

UNIT **PROCESSES** REVIEW

Friedel-Crafts Reactions

I MPORTANT developments have been made in specific areas of application and study of the Friedel-Crafts reactions but the most significant advance has come through the greatly increased number and variety of applications.

The essential features of the pattern established for the 1955 Review have been continued. Discussion has been limited to material that cannot be adequately covered in the tables and bibliography. Space limitations imposed by the large increase in the number of references have dictated necessary changes. The tables for openchain acylation and open-chain alkylation have been arranged in the general order of increasing complexity of the substituting reagent, and increasing complexity of the aromatic compound undergoing substitution. The tables for ringclosure acylation and ring-closure alkylation have been abbreviated. They have been arranged in the order of increasing size and number of rings. Only pertinent products are included. Because of its frequent use, polyphosphoric acid has been indicated as PPA throughout the tables. Related reactions of less general interest such as the Fries rearrangement olefin acylation, and chloromethylation have been eliminated except for brief consideration of important features in the discussion section and complete lists of references in the bibliography. The discussion follows almost the same pattern as the tables.

A number of authors have written minor reviews of the modern aspects of Friedel-Crafts reactions (4A, 36A, 65A,

Advantage has been taken of the bulk and easy removal of the tert-butyl group as a means of obtaining several substances in good yield which were obtained with difficulty by direct means (49A, 77A). The tert-butyl group blocks the two adjacent positions as well as the position it occupies and can be removed readily without disturbing other substituents.

Acylations with phthalic anhydride (54A) and its tetrachloroanalog (55A) provide useful derivatives for characterizing aromatic hydrocarbons. Buu-Hoï and his associates (16A) have found zinc chloride to be a good catalyst for benzylation or allylation of polynuclear aromatic hydrocarbons. Polyphosphoric acid continues in popularity for reactions requiring milder conditions. It does not cleave phenolic ethers (31A). Antimony pentachloride is generally inferior to aluminum chloride except in the benzoylation of benzene (69A). It is presumed that there is less tie-up of the catalyst in this case. Boron trifluoride seems to function better alone at room temperature than it does with phosphoric acid or ether (110A). Silver perchlorate with magnesium oxide is not so good a catalyst as aluminum chloride, antimony pentachloride, or even ferric chloride (17A). The effect of acid concentration, olefin to aromatic ratio, reaction temperature, and reaction time have been investigated for the production of chlorocumene (56A).

Another example of carbon monoxide elimination has been observed in the attempted cyclization of 2,2-dimethyl-5phenylvaleric acid (74A).

Halogen exchange between aluminum halides and 2,4,6-substituted benzoyl halides has been explained by postulating a partial ionization to give trace amounts of acylonium ions (5A). This evidence is claimed to indicate that the acylonium ion is the actual acylating agent. Additives which retard, or even suppress, the reactions do so by solvating the acylonium ion as well as tying up the catalyst. Similar results were obtained using titanium tetrachloride or stannic chloride.

Several kinetic studies have been made which add to mechanistic information (8A, 10A, 11A, 13A, 29A, 39A, 40A, 53A, 82A, 84A, 93A-95A). Acetylation of tertbutylbenzene gives only 1.5% of the meta isomer and none of the ortho product (15A). There is continued interest in the effects of solvents in modifying the distribution of isomers obtained in alkylations and some acylations (3A, 7A, 12A, 35A, 46A, 47A, 72A). Most of these studies have dealt with naphthalene derivatives.

Azulene can be acylated without the use of catalysts (30A). 10-Alkylphenothiazines undergo substitutions of the Friedel-Crafts type in the 2-position (18A). 2,5 - Diphenyl - 1,4 - dithiadiene suffers desulfurization upon formylation to give a thiophene derivative (68A).

Moed and his associates (61A) found that the Hoesch reaction using amino



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OPEN-CHAIN ACYLATION (Aromatics)			
Aromatic 1,2,3-(CH ₃ O) ₃ C ₆ H ₃ C ₆ H ₅ N(CH ₃) ₂	$HCON(CH_3)_2$ or $C_6H_5N(CH_3)CHO$,	Product 1-HCO-2,3,4-(CH ₂ O) ₃ -C ₈ H ₂ 4-HCO-C ₆ H ₄ N(CH ₂) ₂ , 50−71%	Reference (26B) (34B)
2,6-(CH $_3$ O) $_2$ -naphthalene Anthracene	POCl ₃ $C_5H_5N(CH_3)CHO$, POCl ₃ , $C_6H_5CH_3$ $HCON(CH_3)_2$ or $C_6H_5N(CH_3)CHO$,	1-HCO-2,6-(CH₃O)₂-naphthalene 9-HCO-anthracene, 63–84%	(82B) (34B)
Naphthacene Benzene	POCI ₃ C ₆ H ₅ N(CH ₃)CHO, POCI ₃	5-HCO-naphthacene Acetophenone	(121B) (142B, 170B,
Toluene		$4-CH_3C_6H_4COCH_3$	171B, 180B) (39B, 98B,
t-C ₄ H ₉ C ₆ H ₅	CH₃COCI, AlCI₃, CS₂	1.5% 3-(t-C ₄ H ₉)C ₆ H ₄ COCH ₃ and 98.5% 4- (t-C ₄ H ₉)C ₅ H ₄ COCH ₃	180B) (22B)
Biphenyl Diphenylmethane $C_6H_5(CH_2)_3C_6H_6$ $C_6H_5(CH_2)_4C_8H_6$ $C_6H_5(CH_2)_4C_8H_6$ $C_6H_5(CH_2)_5C_6H_6$	(CH ₃ CO) ₂ O, AlCl ₃ CH ₃ COCl, AlCl ₃ , CS ₂ (CH ₃ CO) ₂ O, AlCl ₃ , C ₂ H ₂ Cl ₄ (CH ₃ CO) ₂ O, AlCl ₃ , CS ₂ (CH ₃ CO) ₂ O, AlCl ₃ , C ₂ H ₂ Cl ₄	4-C ₆ H ₃ -C ₆ H ₄ COCH ₃ 4-C ₆ H ₅ CH ₂ -C ₆ H ₄ COCH ₃ 4-[C ₆ H ₅ (CH ₂) ₃]C ₆ H ₄ COCH ₃ , 50% (4-CH ₃ COC ₆ H ₄ CH ₂ CH ₂) ₂ , 74% 4-[C ₆ H ₅ (CH ₂) ₃]C ₆ H ₄ COCH ₃ , 48%, and (4- CH ₃ COC ₆ H ₄ CH ₂ CH ₂) ₂ CH ₂ , 17%	(33B) (57B) (2B) (44B) (2B)
C_6H_5Cl C_6H_5OH Anisole	CH ₃ COCl, AlCl ₃ CH ₃ CO ₂ H, BF ₃ or H ₄ P ₂ O ₇ CH ₃ CO ₂ H or (CH ₃ CO) ₂ O, PPA; or	4-ClC ₆ H ₄ COCH ₃ , 80% 4-HOC ₆ H ₄ COCH ₃ , 60-70%	(98B) (119B, 131B) (35B, 66B,
$C_6H_6OCH_2CH_3$ $C_6H_3OCH_3CH=CH_2$ $C_6H_3OCH_2CH=CHCH_3$ $C_6H_3OCH_2CH=CHC_6H_5$ x - $ClC_5H_4OC_6H_5$ ($x=2,3$ or 4) 4 - $O_2NC_6H_4SC_6H_5$ $C_6H_6NHCOCH_3$ $C_6H_6Si(CH_3)_3$ $C_6H_5CH_2Si(CH_3)_3$ $C_6H_5CH_2CN$	(CH ₃ CO) ₂ O, AlCl ₃ , CS ₂ CF ₃ CO ₂ COCH ₃ CH ₃ CO + ClO ₄ – CH ₃ CO + ClO ₄ – CH ₃ COCl, AlCl ₃ , CS ₂ CH ₃ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ CH ₃ COCl, AlCl ₃ , CS ₂	4-CH ₃ CH ₂ OC ₆ H ₄ COCH ₃ , 21% 4-CH ₃ COC ₆ H ₄ OCH ₂ CH=CH ₂ Resin Resin 4-(x-ClC ₅ H ₄ O)C ₆ H ₄ COCH ₃ (x = 2, 3 or 4) No ketone 4-CH ₃ COC ₆ H ₄ NHCOCH ₂ , 85% CH ₃ COC ₆ H ₄ Si(CH ₃) ₃ 4-CH ₃ COC ₆ H ₄ CH ₂ Si(CH ₅) ₃ 4-CH ₃ COC ₆ H ₄ CH ₂ CN and 3-CH ₃ COC ₆ H ₄ -CH ₃ COC ₆ H ₄ CH ₂ CN and 3-CH ₃ COC ₆ H ₄ -CH ₃ COC ₆ H ₄ CH ₂ CN and 3-CH ₃ COC ₆ H ₄ -CH ₃ COC ₆ CH ₄ -CN in result amounts	134B) (134B) (21B) (21B) (21B) (92B) (167B) (157B) (168B) (141B) (155B)
$\begin{array}{l} 4 \cdot (C_6H_5CH_2CH_2CH_2)C_6H_4CO_2H \\ 1,3 \cdot (CH_3)_2C_5H_4 \\ 4 \cdot CH_3C_6H_4SH \\ 3 \cdot CH_3OC_6H_4C_9H_6 \\ 4 \cdot X \cdot C_6H_4OH \ (X = Br, \ Cl \ or \ F) \end{array}$	(CH ₃ CO) ₂ O, AlCl ₃ , C ₆ H ₅ NO ₂ CH ₃ COCl, AgClO ₄ , MgO CH ₃ COCl, CS ₂ CH ₃ COCl, AlCl ₃ , (CH ₂ Cl) ₂ CH ₃ CO ₂ H, BF ₃	CH ₂ CN, in nearly equal amounts 4-[(4-CH ₃ COC ₆ H ₄)CH ₂ CH ₂ CH ₂ C ₆ H ₄ CO ₂ H 2,4-(CH ₃) ₂ C ₆ H ₃ COCH ₃ , 30% 2-CH ₃ -5-HS-C ₆ H ₃ COCH ₃ 2-CH ₃ O-4-C ₆ H ₅ -C ₆ H ₃ COCH ₃ , 48% 2-HO-5-X-C ₆ H ₃ COCH ₃ (X = Br, Cl or F)	(45B) (39B) (145B) (14B) (93B)
3-ClC ₀ H ₄ OCH ₃ 4-FC ₆ H ₄ OCH ₂ 2-ClC ₆ H ₄ SCH ₃ 1,2-(HO) ₂ C ₆ H ₄ 1,3-(HO) ₂ C ₆ H ₄	CH ₃ COCl, AlCl ₃ , CS ₂ CH ₃ COCl, AlCl ₃ , CS ₂ CH ₃ COCl CH ₃ CO ₂ H, PPA CH ₃ CO ₂ H, PPA or BF ₃	vields range from 44-94% 2-Cl-4-CH ₃ O-C ₆ H ₃ COCH ₃ 2-CH ₃ O-5-F-C ₆ H ₃ COCH ₃ 3-Cl-4-CH ₅ S-C ₆ H ₃ COCH ₃ 3,4-(HO) ₂ C ₆ H ₃ COCH ₃ 2,4-(HO) ₂ C ₆ H ₃ COCH ₃ , 80-90%, (some di-	
2-CH ₃ OC ₆ H ₄ OH 3-CH ₃ OC ₆ H ₄ OH	CH₃CO₂H, PPA CH₃CO₂H, PPA	acctylation) 3-CH ₂ O-4-HO-C ₆ H ₂ COCH ₃ 2-CH ₂ O-4-HO-C ₆ H ₃ COCH ₃ , 2-HO-4-CH ₂ O-C ₆ H ₃ COCH ₃ and	131B) (129B) (129B)
1,2-(CH ₃ O) ₂ C ₆ H ₄ (also for 1,3-) 2-O ₂ NC ₆ H ₄ OH (also for 4-) 3-CH ₃ OC ₆ H ₄ NHCOCH ₃ 3-(n-C ₄ H ₉ O)C ₆ H ₄ NHCOCH ₂ 1,3,5-(CH ₃) ₃ C ₄ H ₃	CH ₃ CO ₂ H, PPA CH ₃ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ CH ₅ COBr, AlCl ₃ , CS ₂ CH ₃ COBr, AlCl ₃ , CS ₂ CH ₃ COCl or (CH ₃ CO) ₂ O, AlCl ₃	2-HO-4-CH ₃ O-1,5-(CH ₃ CO) ₂ C ₆ H ₂ 3,4-(CH ₃ O) ₂ C ₆ H ₃ COCH ₃ 3-O ₂ N-4-HO-C ₆ H ₃ COCH ₅ , 47% 3-HO-4-CH ₃ CO-C ₆ H ₃ NHCOCH ₃ 3-HO-4-CH ₂ CO-C ₆ H ₃ NHCOCH ₃ and 2,4-(CH ₃ CO) ₂ -5-HO-C ₆ H ₂ NH ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCH ₃ , 96%	(129B) (89B) (59B) (59B) (41B, 127B,
3,5-(CH ₃) ₂ C ₆ H ₃ (t-C ₄ H ₉) 3-CH ₃ -5-(i-C ₃ H ₇)C ₆ H ₃ OCH ₃	CH ₃ COCl, AlCl ₃ , CS ₂ RCOCl, AlCl ₃ , CS ₂	(some diacetylation) 2,6-(CH ₃) ₂ -4-(t-C ₄ H ₉)C ₆ H ₂ COCH ₃ 2-CH ₃ -4-CH ₃ O-5-(i-C ₅ H ₇)C ₆ H ₂ COR R Yield, %	180B) (159B) (156B)
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$^{2,5-(CH_3O)_2C_6H_3C_2H_5}_{(3,4-(CH_3O)_2C_6H_3CH_2]_2}$	CH₃COCl	$2-HO-4-C_2H_3-5-CH_3O-C_5H_2COCH_3$ [$2-CH_3CO-3,4-(CH_3O)_2C_6H_2CH_2$] $_2$	(147B) (9B)

	OPEN-CHAIN ACYLATION (Ar	omatics) (Continued)	
Aromatic	Reagent	Product	Reference
2-HO-3-O ₂ N-C ₆ H ₃ CH ₃ 3-CH ₃ -4-Cl-C ₆ H ₃ OH 2,4-(HO) ₂ C ₆ H ₃ COCH ₃ 2-HO-4-CH ₃ O-C ₆ H ₃ COCH ₃ 2-CH ₃ O-4-HO-C ₆ H ₃ COC ₂ H ₃ 1,3,5-(HO) ₃ C ₆ H ₃ 3,5-(CH ₃ O) ₂ C ₆ H ₃ OCH ₃ 3,5-(CH ₃ O) ₂ C ₆ H ₃ OCH 1,3,5-(CH ₃ O) ₃ C ₆ H ₃ 1,2,3-(CH ₃ O) ₃ C ₆ H ₃ 2,5-(C ₂ H ₃ O) ₂ C ₆ H ₃ OCH ₃ 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ OCH ₃	CH ₃ COCl, AlCl ₂ , C ₆ H ₅ NO ₂ CH ₃ CO ₂ H, BF ₃ CH ₅ CO ₂ H, PPA CH ₅ CO ₂ H, PPA CH ₃ CO ₂ H, CH ₃ CO) ₂ O, PPA CH ₃ CO ₂ H, BF ₃ ; or CH ₃ COCl, AlCl ₃ , ether	3-O ₂ N-4-HO-5-CH ₃ -C ₆ H ₂ COCH ₃ , 50% 2-HO-4-CH ₃ -5-Cl-C ₆ H ₂ COCH ₃ , 85% 1,3-(CH ₃ CO) ₂ -4,6-(HO) ₂ C ₆ H ₂ 1,3-(CH ₃ CO) ₂ -4-CH ₃ O-6-HO-C ₆ H ₂ 3-CH ₃ CO-4-HO-6-CH ₃ O-6-H ₂ COC ₂ H ₃ 2,4,6-(HO) ₃ C ₆ H ₂ COCH ₃ , 80-90% 2,4,6-(CH ₃ CO) ₃ -3,5-(HO) ₂ C ₆ OCH ₃ 2,4,6-(CH ₃ CO) ₃ -3,5-(CH ₃ O) ₂ C ₅ OH 1,3,5-(CH ₃ O) ₃ -2,4,6-(CH ₃ CO) ₃ C ₅ 2,3,4-(CH ₃ O) ₂ C ₄ COCH ₃ 2,5-(C ₂ H ₃ O) ₂ -4-CH ₃ O-C ₆ H ₂ COCH ₃ 2,3,4-(CH ₃ O) ₂ -6-HO-C ₆ HCOCH ₃ , 60-70%	(89B) (93B) (129B) (129B) (129B) (129B) (132B) (132B) (132B) (132B) (66B) (94B) (103B, 119B)
Indan 1-(C ₂ H ₅ O ₂ C)-indan 1-(4-CH ₅ OC ₆ H ₄)-2-CH ₃ -3-C ₂ H ₅ -6- CH ₃ O-indan Naphthalene 2-C ₂ H ₅ -naphthalene 1-HO-naphthalene	CH ₃ COCl, AlCl ₃ , C ₈ H ₈ CH ₃ COCl, AlCl ₃ , CS ₂ CH ₃ COCl, AlCl ₃ , CS ₂ CH ₃ COCl or (CH ₃ CO) ₂ O, AlCl ₃ , many solvents CH ₃ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ CH ₃ CO ₂ H, PPA	5-CH ₃ CO-indan 1-(C ₂ H ₃ O ₂ C)-6-CH ₃ CO-indan 1-(3-CH ₃ CO-4-HO-C ₆ H ₃)-2-CH ₃ -3-C ₂ H ₅ -5- CH ₃ CO-6-HO-indan 1- and 2-CH ₃ CO-naphthalene (detailed study) 2-C ₂ H ₅ -6-CH ₂ CO-naphthalene 1-HO-2-CH ₃ CO-naphthalene, 37%;	(50B) (3B) (80B) (8B, 97B, 100B) (7B) (135B)
2-HO-naphthalene 1-HO-2-CH₃CO-naphthalene 1,6-(CH₃)₂-naphthalene 1-HO-2-HO₂C-naphthalene (also for ester) 2-HO-3-HO₂C-naphthalene (also for ester)	CH₃CO₂H, BF₃ CH₃CO₂H, PPA CH₃COCl	1-HO-4-CH ₃ CO-naphthalene, 32%; and some diacetylation 2-HO-1-CH ₃ CO-naphthalene, 93% 1-HO-2,4-(CH ₃ CO) ₂ -naphthalene 1,6-(CH ₃) ₂ -4-CH ₃ CO-naphthalene 1-HO-2-HO ₂ C-4-CH ₃ CO-naphthalene 1-CH ₃ CO-2-HO-3-HO ₂ C-naphthalene	(119B) (135B) (28B) (88B)
5-CH ₈ O-2,3-H ₂ -benzofuran		5-CH ₃ O-6-CH ₃ CO-2,3-H ₂ -benzofuran and 5-HO-6-CH ₃ CO-2,3-H ₂ -benzofuran	(147B)
$2-(C_2H_3O_2C)-4,7-(CH_3O)_2-6-HO-$ benzofuran	$\mathrm{CH_3COCl}$, $\mathrm{AlCl_3}$, $\mathrm{C_6H_5NO_2}$	2-(C ₂ H ₅ O ₂ C)-4,7-(CH ₃ O) ₂ -5-CH ₃ CO-6-HO- benzofuran	(154B)
4-CH ₃ -5-HO-coumarin 4-CH ₃ -7-HO-coumarin 4,7-(CH ₃) ₂ -5-HO-coumarin 4-CH ₃ -5,7-(HO) ₂ -coumarin	(CH ₃ CO) ₂ O, AlCl ₃ (CH ₃ CO) ₂ O, AlCl ₃ (CH ₃ CO) ₂ O, AlCl ₃ CH ₃ CO ₂ H, BF ₅ ; or (CH ₃ CO) ₂ O, AlCl ₃	4-CH ₃ -5-HO-6-CH ₃ CO-coumarin 4-CH ₃ -7-HO-8-CH ₃ CO-coumarin 4,7-(CH ₃) ₂ -5-HO-6-CH ₃ CO-coumarin 4-CH ₃ -5,7-(HO) ₂ -6-CH ₃ CO-coumarin; and some diacetylation	(140B) (140B) (140B) (53B, 140B)
8-HO-quinoline Diphenylene 1-CH ₃ -7-(<i>i</i> -C ₃ H ₇)phenanthrene	CH ₃ COCl or (CH ₃ CO) ₂ O, AlCl ₃ CH ₃ COCl, AlCl ₃ , CS ₂ CH ₃ COCl, AlCl ₃	5-CH ₃ CO-8-HO-quinoline 2-CH ₃ CO-diphenylene 1-CH ₃ -3-CH ₃ CO-7-(i-C ₃ H ₇)-phenanthrene	(172B) (6B) (166B)
(Retene) 1,1,4a-(CH ₃) ₃ -6-CH ₃ O-1,2,3,4,4a,- 9,10,10a-H ₃ -phenanthrene Chrysene 3-CH ₃ -filicinic acid Toluene Phenol Phenol	CH ₃ COCl, AlCl ₃ , C ₆ H ₃ NO ₂ CH ₃ COCl, AlCl ₅ CH ₃ COCl, AlCl ₅ (C ₂ H ₅ CO) ₂ O, BF ₃ C ₂ H ₅ CO ₂ H, BF ₃ or PPA RCO ₂ H, PPA	1,1,4a-(CH ₃) ₃ -6-CH ₃ O-7-CH ₅ CO-1,2,3,4,4a,-9,10,10a-phenanthrene 2-, 4- and 5-CH ₃ CO-chrysene 3-CH ₃ -5-CH ₃ CO-filicinic acid 4-CH ₃ C ₅ H ₄ COC ₂ H ₅ , 23-30% 4-HOC ₆ H ₄ COC ₂ H ₅ , 58% 4-RCO-C ₆ H ₄ OH	(95B) (36B) (152B) (180B) (30B, 134B) (134B)
		R Yield, %	
		$\begin{array}{lll} \textit{n-}C_3H_7 & 54 \\ \textit{n-}C_4H_9 & 47 \\ \textit{n-}C_5H_{11} & 41 \\ C_6H_5CH_2 & 28 \\ C_6H_5CH_2CH_2 & 27 \end{array}$	
Anisole	C ₂ H ₅ COCl; or C ₂ H ₅ CO ₂ H, PPA	4-CH₃OC₅H₄COC₂H₃, 64% 4-CH₃OC₅H₄COR	(109B, 134B) (134B)
Anisole	RCO₂H, PPA	R Yield, %	(7542)
		n-C₃H₁ 60	
		n-C ₃ H ₇ n-C ₄ H ₉ 72 n-C ₅ H ₁₁ C ₆ H ₆ CH ₂ 73 4-CH ₃ OC ₆ H ₄ CH ₂ 74 C ₆ H ₅ CH ₂ CH ₂ 50	
C ₆ H ₅ SC ₂ H ₅ 4-CH ₃ O-biphenyl Diphenyl ether	C ₂ H ₅ COCl, AlCl ₃ C ₂ H ₆ COCl	4-C ₂ H ₅ SC ₆ H ₄ COC ₂ H ₅ 4-(4-CH ₅ OC ₆ H ₄)C ₆ H ₄ COC ₂ H ₅ 4-(C ₆ H ₅ O)C ₅ H ₄ COC ₂ H ₅ and (4-C ₂ H ₅ COC ₅ H ₄) ₂ O	(29B) (32B, 176B) (30B)
C ₆ H ₆ CH ₂ C ₆ H ₅ (C ₆ H ₅ CH ₂ CH ₂) ₂ (C ₆ H ₅ CH ₂ CH ₂) ₂ (C ₆ H ₆ CH ₂ CH ₂ CH ₂) ₂ 4-HO ₂ CC ₆ H ₄ (CH ₂) ₃ C ₆ H ₅ 4-CH ₃ COC ₆ H ₄ (CH ₂) ₅ C ₆ H ₅ 3-CH ₃ O-biphenyl 4-BrC ₆ H ₄ OH 4-ClC ₆ H ₄ OH	(C ₂ H ₅ CO) ₂ O, AlCl ₃ , CS ₂ (C ₂ H ₅ CO) ₂ O, AlCl ₃ , CS ₂ (C ₂ H ₅ CO) ₂ O, AlCl ₃ , C ₆ H ₅ NO ₂ (C ₂ H ₅ CO) ₂ O, AlCl ₃ , C ₃ H ₅ NO ₂ (C ₂ H ₅ CO) ₂ O, AlCl ₃ , C ₂ H ₂ Cl ₄ C ₂ H ₅ COCl, AlCl ₃ , (CH ₂ Cl) ₂ C ₂ H ₅ CO ₂ H, BF ₃ C ₂ H ₅ CO ₂ H, BF ₃	(4-C ₂ H ₃ COC ₃ H ₄) ₂ CH ₂ , 79% (4-C ₂ H ₃ COC ₆ H ₄ CH ₂ CH ₂) ₂ , 70% (4-C ₂ H ₃ COC ₆ H ₄ CH ₂ CH ₂ CH ₂) ₂ , 63% 4-[4-HO ₂ CC ₆ H ₄ (CH ₂) ₃]C ₆ H ₄ COC ₂ H ₅ , 70% 4-[4-CH ₃ COC ₆ H ₄ (CH ₂) ₃]C ₆ H ₄ COC ₂ H ₅ , 76% 2-CH ₃ O-4-C ₅ H ₅ -C ₅ H ₄ COC ₂ H ₅ , 37% 2-HO-5-Br-C ₆ H ₃ COC ₂ H ₅ , 33–59% 2-HO-5-Cl-C ₆ H ₃ COC ₂ H ₅ , 82%	(1B) (1B) (1B) (2B) (2B) (14B) (93B) (93B)

OPEN-CHAIN ACYLATION (Aromatics) (Continued)

Aromatic	Reagent	Product	Reference
2-ClC₀H₄OCH₃ 2-FC₀H₄OCH₃	C_2H_5COCl C_2H_5COCl , AlCl $_3$, CS $_2$	3-Cl-4-CH ₃ O-C ₆ H ₃ COC ₂ H ₅ 3-F-4-CH ₃ O-C ₆ H ₃ COC ₂ H ₅ , and some	(30B) (31B)
4-FC ₆ H ₄ OCH ₃	C ₂ H ₅ COCl, AlCl ₃ , CS ₂	(3-F-4-CH ₃ O-C ₆ H ₃) ₂ C=CHCH ₃ 2-CH ₃ O-5-F-C ₆ H ₃ COC ₂ H ₅	(27B) (178B)
2-ClC ₆ H ₄ SCH ₃ 1,2-(HO) ₂ C ₆ H ₄ (also for 1,3-) 2-CH ₃ OC ₆ H ₄ OH	C ₂ H ₅ COCl C ₂ H ₅ CO ₂ H, PPA C ₂ H ₅ CO ₂ H, PPA	3-Cl-4-CH ₃ S-C ₆ H ₃ COC ₂ H ₅ 3,4-(HO) ₂ C ₆ H ₃ COC ₂ H ₅ 3-CH ₃ O-4-HO-C ₈ H ₃ COC ₂ H ₅	(129B) (129B)
3-CH₃OC₅H₄OH	C ₂ H ₅ CO ₂ H, PPA	2-HO-4-CH ₃ O-C ₆ H ₃ COC ₂ H ₃ , 2-CH ₃ O-4-HO-C ₆ H ₃ COC ₂ H ₅ , and	(129B)
1,2-(CH ₂ O) ₂ C ₆ H ₄ (also for 1,3-)	C ₂ H ₅ CO ₂ H, PPA	2-HO-4-CH ₃ O-1,5-(C ₂ H ₅ CO) ₂ -C ₆ H ₂ 3,4-(CH ₃ O) ₂ C ₆ H ₃ COC ₂ H ₅	(129B)
3-CH ₃ -4-Cl-C ₆ H ₃ OH 2,4-(HO) ₂ C ₆ H ₃ COCH ₃	C ₂ H ₅ CO ₂ H, BF ₃ C ₂ H ₅ CO ₂ H, PPA	2-HO-4-CH ₃ -5-Cl-C ₆ H ₂ COC ₂ H ₅ , 46% 2,4-(HO) ₂ -5-CH ₃ CO-C ₆ H ₂ COC ₂ H ₅	(93B) (129B)
$2,4-(HO)_2C_6H_3COC_2H_3$ $2-CH_3O-4-HO-C_6H_2COC_2H_3$ $1,2,3-(HO)_3C_6H_3$	C ₂ H ₆ CO ₂ H, PPA C ₂ H ₆ CO ₂ H, PPA C ₂ H ₅ COCl	2,4-(HO) ₂ -1,5-(C ₂ H ₆ CO) ₂ -C ₆ H ₂ 2-CH ₃ O-4-HO-1,5-(C ₂ H ₅ CO) ₂ -C ₆ H ₂ 2,3,4-(HO) ₃ C ₆ H ₂ COC ₂ H ₅ , 75%	(129B) (129B) (23B)
1,3,5-(HO) ₃ C ₆ H ₃ 3,5-(HO) ₂ C ₆ H ₃ OCH ₃ (also for di-	$C_2H_5CO_2H$, PPA	2,4,6-(HO) ₂ -1,3,5-(C ₂ H ₃ CO) ₃ -C ₆ 3,5-(HO) ₂ -2,4,6-(C ₂ H ₃ CO) ₃ C ₆ OCH ₃	(132B) (132B)
and tri- ether 2-CH ₃ O-naphthalene	C ₂ H ₅ COCl, AlCl ₃ , C ₆ H ₆ NO ₂	2-CH ₃ O-6-C ₂ H ₅ CO-naphthalene	(85B)
1-HO-naphthalene	RCO₂H, PPA	1-HO-2-(or 4-)RCO-naphthalene	(<i>135B</i>)
		Yield, % R 2-RCO 4-RCO	
		$\begin{array}{ccccccc} C_2H_5 & 42 & 1 \\ n-C_3H_7 & 72 & 3 \end{array}$	
		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	
1-HO-2-CH₃CO-naphthalene Chrysene	C ₂ H ₅ CO ₂ H, PPA C ₂ H ₅ COCl, AiCl ₃ , CS ₂	1-HO-2-CH3CO-4-C2H3CO-naphthalene 6-C2H3CO-chrysene, 57%	(135B) (24B)
Biphenyl	RCOCl, AÍCl₃, CS₂	4-RCO-biphenyl ($R = n-C_3H_7$, $n-C_7H_{13}$, $n-C_{11}H_{23}$, $n-C_{15}H_{31}$)	(122B)
${ m C_6H_5SC_2H_5} \ { m C_6H_5NHCOCH_8}$	RCOCI	4-C2H5SC6H4CO-(n-C5H7) 4-RCOC6H4NHCOCH3 (R = n-C8H7,	$(29B) \ (84B)$
$C_6H_5CH_2NHCHO$	RCOCl, AlCl $_{\flat}$, CS $_{2}$	$n-C_4H_9$, $n-C_5H_{11}$) $4-RCOC_6H_4CH_2NH_2$, $25-30\%$ (R = $n-C_3H_7$, $n-C_4H_9$, $n-C_5H_{11}$, $i-C_5H_{11}$, $n-C_{11}H_{23}$)	(84B)
$C_6H_5CH_2Si(CH_8)_8$	RCOCI, AlCl ₃	$4-RCOC_5H_4CH_2Si(CH_3)_3, 33-55\%$ $(R = n-C_3H_7, n-C_5H_{11}, n-C_7H_{15})$	(141B)
4-ClC ₆ H ₄ OH 4-FC ₆ H ₄ OH	n-C ₃ H ₇ CO ₂ H, BF ₃ n-C ₃ H ₇ CO ₂ H, BF ₃	2-HO-5-Cl-C ₆ H ₃ CO-(<i>n</i> -C ₃ H ₇), 86% 2-HO-5-F-C ₆ H ₃ CO-(<i>n</i> -C ₃ H ₇), 80%	(93B) (93B)
3-CH₃O-biphenyl 1,3-(HO)₂C₀H₄ 3-CH₃-4-Cl-C₀H₃OH	n-C ₃ H ₇ COCl, AlCl ₃ , (CH ₂ Cl) ₂ n-C ₃ H ₇ CO ₂ H, PPA n-C ₃ H ₇ CO ₂ H, BF ₃	$2-HO-4-C_6H_3-C_6H_3CO-(n-C_3H_7), 60\%$ $2,4-(HO)_2C_6H_3CO-(n-C_3H_7)$ $2-HO-4-CH_3-5-Cl-C_6H_2CO-(n-C_3H_7)$	(14B) (129B) (93B)
2,4,6-(HO) $_{3}$ C $_{8}$ H $_{2}$ CH $_{3}$ Filicinic acid (also for 3-CH $_{2}$)	n-C ₃ H ₇ COCl, AlCl ₃ n-C ₃ H ₇ COCl, AlCl ₃	2,4,6-(HO) ₃ -3-CH ₃ -C ₃ HCO-($(n$ -C ₃ H ₇), 41% 3-($(n$ -C ₃ H ₇ CO)-filicinic acid	(151B) (152B)
2-FC ₆ H ₄ OCH ₃	RCOCI	3-F-4-CH ₃ O-C ₆ H ₃ COR (R = n -C ₄ H ₉ , n -C ₅ H ₁₁ , n -C ₉ H ₁₉)	`(30B)
3-CH₃-4-Cl-C₅H₃OH 1,2,3-(HO)₃C₅H₃	n•C₄H₃CO₂H, BF₃ RCO₂H, ZnCl₂	2-HO-4-CH ₃ -5-Cl-C ₆ H ₂ CO-(n -C ₄ H ₉), 86% 2,3,4-(HO) ₈ C ₆ H ₂ COR	$(93B) \ (23B)$
		R Yield, %	
	•	<i>n</i> -C ₄ H ₉ 70 <i>n</i> -C ₅ H ₁₁ 70	
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
Benzene	CH₃(CH₂) _n COCl, AlCl₃	$n \cdot C_{14}H_{29}$ $CH_3(CH_2)_nCOC_6H_5 (n = 4 \text{ to } 18)$	(15B)
4-CH₃O-biphenyl	CH ₃ (CH ₂), COCl, AlCl ₃ , C ₆ H ₅ NO ₂	4-(4-CH3OC6H4)C6H4CO(CH2)nCH3 (n = 4, 5, 6)	(32B)
Diphenyl ether Naphthalene	RCOCl $CH_3(CH_2)_nCOCl$, AlCl $_3$, $C_6H_5NO_2$	4- $(C_{\delta}H_{\delta}O)C_{\delta}H_{\vartheta}COR(R = n - C_{\delta}H_{11}, n - C_{7}H_{1\delta})$ 2- $CH_{\vartheta}(CH_{2})_{n}CO$ -naphthalene (n = 4, 6, 8, 10, 12)	(30B) (181B)
Chrysene RC_6H_5	n-C ₆ H ₁₃ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ n-C ₉ H ₁₉ COCl, AlCl ₃ , CS ₂	2.(n-C ₅ H ₁₃ CO)-chrysene 4-RC ₅ H ₄ CO-(n-C ₅ H ₁₉)	(37B) (101B)
$C_6H_5N(CH_3)_2$	n-C ₉ H ₁₉ COCl, ZnCl ₂	$(R = H, HO, CH_3, Cl, or NHCOCH_3)$ $4\cdot(n\cdot C_0\cdot H_1)CO)C_0\cdot H_4N(CH_3)$	(101B)
1,3-(HO)₂C₀H₄ 2-HOC₀H₄CO₂H 2,4-(HO)₂C₀H₃CO₂H	n-C ₉ H ₁₉ CO ₂ H, ZnCl ₂ n-C ₉ H ₁₉ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ n-C ₉ H ₁₉ COCl, AlCl ₃ , CS ₂	$2,4-(HO)_2C_6H_3CO-(n-C_9H_{19})$ $2-HO-5-(n-C_9H_{19}CO)C_6H_3CO_2H$ $2,4-(HO)_2-5-(n-C_9H_{19}CO)C_6H_3CO_2H$	(101B) (101B) (101B)
1-HO-naphthalene 1,4-(HO) ₂ -naphthalene	n-C ₉ H ₁₉ CO ₂ H, ZnCl ₂ n-C ₉ H ₁₉ CO ₂ H, ZnCl ₂	1-HO-4-(n-C ₉ H ₁₉ CO)-naphthalene 1,4-(HO) ₂ -4-(n-C ₉ H ₁₉ CO)-naphthalene	(101B) (101B)
$3,5-(CH_3)_2C_6H_3-(t-C_4H_9)$	RCOCl, AlCl ₃ , CS ₂	$2,6-(CH_3)_2-4-(t-C_4H_9)-C_0H_2COR$ $(R = n-C_9H_{19}, n-C_{17}H_{35})$	(159B)
$ ext{4-}(\mathrm{C_6H_6S})\mathrm{C_6H_4NO_2}$ Benzene Benzene	n-C ₁₇ H ₂₅ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ Karite oil, AlCl ₃ Hydrographed palm oil AlCl ₂	No ketone $58\% \text{ C}_6\text{H}_5\text{COR}$ and some $\text{C}_6\text{H}_5\text{R}'$ $3539\% \text{ C}_4\text{H}_5\text{COR}$	(167B) (124B) (124B)
Deliberie	Hydrogenated palm oil, AlCl ₃	35–39% C ₆ H ₅ COR	(.272)

	OPEN-CHAIN ACYLATION (Ar	omatics) (Continued)	
Aromatic	Reagent	Product	Reference
Benzene	Hydrogenated olive oil, AlCl ₃	Tar	(124B)
Biphenyl Diphenyl ether	$(i-C_3H_7)$ COCl, AlCl ₃ , CS ₂ $(i-C_3H_7)$ COCl	$4-C_5H_5C_6H_4CO-(i-C_3H_7), 92\%$ $4-(C_6H_5O)C_6H_4CO-(i-C_3H_7)$	(164B) (30B)
Mesitylene	$(i-C_3H_7)COCl$	$2,4,6-(CH_3)_3C_6H_2CO-(i-C_3H_7), 75\%$	(10B)
1,2,3-(HO)₃C₀H₃	(i-C ₃ H ₇)CO ₂ H, ZnCl ₂	$2,3,4-(HO)_3C_6H_2CO-(i-C_3H_7), 40\%$	(23B)
1,3,5-(HO);C6H3 Biphenyl	$(i-C_3H_7)$ COCl, AlCl ₃ , C ₆ H ₆ NO ₂ C ₂ H ₅ CH(CH ₃)COCl, AlCl ₃ , CS ₂	$2,4,6-(HO)_3C_6H_2CO-(i-C_3H_7), 20\%$ $4-C_6H_3C_6H_4COCH(CH_3)C_2H_5, 86\%$	(83B) (165B)
$2,5-(CH_3O)_2C_6H_3-(n-C_7H_{15})$	(i-C₄H₀)ĈOCl, AlCl₃, CS₂	2,5-(HO) ₂ -4-(n -C ₇ H ₁₅)-C ₆ H ₂ CO-(i -C ₄ H ₉), mono ether	(139B)
Benzene	Cyclopentyl-COCl	Cyclopentyl-COC ₅ H ₅	(40B)
Toluene $1,2-(CH_3O)_2C_6H_4$ (also for $1,4-$)	Gyclohexyl-COCl, AlCl₃ Gyclohexyl-COCl, AlCl₃, C₄H₄NO₂	4-ĆH₃̂C₀H₄CO-cyclohexyl 3,4-(CH₃O)₂C₀H₃CO-cyclohexyl	(81B) (18B)
Anisole	Cyclohexyl-CH ₂ COCl, AlCl ₃ , C ₈ H ₅ NO ₂	4-CH ₃ OC ₆ H ₄ COCH ₂ -cyclohexyl	(20B)
1,3-(HO) ₂ C ₆ H ₄ Biphenyl	Cyclohexyl-(CH ₂) ₄ CO ₂ H, ZnCl ₂ CH ₃ CH=CHCOCl, AlCl ₃ , (CHCl ₂) ₂	2,4- $(HO)_2C_6H_3CO(CH_2)_4$ -cyclohexyl 4- C_6H_3COCH =CHCH3	(18B) (47B)
Phenol	C ₆ H ₅ CH=CHCO ₂ H, PPA	$4-HOC_6H_4COCH=CHC_6H_5$, 20%	(134B)
Anisole	C ₆ H ₅ CH=CHCO ₂ H, PPA	4-CH ₃ OC ₃ H ₄ COCH=CHC ₅ H ₅ , 45%	(134B)
Anisole 3-CH₃O-4-HO-C₀H₃CHO	C_6H_5CH =CHCOCl, AgClO ₄ C_6H_5CH =CHCOCl, C_6H_6	4-CH₃OC₀H₄COCH—CHC₀H₅ Cinnamoylvanillin	(21B) (148B)
3-CH₃O-4-HO-C₅H₃CO₂H	$C_{\mathfrak{b}}H_{\mathfrak{b}}CH=CHCOCl, C_{\mathfrak{b}}H_{\mathfrak{b}}$	Cinnamoylvanillic acid	(148B)
3,4,5-(CH₃O)₃C₅H₂OH Toluene	C_6H_5CH =CHCO ₂ H, BF ₃ $C_6H_5CH_2COCl$	$2,3,4-(CH_3O)_3-6-HO-C_6HCOCH=CHC_6H_6$ $4-CH_3C_6H_4COCH_2C_6H_5$, 93%	(119B) (48B)
Anisole	$C_6H_5CH_2COCl$, $AlCl_5$, CS_2	$4-CH_3OC_6H_4COCH_2C_6H_5$	(48B)
C₀H₅Cl 4-ClC₀H₄OH	$C_6H_5CH_2COCl$ $C_5H_5CH_2CO_2H$, BF ₃	4-ClC ₆ H ₄ COCH ₂ C ₆ H ₅ 2-HO-5-Cl-C ₆ H ₃ COCH ₂ C ₆ H ₅ , 68%	(48B) (93B)
2-FC ₆ H ₄ OCH ₃	C ₆ H ₅ CH ₂ COCl	3-F-4-CH ₃ O-C ₆ H ₃ COCH ₂ C ₆ H ₅	(30B, 31B)
4-FC ₆ H ₄ OCH ₃	$C_6H_5CH_2COCl$, $AlCl_3$, CS_2	2-CH ₃ O-5-F-C ₆ H ₃ COCH ₂ C ₆ H ₅	(27B)
3,4,5-(CH3O)3C6H2OH Carbazole	C ₆ H ₅ CH ₂ COCl, AlCl ₃ , ether C ₆ H ₅ CH ₂ COCl, AlCl ₃ , C ₆ H ₆	2,3,4-(CH ₃ O) ₃ -6-HO-C ₆ HCO-CH ₂ C ₆ H ₆ 3,6-(C ₆ H ₆ CH ₂ CO)-carbazole	$(105B) \\ (96B)$
N-(C ₆ H ₅ CO)-carbazole	$C_6H_5CH_2COCl, AlCl_3, CS_2$	$2-(C_6H_5CH_2CO)-N-(C_6H_5CO)$ -carbazole and	
Benzene	4-CH ₃ C ₆ H ₄ CH ₂ COCl	2-($C_6H_5CH_2CO$)-carbazole 4- $CH_3C_6H_4CH_2COC_6H_5$, 60%	(48B)
Anisole	4-CH ₃ C ₆ H ₄ CH ₂ COCl	4-(4-CH ₂ C ₆ H ₄ CH ₂ CO)C ₆ H ₄ OCH ₃ , 67%	(48B)
Benzene	4-ClC ₆ H ₄ CH ₂ COCl	4-CIC ₆ H ₄ CH ₂ COC ₆ H ₅ , 89%	(48B)
$egin{aligned} \mathbf{Benzene} \\ \mathbf{C_6H_5OC_2H_5} \end{aligned}$	4-(C ₆ H ₅ CH ₂)C ₆ H ₄ CH ₂ COCl, AlCl ₂ 4-CH ₃ OC ₆ H ₄ CH ₂ COCl, SnCl ₄	$\begin{array}{l} \textbf{4-}(C_6H_5CH_2)C_6H_4CH_2COC_6H_5\\ \textbf{4-}(\textbf{4-}CH_2OC_6H_4CH_2CO)C_6H_4OC_2H_5 \end{array}$	(67B) (169B)
$3,4,5-(CH_3O)_3C_6H_2OH$	4-CH ₃ OC ₆ H ₄ CH ₂ COCl, AlCl ₃ , ether	2,3,4-(CH ₃ O) ₃ -6-HO-	(105B)
$3,5-(\mathrm{CH_3O})_2$ -4- $\mathrm{C_2H_5O-C_6H_2OH}$	4-C ₂ H ₅ OC ₆ H ₄ CH ₂ COCl, AlCl ₃ , ether	1-(4-CH₃OC₅H₄CH₂CO)-C₅H 2,4-(CH₃O)₂-3-C₂H₃O-6-HO- 1-(4-C₂H₅OC₅H₄CH₂CO)-C₅H	(104B)
$3,5-(C_2H_5O)-4-CH_3O-C_6H_2OH$	$4-C_2H_5OC_6H_4CH_2COCl$, AlCl $_3$	$2,4-(C_2H_5O)_2-3-CH_3O-6-HO-$	(105B)
$1,2-(CH_{3}O)_{2}C_{6}H_{4}$	$3,4-(\mathrm{CH_3O})_2\mathrm{C_6H_3CH_2COCl}$	1-(4-C ₂ H ₃ OC ₈ H ₄ CH ₂ CO)-C ₆ H 1-[3,4-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CO]-3,4-(CH ₃ O) ₂ , 31%	(179B)
$1,2-(CH_3O)_2C_6H_4$	$2,4,6-(CH_3O)_3C_6H_2CH_2CO_2H$	1-[2,4,6-(CH ₃ O) ₃ C ₆ H ₂ CH ₂ CO]- 3,4-(CH ₃ O) ₂ C ₆ H ₃	(134B)
Benzene	FCH ₂ COCl, AlCl ₃ , CH ₂ Cl ₂	FCH ₂ COC ₆ H ₅	(12B)
Diphenyl ether Diphenyl sulfide	ClCH ₂ COCl, AlCl ₃ , CS ₂ ClCH ₂ COCl, AlCl ₃ , CS ₂	$(4-\text{ClCH}_2\text{COC}_6\text{H}_4)_2\text{O}$ $(4-\text{ClCH}_2\text{COC}_6\text{H}_4)_2\text{S}$	(<i>175B</i>) (<i>175B</i>)
4-ÊC₅H₄OCH₃		2-CH ₃ O-5-F-C ₆ H ₃ COCH ₂ Br	(27B)
1,3-(CH ₃ O) ₂ C ₆ H ₄ 2-Cl-3,5-(CH ₃ O) ₂ C ₆ H ₂ OH (also	ClCH2COCl, AlCl3, CS2 ClCH2COCl, AlCl3, C6H5NO2	2-HO-4-CH ₃ O-C ₆ H ₃ COCH ₂ Cl, 55% 2-HO-3-Cl-4,6-(CH ₃ O) ₂ C ₆ HCOCH ₂ Cl	(106B) (117B, 118 B)
for 2-Br) Biphenyl	BrCH ₂ COBr, AlCl ₃ , CS ₂	(4-BrCH ₂ COC ₆ H ₄) ₂ , 35%	(113B)
2-CH ₃ CO ₂ -fluorene	CICH COCL AICL (CHCL)	2-CH ₃ CO ₂ -7-ClCH ₂ CO-fluorene, 64% 2-CH ₃ O-5-cyclohexyl-C ₆ H ₃ COCH ₂ Cl	(116B) (20B)
4-Cyclohexyl-C₅H₄OCH₃ Benzene	$ClCH_2COCl, AlCl_3, (CHCl_2)_2 \ XCH_2CH_2COCl, AlCl_3, C_6H_6$	XCH ₂ CH ₂ COC ₆ H ₅ ($X = Br$, Cl, I)	(136B)
C ₆ H ₅ NHCOCH ₃	XCH ₂ CH ₂ COCl, AlCl ₃ , CS ₂	4-(XCH2CH2CO)C6H4NHCOCH3 $(X = Br, Cl, I)$	(136B)
C ₆ H ₅ CH ₂ NHCHO	XCH ₂ CH ₂ COCl, AlCl ₃ , CS ₂	4- $(X \subset H_2 \subset H_2 \subset G)$ C ₆ H ₄ CH ₂ NHCHO (X = Br, Cl, I)	(136B)
C ₆ H ₅ NHCOCH ₂	BrCH ₂ CHBrCOCl, AlCl ₃ , CS ₂	4-(CH ₃ CONH)C ₆ H ₄ COCHBrCH ₂ Br	(84B)
Benzene Benzene	Cl_3CCOCl $F_3C(CF_2)_nCOCl$, $AlCl_3$	$C_6H_5COCCl_3$ $F_3C(CF_2)_nCOC_6H_5$, 33-44% (n = 0 to 4)	(90B) (160B)
Toluene	$F_3C(CF_2)_nCOCI$, AlCl ₅	$4-CH_3C_6H_4CO(CF_2)_nCF_3$, 21-66%	(160B)
1,3-(CH ₃) ₂ C ₆ H ₄	n -C _{δ} F ₁₁ COCl, Al(Hg) + Br ₂	(n = 0 to 4) 2,4-(CH ₃) ₂ C ₆ H ₃ CO-(n-C ₅ F ₁₁), 81%	(160B)
Benzene	CH₃SCH₂CH₂COCl, AlCl₃	CH ₃ SCH ₂ CH ₂ COC ₆ H ₅	(146B)
Benzene Benzene	HO ₂ CCH ₂ CO ₂ H, SiCl ₄ , AlCl ₃ C ₂ H ₅ O ₂ CCH ₂ CO ₂ H, SiCl ₄ , AlCl ₃	$CH_3COC_6H_5$, 44% 33% $C_2H_5O_2CCH_2COC_6H_5$ and some	(185B) (185B)
1,5-(Cyclohexyl) ₂ -2,4-(C ₂ H ₅ O) ₂ -	CH ₃ O ₂ CCH ₂ CH ₂ COCl, AlCl ₃ , C ₆ H ₆	$C_2H_5C_6H_5$ 2,4- $(C_2H_5O)_2$ -5-cyclohexyl-	(18B)
C_6H_2 1,5-(Cyclohexyl) ₂ -2,4-(C_2H_6O) ₂ -	CH ₃ O ₂ CCH ₂ CH ₂ CH ₂ COCl, AlCl ₃ , C ₆ H ₆	$C_6H_2COCH_2CH_2CO_2CH_3$ 2,4- $(C_2H_5O)_2$ -5-cyclohexyl-	(18B)
C_6H_2	C_6H_6	$C_6H_2COCH_2CH_2CO_2CH_3$	
Benzene	HO ₂ C(CH ₂) _n CO ₂ H, SiCl ₄ , AlCl ₃	$HO_2C(CH_2)_nCOC_6H_5$, 51-80% (n = 2, 3, 4, 8)	(185B)
$2,4-(C_2H_5O)_2C_6H_8$ -cyclohexyl	CH ₃ O ₂ CCH ₂ CH ₂ COCl, C ₂ H ₂ Cl ₄	2,4-(C ₂ H ₅ O) ₂ -5-cyclohexyl- C ₆ H ₂ COCH ₂ CH ₂ CO ₂ H	(19B)
1,2,3-(CH ₃ O) ₃ C ₆ H ₃ 2-Cyclohexyl-C ₆ H ₄ OCH ₃ (also for 4-)	C ₂ H ₅ O ₂ C(CH ₂) ₃ COCl, AlCl ₃ CH ₃ O ₂ C(CH ₂) ₄ COCl, AlCl ₃	2,3,4-(CH ₃ O) ₃ C ₅ H ₂ CO(CH ₂) ₃ CO ₂ C ₂ H ₅ 3-Cyclohexyl-4-CH ₃ O-C ₆ H ₃ CO-(CH ₂) ₄ - CO ₂ CH ₃	(112B) (19B, 20B)

Anomatia	OPEN-CHAIN ACYLATION (Ar	omatics) (Continued) Product	Reference
Aromatic Diphenvlmethane	Reagent $CH_3O_2C(CH_2)_2COCl$, AlCl $_3$, $C_2H_2Cl_4$	Proauct [4-CH ₃ O ₂ C(CH ₂) ₂ COC ₆ H ₄] ₂ CH ₂ , 70%	(1B)
Anisole $1,2,3-(CH_3O)_3C_6H_3$	CH ₃ O ₂ CCH(CH ₃)CO ₂ H, PPA CH ₃ O ₂ CCH(CH ₃)CO ₂ H, PPA	4-CH ₃ OC ₆ H ₄ COCH(CH ₃)CO ₂ CH ₃ 2,3,4-(CH ₃ O) ₃ C ₆ H ₂ COCH(CH ₃)CO ₂ CH ₃	(66B) (66B)
4-Cyclohexyl-C ₆ H ₄ OCH	$CH_3O_2CCH(C_0H_5)CH_2COCI$, AlCl ₃ ,	2-CH ₃ O-5-cyclohexyl-C ₆ H ₃ CO-	(20B)
Indan	C_8H_5 1-HO ₂ C-1-HO ₂ CCH ₂ -2-CH ₃ -	$CH_2CH(C_6H_5)CO_2CH_3$ 1- HO_2C -1-(5-indanyl-COCH ₂)-2- CH_3 -	(73B)
Tetralin	cyclopentane, AlCl3, C6H3NO2 1-HO2C-1-HO2CCH2-2-CH3-	cyclopentane 1-HO ₂ C-1-(5,6,7,8-H ₄ -2-naphthyl-COCH ₂)-	(73B)
Benzene	cyclopentane, AlCl ₃ , C ₆ H ₅ NO ₂ Succinic anhydride, AlCl ₃	2-CH ₃ -cyclopentane C ₆ H ₅ COCH ₂ CH ₂ CO ₂ H	(128B)
Toluene C ₂ H ₅ CH(CH ₃)C ₆ H ₅	Succinic anhydride, AlCl ₃ Succinic anhydride, AlCl ₃ , C ₂ H ₂ Cl ₄	4-CH ₃ C ₆ H ₄ COCH ₂ CH ₂ CO ₂ H 4-[C ₂ H ₅ CH(CH ₃)]C ₆ H ₄ COCH ₂ CH ₂ CO ₂ H, 67% (28 known compounds were prepared in 31-85% yields)	(128B) (144B)
$(C_2H_5)_2CHC_6H_5$ $C_6H_3(CH_2)_3CO_2C_2H_5$	Succinic anhydride, AlCl ₃ , C ₂ H ₂ Cl ₄ Succinic anhydride, AlCl ₃ , (CHCl ₂) ₂	4-[(C ₂ H ₅) ₂ CH]C ₆ H ₄ COCH ₂ CH ₂ CO ₂ H, 83% 4-[C ₂ H ₅ O ₂ C(CH ₂) ₃]C ₆ H ₄ COCH ₂ CH ₂ CO ₂ H	(149B) (45B)
$C_6H_5COCH_3$ Anisole	Succinic anhydride, AlCl ₃ Succinic anhydride, AlCl ₃	4-CH3COC6H4COCH2CH2CO2H 4-CH3OC6H4COCH2CH2CO2H	(128B) (128B)
C_6H_5Cl 1,3-(CH_3) C_6H_4 (also for 1,4-)	Succinic anhydride, AlCl ₃ Succinic anhydride, AlCl ₃	4-ClC ₆ H ₄ ČOCH ₂ CH ₂ CO ₂ H 2,4-(CH ₃) ₂ C ₃ H ₃ COCH ₂ CH ₂ CO ₂ H	(128B) (58B, 87B,
			(128B) (128B)
1,4-(CH ₃ O) ₂ C ₆ H ₄ 4-CH ₃ C ₆ H ₄ OCH ₃	Succinic anhydride, AlCl ₃ Succinic anhydride	2,5-(CH ₃ O) ₂ C ₅ H ₃ COCH ₂ CH ₂ CO ₂ H 2-CH ₃ O-5-CH ₃ -C ₅ H ₃ COCH ₂ CH ₂ CO ₂ H, 84%	(56B)
1.3- $(CH_3O)_2C_6H_4$ (also for 1,4-) 4-Cyclobutyl- $C_6H_4OCH_3$ 4-Cyclopentyl- $C_6H_4OCH_3$	Succinic anhydride Succinic anhydride Succinic anhydride	2,4-(CH ₃ O) ₂ C ₆ H ₃ COCH ₂ CH ₂ CO ₂ H 2-CH ₃ O-5-cyclobutyl-C ₆ H ₃ CO-CH ₂ CH ₂ CO ₂ H 2-CH ₃ O-5-cyclopentyl-C ₆ H ₃ CO-	(52B, 125B) (19B) (19B)
2-Cyclohexyl-C ₆ H ₄ OCH ₃	Succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	CH₂CH₂CO₂H 3-Cyclohexyl-4-CH₃O-C₀H₃CO-	(19B, 20B)
4-Cyclohexyl-C ₆ H ₄ OR	Succinic anhydride, AlCl ₅ , C ₆ H ₅ NO ₂	CH ₂ CH ₂ CO ₂ H 2-RO-5-cyclohexyl-C ₆ H ₃ COCH ₂ CH ₂ CO ₂ H	(19B)
1,2,4-(C ₂ H ₅) ₃ C ₆ H ₃	Succinic anhydride, AlCl ₃ , C ₂ H ₂ Cl ₄	$(R = CH_3, i-C_3H_7)$ 2,4,5- $(C_2H_5)_3$ - $C_6H_2COCH_2CH_2CO_2H_1$, 70 C_6	(149B)
$(\hat{2}-\hat{C}\hat{H}_3\hat{O}\hat{C}_6\hat{H}_4\hat{C}\hat{H}_2)_2$	Succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	3-(2-CH ₃ OC ₆ H ₄ CH ₂ CH ₂)-4-CH ₃ O-C ₆ H ₃ CO- CH ₂ CH ₂ CO ₂ H and [2-CH ₃ O-5- (HO ₂ CCH ₂ CO)-C ₆ H ₃ CH ₂] ₂	(20B)
3-CH ₃ -4-cyclohexyl-C ₆ H ₃ OCH ₃	Succinic anhydride	2-CH ₃ O-4-CH ₃ -5-cyclohexyl- C ₆ H ₂ COCH ₂ CH ₂ CO ₂ H	(19B)
2-Cyclohexyl-4-Cl-C ₆ H ₃ OCH ₃	Succinic anhydride	2-CH ₃ O-3-cyclohexyl-5-Cl- C ₆ H ₂ COCH ₂ CH ₂ CO ₂ H	(19B)
$1.3-(CH_3O)_2$ -4-cyclopentyl- C_6H_2	Succinic anhydride	2,4-(CH ₃ O) ₂ -5-cyclopentyl-	(19B)
$1,3-(CH_3O)_2-4$ -cyclohexyl- C_6H_3	Succinic anhydride	C ₆ H ₂ COCH ₂ CH ₂ CO ₂ H 2,4-(CH ₃ O) ₂ -5-cyclohexyl-	(19B)
$1,3-(CH_3O)_2-2$ -cyclohexyl- C_6H_3	Succinic anhydride	C ₆ H ₂ COCH ₂ CH ₂ CO ₂ H 2,4-(CH ₃ O) ₂ -3-cyclohexyl-	(19B)
[2,4-(CH ₃ O) ₂ C ₆ H ₃] ₂	Succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	C ₆ H ₂ COCH ₂ CH ₂ CO ₂ H [2.4-(CH ₃ O) ₂ -5-(HO ₂ CCH ₂ CH ₂ CO)-C ₆ H ₂] ₂	(18B)
Indan Tetralin	Succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂ Succinic anhydride, AlCl ₃	5-Indanyl-COCH ₂ CH ₂ CO ₂ H, ~100 ° _ℓ 5,6,7,8-H ₄ -2-naphthyl-COCH ₂ CH ₂ CO ₂ H	(55B) (128B)
Naphthalene 1-CH ₃ O-naphthalene (also for 2-)	Succinic anhydride, AlCl ₃ Succinic anhydride, AlCl ₃	1- and 2-Naphthyl-COCH ₂ CH ₂ CO ₂ H 1-(HO ₂ CCH ₂ CH ₂ CO)-4-CH ₃ O-naphthalene	(128B) (68B, 128B)
9,10-H ₂ -phenanthrene	Succinic anhydride, AlCl ₂	2-(HO ₂ CCH ₂ CH ₂ CO)-9,10-H ₂ -phenanthrene, 90%	(144B)
$2-C_2H_5-9,10-H_2$ -phenanthrene	Succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	3-C ₂ H ₅ -7-(HO ₂ CCH ₂ CH ₂ CO)- 9,10-H ₂ -phenanthrene	(36B)
4,5-Cyclopenteno-6,7,8,8a-H ₄ -acenaphthene	Succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	3-(HO ₂ CCH ₂ CH ₂ CO)-4,5-cyclopenteno- 6,7,8,8a-H ₄ -acenaphthene	(49B)
Dehydroabietic acid, ester	Succinic anhydride, AlCl $_3$, C $_6H_5NO_2$	6-(HO ₂ CCH ₂ CH ₂ CO)-dehydroabietic acid.	(174B)
Cumene	2-CH ₃ -succinic anhydride, AlCl ₃	methyl ester $4-(i-C_3H_7)C_6H_4COCH_2CH(CH_3)CO_2H$	(77 B)
$1,3-(CH_3)_2C_6H_4$	C ₆ H ₆ NO ₂ 2-CH ₃ -succinic anhydride, AlCl ₃ ,	$2,4\text{-}(CH_3)_2C_6H_3COCH_2CH(CH_3)CO_2H$	(79B)
4-Cyclohexyl-C ₆ H ₄ OCH ₈	C6H6NO2 2-CH3-succinic anhydride	2-CH ₃ O-5-cyclohexyl-	(19 B)
2,5-(CH ₃ O) ₂ C ₆ H ₃ OCH ₃	2-CH ₃ -succinic anhydride, AlCl ₃ ,	C ₆ H ₃ COCH ₂ CH(CH ₃)CO ₂ H 2,5-(CH ₃ O) ₂ -4-CH ₃ O-C ₆ H ₂ CO-CHR ₁	(4B)
2-(i-C ₃ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₅	C ₆ H ₅ NO ₂ or C ₂ H ₂ Cl ₄ 2-CH ₃ -succinic anhydride	$CHR_2CO_2H (R_1 \text{ or } R_2 = CH_3)$ 2- CH_3 -4- CH_3 O-5- $(i$ - $C_3H_7)$ - C_6H_2 CO-	(108B)
1.5-(C ₂ H ₆ O) ₂ -2,4-(cyclohexyl) ₂ -	2-CH ₃ -succinic anhydride, AlCl ₃ ,	$CH_2CH(CH_3)CO_2H$ 2,4- $(C_2H_5O)_2$ -5-cyclohexyl-	(18B)
$\frac{\mathrm{C_6H_2}}{1.3\text{-}(\mathrm{CH_3O})_2\mathrm{C_6H_4}}$	C ₆ H ₅ NO ₂ 2-C ₂ H ₅ -succinic anhydride, AlCl ₃ ,	$C_6H_2COCH_2CH(CH_3)CO_2H$ 2,5- $(CH_3O)_2C_6H_3COCH_2CH(C_2H_5)CO_2H$.	(17B)
Benzene 4-Cyclohexyl-C ₆ H ₄ OCH ₈	n-C₃H;NO₂ 2-C₅H₃-succinic anhydride 2-C₅H₃-succinic anhydride	85°C $C_8H_3COCHR_1CHR_2CO_2H$ (R ₁ or R ₂ = CH ₃) 2-CH ₃ O-5-cyclohexyl-C ₈ H ₃ CO-	(16B) (19B)
Cumene	2,3-(CH ₃) ₂ -succinic anhydride,	$CH_{2}CH(\acute{C}_{6}H_{5})C\acute{O}_{2}H$ 4- $(i$ - $C_{3}H_{7})C_{6}H_{4}CO[CH(CH_{3})]_{2}CO_{2}H$	(78B)
	$AlCl_3$, $C_6H_5NO_2$	2 077 5 (1 0 77) 0 77 00 1077 (017 -1 010 17	(76B)
$1-CH_3-4-(i-C_3H_7)-C_6H_4$	2,3-(CH ₃) ₂ -succinic anhydride,	$2-\mathrm{CH}_3-5-(i-\mathrm{C}_3\mathrm{H}_7)\mathrm{C}_6\mathrm{H}_3\mathrm{CO}-[\mathrm{CH}(\mathrm{CH}_3)]_2\mathrm{CO}_2\mathrm{H}$	(101)
$1-CH_3-4-(i-C_3H_7)-C_6H_4$ Anisole	2,3-(CH ₃) ₂ -succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂ H ₆ -phthalic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	2-CH ₃ -5-(<i>i</i> -C ₃ H ₇)C ₆ H ₃ CO-[CH(CH _{3.7}] ₂ CO ₂ H 1-HO ₂ C-2-(4-CH ₃ OC ₆ H ₄ CO)-cyclohexane	(126B)

OPEN-CHAIN ACYLATION (Aromatics) (Continued)

	OPEN-CHAIN ACTUATION (AR	oma resj (Continuea)	
Aromatic	Reagent	Product	Reference
Benzene (also for toluene)	α,α-(2'-CH ₃ -cyclopentano)-succinic anhydride, AlCl ₂	1-HO ₂ C-1-(C ₆ H ₅ COCH ₂)-2-CH ₃ -cyclopentane	(72B)
Benzene (also for toluene and tetralin)	α, α -(2'-C ₂ H ₅ -cyclopentano)-succinic anhydride, AlCl ₃	1-HO ₂ C-1-(C ₆ H ₅ COCH ₂)-2-C ₂ H ₅ - cyclopentane	(74B, 75B)
4-CH₃C _€ Ĥ₄OH	Maleic anhydride, AlCl ₃ , (CH ₂ Cl) ₂	2-HO-5-CH₃-C₀H₃COCH==CHCO₂H	(5B)
4-ClC ₆ H ₄ OCH ₃ 1,2-(HO) ₂ C ₆ H ₄	Maleic anhydride Maleic anhydride	$2-CH_3O-5-Cl-C_6H_3COCH=CHCO_2H$ $3.4-(HO)_2C_6H_3COCH=CHCO_2H$	(5B) $(5B)$
1,2-(CH ₃ O) ₂ C ₆ H ₄ (also for 1,3- and 1.4-)	Maleic anhydride, AlCl ₃ , CH ₂ Cl ₂	$3,4-(CH_3O)_2C_6H_3COCH=CHCO_2H$	(<i>5B</i>)
2,4-(CH ₃) ₂ C ₆ H ₃ OH (also for 3,4- and 3,5-)	Maleic anhydride	2-HO-3,5-(CH ₃) ₂ C ₆ H ₂ COCH=CHCO ₂ H	(5B)
3,5-(CH ₃) ₂ C ₆ H ₃ OC ₂ H ₅ 2-Cyclohexyl-C ₆ H ₄ OCH ₃ (also for 4-)	Maleic anhydride Maleic anhydride, AlCl ₃ , C ₆ H ₆ NO ₂	$2-C_2H_3O-4,6-(CH_3)_2C_6H_2COCH=CHCO_2H$ $3-Cyclohexyl-4-CH_3O-C_6H_3COCH=CHCO_2H$	$\begin{array}{c} (5B) \\ (19B) \end{array}$
1-Cyclohexyl-2,4-(CH ₃ O) ₂ -C ₆ H ₃	Maleic anhydride	2,4-(CH ₃ O) ₂ -5-cyclohexyl- C ₆ H ₂ COCH=CHCO ₂ H	(19B)
2-CH ₈ O-biphenyl 1,5-(C_2H_6O) ₂ -2,4-(cyclohexyl) ₂ - C_6H_2	Maleic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂ Maleic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	3-C ₆ H ₃ -4-CH ₃ -O-C ₆ H ₃ COCH=CHCO ₂ H 2,4-(C ₂ H ₄ O) ₂ -5-cyclohexyl- C ₆ H ₂ COCH=CHCO ₂ H	(20B) (18B)
Benzene	2-C ₆ H ₅ -maleic anhydride, AlCl ₃	$C_6H_5COC(C_6H_5)$ =CHCO ₂ H, 50% $C_6H_5COCH_2C(CO_2H)$ =CH ₂ , 63%	(114B) (115B)
Benzene (also for C ₆ H ₅ Br) Benzene	Itaconic anhydride, AlCl ₃ , CS ₂ Citraconic anhydride, AlCl ₃ , CS ₂	46% C ₆ H ₃ COCH(CH ₃)=CHCO ₂ H and 14% C ₆ H ₃ COCH=CHCO ₂ H	(115B)
Indan	1-Cyclopentene-1,2-dicarboxylic acid	2-(5-indanylcarbonyl)-1-cyclopentene-1-	(71B)
Tetralin	anhydride, AlCl ₃ , C ₆ H ₅ NO ₂ 1-Cyclopentene-1,2-dicarboxylic acid	carboxylic acid 1-(5,6,7,8-H ₄ -2-naphthylcarbonyl)-1-	(71B)
Benzene	anhydride, AlCl ₃ , C ₆ H ₅ NO ₂ Glutaric anhydride, AlCl ₃	cyclopentene-2-carboxylic acid C ₆ H ₆ CO(CH ₂) ₃ CO ₂ H	(46B)
$C_6H_5(CH_2)_4CO_2C_2H_5$ 2-CH ₃ O-naphthalene	Glutaric anhydride, AlCl ₃ , C ₂ H ₂ Cl ₄ Glutaric anhydride, AlCl ₃ , C ₆ H ₆ NO ₂	4- $[C_2H_5O_2C(CH_2)_4]C_6H_4CO(CH_2)_3CO_2H$ 1- and 6- $[HO_2C(CH_2)_3CO]$ -2- CH_3O -naphthale	(46B) ne (70B)
Benzene 2-Cyclohexyl-C ₆ H ₄ OC ₂ H ₅	3-CH₃-glutaric anhydride Sebacic anhydride	$C_bH_bCOCH_2CH(CH_3)CH_2CO_2H$, 90% 3-Cyclohexyl-4- $C_2H_bO-C_bH_3CO(CH_2)_3CO_2H$	(158B) (19B)
1,2-(CH ₃ O) ₂ C ₆ H ₄	Glutaric acid, BF ₃ ; or bis-chloride, AlCl ₃ , CS ₂	[3,4-(CH ₃ O) ₂ C ₆ H ₃ COCH ₂] ₂ CH ₂	(138B)
Benzene C ₆ H ₅ CH ₂ CH ₂ CO ₂ C ₂ H ₅ 1,3-(CH ₈ O) ₂ C ₆ H ₄ (also for bis-	CICOCH ₂ C(CH ₃) ₂ CH ₂ COCl. AlCl ₃ ClCO(CH ₂) ₄ COCl, AlCl ₃ , CS ₂ COCl ₂ , AlCl ₃ , C ₂ H ₂ Cl ₂	$(C_6H_6COCH_2)_2C(CH_3)_2$, 70% $[4-(C_2H_6O_2CH_2CH_2)C_6H_4COCH_2CH_2]_2$, 50% $[2,4-(HO)_2C_6H_3]_2CO$, $35-40\%$, and mono	(162B) (1B) (182B, 183 B)
C ₂ H ₅) Benzene	C ₆ H ₅ COCl, AlCl ₃ or SbCl ₅	ether $C_6H_6COC_6H_5$, 22 and $72\frac{C_6}{C_6}$	(142B)
Toluene (also for benzene) Toluene	C ₆ H ₅ COCl, AgClO ₄ , MgO C ₆ H ₅ COCl, AlCl ₃	4-CH ₃ C ₆ H ₄ COC ₆ H ₅ , 43 % (0% for benzene) 4-CH ₃ C ₆ H ₄ COC ₆ H _δ , 40-90%	(39B) (51B, 98B)
Phenol Anisole	C ₆ H ₅ CO ₂ H C ₆ H ₅ CO ₂ H, PPA; C ₆ H ₅ COCl, AlCl ₃ ,	4-HOC ₆ H₄COC ₆ H₅	(133B) (13B, 66B,
Amsor	CS_2 ; or $CF_3CO_2COC_6H_5$, CF_3CO_2H		133B)
$egin{array}{l} \mathbf{C_6H_5OC_2H_5} \ \mathbf{C_6H_5Cl} \end{array}$	C_6H_5COCl, I_2 $C_6H_5COCl, AlCl_3$	$4-C_2H_5OC_6H_4COC_6H_5$, 83% $4-ClC_6H_4COC_6H_5$, $9-72\%$ (also some 3-Cl)	(91B) (98B)
C ₆ H ₅ CH ₂ CH ₂ NHCOCH ₃ C ₆ H ₅ CH ₂ Si(CH ₃) ₅	C ₆ H ₆ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ C ₆ H ₅ COCl, AlCl ₃	4-C ₆ H ₅ COC ₆ H ₄ CH ₂ CH ₂ NHCOCH ₈ 4-C ₆ H ₅ COC ₆ H ₄ CH ₂ Si(CH ₃) ₃ , 65%	(177B) (141B)
$\mathrm{C_6H_5Si}(\mathrm{CH_3})_3$	C_6H_5COF , BF_3 , $CHCl_3$	$C_6H_5COC_6H_4Si(CH_3)_3$	(168B)
Biphenyl 4-ClC ₆ H ₄ OH	C_6H_5COCI , I_2 $C_6H_5CO_2H$, BF_3	4-C ₆ H ₅ CO-biphenyl, 50% 2-HO-5-Cl-C ₆ H ₃ COC ₆ H ₅ , 70%	(91B) (93B)
2-FC ₆ H ₄ OCH ₃ (also for 4-) 2-ClC ₆ H ₄ SCH ₃	C ₆ H ₅ COCl C ₆ H ₅ COCl	3-F-4-CH₃O-C ₆ H₃COC ₆ H₅ 3-Cl-4-CH₃S-C ₆ H₃COC ₆ H₅	(27B, 30B) (178B)
4-(t-C ₄ H ₉)C ₆ H ₄ OCH ₃ 1,2-(CH ₃ O) ₂ C ₆ H ₄	C_6H_5COCl , $ZnCl_2$, $(CHCl_2)_2$ C_6H_5COCl , $AlCl_3$, CS_2 ; $C_6H_5CO_2H$,	$2-CH_3O-5-(t-C_4H_9)C_6H_3COC_6H_5$ $3,4-(CH_3O)_2C_6H_3COC_6H_5$, $68-81\%$, (some	(107B) (91B, 129B,
, ,	PPA or I_2	demethylation) 2,4-(CH ₃ O) ₂ C ₆ H ₄ COC ₆ H ₅	150 <i>B</i> , 179 <i>B</i>) (129 <i>B</i>)
1,3-(CH ₃ O) ₂ C ₆ H ₄ [4-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)] ₂	C ₆ H ₅ CO ₂ H, PPA C ₆ H ₅ COCl, AlCl ₃ , C ₆ H ₅ NO ₂	2.+(Ch ₃ O) ₂ C ₆ H ₃ COC ₆ H ₅ 2-CH ₃ O-5-[4-CH ₅ OC ₆ H ₄ CH(C ₂ H ₅)- CH(C ₂ H ₅)]C ₆ H ₃ COC ₆ H ₅	(30B)
Mesitylene 1,2,3-(CH ₃ O) ₃ C ₆ H ₃	C_6H_5COCl, I_2 $C_6H_5CO_2H, PPA$	$2,4,6-(CH_3)_3C_6H_2COC_6H_5,65\%$ $2,3,4-(CH_3O)_3C_6H_2COC_6H_5$	$(91B) \\ (66B)$
$2,4,6-(i-C_3H_7)_3C_6H_2N(CH_3)_2$	C ₆ H ₅ COCl, AlCl ₃ , CS ₂	2,4,6-(<i>i</i> -C ₃ H ₇) ₃ -3-H ₂ N-C ₆ HCOC ₆ H ₅ , 25% 2.4,6-(<i>i</i> -C ₃ H ₇) ₃ -3-C ₂ H ₅ NH-C ₆ HCOC ₆ H ₆ , 69%	(173B) (173B)
2,4,6-(i-C ₂ H ₇) ₂ C ₆ H ₂ NHC ₂ H ₅ Naphthalene	C_6H_5COCl , AlCl $_3$, CS $_2$ C_6H_5COCl	70% 1-C ₆ H ₅ CO-naphthalene and 30% 2-C ₆ H ₅ CO-naphthalene	(97B)
2-CH₃O-naphthalene	C ₆ H ₅ COCl, I ₂	1-C ₆ H ₅ CO-2-CH ₃ O-naphthalene	(91B) (99B)
1-C ₆ H ₅ CH ₂ -naphthalene 1-HO-2-HO ₂ C-naphthalene (also	C_6H_8COCl , $AlCl_3$	4-C ₆ H ₆ CH ₂ -1-C ₆ H ₅ CO-naphthalene, 79% 1-HO-2-HO ₂ C-4-C ₆ H ₅ CO-naphthalene	(88B)
for ester) 2-HO-3-HO ₂ C-naphthalene (also		1-C ₆ H _{&} CO-2-HO-3-HO ₂ C-naphthalene	(88B)
for ester) 7-HO-coumarin	C ₆ H ₆ COCl, AlCl₃	7-HO-8-C ₆ H ₆ CO-coumarin	(120B)
4-CH ₃ -5-HO-coumarin 4-CH ₃ -5,7-(HO) ₂ -coumarin	C ₆ H ₅ COCl, AlCl ₃ C ₆ H ₅ COCl, AlCl ₃	$4-CH_3-5-HO-6-C_6H_5CO$ -coumarin $4-CH_3-5,7-(HO)_2-6,8-(C_6H_5CO)_2$ -coumarin	(140B) (140B)
8-HO-quinoline 1,4-(C ₆ H ₅) ₂ C ₆ H ₄	C ₆ H ₆ COCl C ₆ H ₅ COCl, AlCl ₃ , CS ₂	5- C_6H_5CO -8- HO -quinoline 1- C_6H_5 -4-[4-(C_6H_5CO) C_6H_4] C_6H_4	(172B) (25B)
Phenanthrene	C ₆ H ₅ COCl, AlCl ₃	3,6-(C ₆ H ₅ CO) ₂ -phenanthrene and isomers	(42B) (86B)
Dibenzofuran	C ₆ H ₅ COCl, AlCl ₃ , C ₆ H ₅ NO ₂	$2-C_6H_5CO$ -dibenzofuran and $1,7-(C_6H_5CO)_2$ -dibenzofuran	(501)

OPEN-CHAIN ACYLATION (Aromatics) (Continued)			
Aromatic 4,5-Cyclopenteno-6,7,8,8a-H ₄ - acenaphthene 4-(t-C ₄ H ₉)C ₆ H ₄ OCH ₃	Reagent C ₆ H ₅ COCl, AlCl ₃ , C ₆ H ₅ NO ₂ R-C ₆ H ₄ COCl, ZnCl ₂ , (CHCl ₂) ₂	Product 3-C ₆ H ₆ CO-4,5-cyclopenteno- 6,7,8,8a-H ₄ -acenaphthene 1-(RC ₆ H ₄ CO)-2-CH ₈ O-5-(t-C ₄ H ₉)-C ₆ H ₃	Reference (49B) (107B)
		R Yield, %c 4-CH ₃ 76 2-Cl 62 4-Cl 60 2-Br 68 3-Br 61 2-CH ₃ O 50 4-CH ₃ O 60	
$1,2,3,4,5$ -(CH $_3$) $_6$ C $_6$ H Phenanthrene	4-CH ₃ C ₆ H ₄ COCl, AlCl ₃ , CS ₂ 2-CH ₃ C ₆ H ₄ COCl, AlCl ₃	1-(4-CH $_3$ C $_6$ H $_4$ CO)-2,3,4,5,6-(CH $_3$) $_5$ -C $_6$ 3,6-(2-CH $_3$ C $_6$ H $_4$ CO) $_2$ -phenanthrene and	(161B) (42B)
Biphenyl Benzene Durene Toluene Anisole 2-ClC ₈ H ₄ OCH ₃ (also for 4-1) Durene Durene Anisole Phenol Benzene (also for toluene Anisole Durene Tetralin [4-CH ₃ OC ₆ H ₄ CH(C ₂ H ₅)] ₂ 2-(i-C ₈ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₃ 2-(i-C ₈ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₃	4-C ₆ H ₅ -C ₆ H ₄ COCl, AlCl ₃ , CS ₂ 2-BrC ₆ H ₄ COCl, AlCl ₃ 4-BrC ₆ H ₄ COCl 2-ClC ₆ H ₄ COCl 4-ClC ₆ H ₄ COCl, I ₂ 2-ClC ₆ H ₄ COCl, I ₂ 2-ClC ₆ H ₄ COCl, AlCl ₃ , CS ₂ (also 4-) 2-ClC ₆ H ₄ COCl, AlCl ₃ , CS ₂ (also 4-) 4-HOC ₆ H ₄ CO ₂ H, PPA 4-CH ₃ OC ₆ H ₄ COCl 4-CH ₃ OC ₆ H ₄ COCl 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , or I ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂ 4-CH ₃ OC ₆ H ₄ COCl, AlCl ₃ , CS ₂	isomers [4-C ₆ H ₅ -C ₆ H ₄] ₂ CO 2-Br-C ₆ H ₄ COC ₆ H ₅ 1-(4-BrC ₆ H ₄ CO)-2,3,5,6-(CH ₃) ₄ -C ₆ H 4-(2-ClC ₆ H ₄ CO)-C ₆ H ₄ CH ₃ 4-(4-ClC ₆ H ₄ CO)-C ₆ H ₄ CCH ₃ 1-(2-ClC ₆ H ₄ CO)-3-Cl-4-CH ₃ O-C ₆ H ₂ 1-(2-ClC ₆ H ₄ CO)-2,3,5,6-(CH ₃) ₄ -C ₆ H 1-(2-FC ₆ H ₄ CO)-2,3,5,6-(CH ₃) ₄ -C ₆ H, 80% 4-(4-HOC ₆ H ₄ CO)-6,H ₄ OCH ₃ 2-CH ₃ O-C ₆ H ₄ COC ₆ H ₄ OCH ₃ 2-CH ₃ O-C ₆ H ₄ COC ₆ H ₄ OCH ₃ 2-CH ₃ O-C ₆ H ₄ CO)-5,5,7,8-H ₄ -naphthalene 2-CH ₃ O-4-[4-CH ₃ OC ₆ H ₄ CO]-5,6,7,8-H ₄ -naphthalene 2-CH ₃ O-4-[4-CH ₃ OC ₆ H ₄ CO]-5-CH ₃ -CH(C ₂ H ₅)]C ₆ H ₃ COC ₆ H ₅ 2-(i-C ₃ H ₇)-4-(2-CH ₃ OC ₆ H ₄ CO)-5-CH ₃ -C ₆ H ₂ OCH ₃ , 40% 2-(i-C ₃ H ₇)-4-(4-CH ₃ OC ₆ H ₄ CO)-5-CH ₃ -	(33B) (163B) (62B) (54B) (91B) (30B) (63B) (61B) (133B) (133B) (54B) (91B, 133B) (60B) (38B) (30B) (156B)
Anisole	4-O ₂ NC ₆ H ₄ COCl, I ₂	C ₆ H ₂ OCH ₂ , 74% 4-(4-CH ₃ OC ₆ H ₄ CO)C ₆ H ₄ NO ₂	(91B)
Aromatic	Reagent	Product	Reference
Benzene (also for toluene and	Reagent 2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl	Product 2-H ₂ NC ₆ H ₄ COC ₆ H ₅	Reference (54B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene	2-(4-CH ₈ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4-[(CH ₈) ₈ Si]C ₆ H ₄ COCl 2-[(CH ₈) ₈ Si]C ₆ H ₄ COCl 3-[(CH ₈) ₈ Si]C ₆ H ₄ COCl, AlCl ₈	2-H ₂ NC ₆ H ₄ COC ₆ H ₅ 4-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 66 Resin 3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 43%	(54B) (11B) (11B) (11B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4-[(CH ₃) ₃ Si]C ₆ H ₄ COCl 2-[(CH ₃) ₃ Si]C ₆ H ₄ COCl 3-[(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂	2-H ₂ NC ₆ H ₄ COC ₆ H ₅ 4-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₈ , 66 ° _C Resin 3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₈ , 43 % 1-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-2,3,4,5,6-(CH ₃) ₅ -C ₈ , 82 ° _C 5-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-acenaphthene, 71 ° _C	(54B) (11B) (11B) (11B) (161B) (64B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene 4-CH ₃ C ₆ H ₄ OCH ₃	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4-[(CH ₃) ₃ Si]C ₆ H ₄ COCl 2-[(CH ₃) ₃ Si]C ₆ H ₄ COCl 3-[(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂	2- $H_2NC_6H_4COC_6H_5$ 4- $(4-CH_3C_6H_4CO)C_6H_4Si(CH_3)_3$, 66% Resin 3- $(4-CH_3C_6H_4CO)C_6H_4Si(CH_3)_3$, 43% 1- $[2.4.6-(CH_3)_3C_6H_2CO]-2.3,4,5,6-(CH_3)_5-C_5$, 82% 5- $[2.4.6-(CH_3)_3C_6H_2CO]$ -acenaphthene, 71% 1- $[2-CH_3-4-CH_3O-5-(i-C_3H_7)-C_6H_2CO]-2-CH_3O-5-CH_3-C_6H_3$, 35%	(54B) (11B) (11B) (11B) (161B) (64B) (156B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 2- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 3- [(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-	2-H ₂ NC ₆ H ₄ COC ₆ H ₅ 4-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 66 $\frac{6}{C}$ Resin 3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 43 $\frac{6}{C}$ 1-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-2,3,4,5,6-(CH ₃) ₅ -C ₅ , 82 $\frac{6}{C}$ 5-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-acenaphthene, 71 $\frac{6}{C}$ 1-[2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ CO]-	(54B) (11B) (11B) (11B) (161B) (64B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene 4-CH ₃ C ₆ H ₄ OCH ₂ 1,3-(CH ₃ O) ₂ C ₆ H ₄	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 2- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 3- [(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4.6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂	2-H ₂ NC ₆ H ₄ COC ₆ H ₅ 4-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 66% Resin 3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 43% 1-[2.4,6-(CH ₃) ₃ C ₆ H ₂ CO]-2,3,4,5,6-(CH ₃) ₅ -C ₆ , 82% 5-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-acenaphthene, 71% 1-[2-CH ₃ -4-CH ₃ O-5-(i-C ₃ H ₇)-C ₆ H ₂ CO]-2-CH ₃ O-5-CH ₃ -C ₆ H ₃ , 35% 1-[2-CH ₃ -4-CH ₃ O-5-(i-C ₃ H ₇)-C ₆ H ₂ CO]-2,4-(CH ₃ O) ₂ -C ₆ H ₃ , 60% [2-CH ₃ -4-CH ₃ O-5-(i-C ₃ H ₇)-C ₆ H ₂] ₂ CO, 69% 1-[2,5-(CH ₃) ₃ C ₆ H ₂ CO]-2,3,6-(CH ₃ O) ₃ -C ₆ H ₂ 2-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-furan, 83% 2-(2-CH ₃ O-5-Cl-C ₆ H ₃ CO)-furan 2-(3-Br-4-CH ₃ O-C ₆ H ₃ CO)-5-CH ₃ -thiophene 2-[4-(CH ₃) ₂ NCH ₂ CH ₂ CO]-furan 2-(3-Br-4-CH ₃ O-C ₆ H ₃ CO)-5-CH ₃ -thiophene 2-[4-(CH ₃) ₂ NCH ₂ CH ₂ CH ₄ CO]-pyridine 2-HO ₂ CC ₆ H ₄ CO ₆ H ₃ , 96% 1,4-(CH ₃) ₂ -2-(2-HO ₂ CC ₆ H ₄ CO)C ₆ H ₃ and	(54B) (11B) (11B) (11B) (11B) (161B) (64B) (156B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene 4-CH ₃ C ₆ H ₄ OCH ₃ 1,3-(CH ₃ O) ₂ C ₆ H ₄ 2-(i-C ₃ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₄ 1,4-(CH ₃ O) ₂ C ₆ H ₄ Mesitylene (also for durene 4-ClC ₆ H ₄ OCH ₃ 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) C ₆ H ₃ CH ₂ CH ₂ N(CH ₃) ₂ Benzene 1,4-(CH ₃) ₂ C ₆ H ₄ (also for 1,3-) Toluene Benzene and 24 homologs and	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 2- [(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ -[(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ -[(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4.6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4.6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O ₃ C ₆ H ₂ COCl 2-ClCO-furan AlCl ₃ , CS ₂ 2-ClCO-furan AlCl ₃ , CS ₂ 2-ClCO-furan 2-ClCO-thiophene 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene	$\begin{array}{l} 2\text{-}H_2NC_6H_4COC_6H_5\\ \\ 4\text{-}(4\text{-}CH_3C_6H_4CO)C_6H_4Si(CH_3)_8, 66\%\\ \\ Resin\\ 3\text{-}(4\text{-}CH_3C_6H_4CO)C_6H_4Si(CH_3)_8, 43\%\\ 1\text{-}[2,4,6\text{-}(CH_3)_3C_6H_2CO]\text{-}2,3,4,5,6\text{-}(CH_3)_5\text{-}C_8, 82\%\\ 5\text{-}[2,4,6\text{-}(CH_3)_3C_6H_2CO]\text{-}acenaphthene, 71\%\\ 1\text{-}[2\text{-}CH_3\text{-}4\text{-}CH_3O\text{-}5\text{-}(i\text{-}C_8H_7)\text{-}C_6H_2CO]\text{-}2\text{-}CH_3O\text{-}5\text{-}(i\text{-}C_3H_7)\text{-}C_6H_2CO]\text{-}2\text{-}CH_3O\text{-}5\text{-}(i\text{-}C_3H_7)\text{-}C_6H_2CO]\text{-}2,4\text{-}(CH_3O)_2\text{-}C_6H_3, 35\%\\ [2\text{-}CH_3\text{-}4\text{-}CH_3O\text{-}5\text{-}(i\text{-}C_3H_7)\text{-}C_6H_2CO]\text{-}2,4\text{-}(CH_3O)_2\text{-}C_6H_3, 60\%\\ [2\text{-}CH_3\text{-}4\text{-}CH_3O\text{-}5\text{-}(i\text{-}C_3H_7)\text{-}C_6H_2]_2CO, 69\%\\ \\ 1\text{-}[2,5\text{-}(CH_3)_2C_6H_3CO]\text{-}2,3,6\text{-}(CH_3O)_3\text{-}C_6H_2\\ 2\text{-}[2,4,6\text{-}(CH_3)_3C_6H_2CO]\text{-}furan, 83\%\\ 2\text{-}(2\text{-}CH_2O\text{-}5\text{-}Cl\text{-}C_6H_3CO)\text{-}furan\\ 2\text{-}(3\text{-}Br\text{-}4\text{-}CH_3O\text{-}C_6H_3CO)\text{-}5\text{-}CH_3\text{-}thiophene\\ 2\text{-}(4\text{-}(CH_3)_2\text{-}CG_6H_3CO)\text{-}5\text{-}CH_3\text{-}thiophene\\ 2\text{-}(4\text{-}(CH_3)_2\text{-}CG_6H_2CO_6H_3\text{-}C_6\text{-}G)\text{-}pyridine}\\ 2\text{-}HO_2CC_6H_4COC_6H_5, 96\%\\ \end{array}$	(54B) (11B) (11B) (11B) (161B) (64B) (156B) (156B) (156B) (156B) (30B) (30B) (30B) (30B) (30B) (177B) (185B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene 4-CH ₃ C ₆ H ₄ OCH ₃ 1,3-(CH ₃ O) ₂ C ₆ H ₄ 2-(i-C ₃ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₄ 1,4-(CH ₃ O) ₂ C ₆ H ₄ Mesitylene (also for durene) 4-ClC ₆ H ₄ OCH ₃ 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) C ₆ H ₅ CH ₂ CH ₂ N(CH ₃) ₂ Benzene 1,4-(CH ₃) ₂ C ₆ H ₄ (also for 1,3-) Toluene	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 2- [(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2.4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2.4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(i-C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(i-C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(i-C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(i-C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O ₃ C ₆ H ₂ COCl 2-ClCO-furan, AlCl ₃ , CS ₂ 2-ClCO-furan 2-ClCO-furan 2-ClCO-5-CH ₃ -thiophene	2-H ₂ NC ₆ H ₄ COC ₆ H ₆ 4-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₈ , 66 ° _C Resin 3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₈ , 43 % 1-[2,4,6-(CH ₃) ₈ C ₆ H ₂ CO]-2,3,4,5,6-(CH ₃) ₅ -C ₅ , 82 % 5-[2,4,6-(CH ₃) ₈ C ₆ H ₂ CO]-acenaphthene, 71 % 1-[2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ CO]- 2-CH ₃ O-5-CH ₃ -C ₆ H ₃ , 35 % 1-[2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ CO]- 2,4-(CH ₃ O) ₂ -C ₆ H ₃ , 60 % [2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂] ₂ CO, 69 % 1-[2,5-(CH ₃) ₂ C ₆ H ₃ CO]-2,3,6-(CH ₃ O) ₃ -C ₆ H ₂ 2-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-furan, 83 % 2-(2-CH ₂ O-5-Cl-C ₆ H ₃ CO)-furan 2-(3-Br-4-CH ₃ O-C ₆ H ₃ CO)-5-CH ₃ -thiophene 2-[4-(CH ₃)) ₂ C ₆ H ₃ CO]-5-CH ₃ -thiophene 2-[4-(CH ₃)) ₂ C ₆ H ₄ COC ₆ H ₃ CO]-5-CH ₃ -thiophene 2-[4-(CH ₃)) ₂ C ₂ C ₆ H ₄ COC ₆ H ₃ CO]-5-CH ₃ -thiophene 2-[4-(CH ₃)) ₂ C ₂ C ₆ H ₄ COC ₆ H ₃ -C ₆ H ₃ -CO]-furan 1-4% 3,3-bis-[2,5-(CH ₃) ₂ C ₆ H ₄ CO]C ₆ H ₃ and 1-4% 3,3-bis-[2,5-(CH ₃) ₂ C ₆ H ₄ CO]C ₆ H ₄ 1-HO ₂ C-2-ArCO-C ₆ H ₄ 3,6-(2-HO ₂ CC ₆ H ₄ CO) ₂ -phenanthrene and	(54B) (11B) (11B) (11B) (161B) (64B) (156B) (156B) (156B) (156B) (156B) (30B) (30B) (30B) (30B) (30B) (43B) (185B) (43B) (102B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene 4-CH ₃ C ₆ H ₄ OCH ₃ 1,3-(CH ₃ O) ₂ C ₆ H ₄ 2-(i-C ₃ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₄ 1,4-(CH ₃ O) ₂ C ₆ H ₄ Mesitylene (also for durene 4-ClC ₆ H ₄ OCH ₃ 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) C ₆ H ₅ CH ₂ CH ₂ N(CH ₃) ₂ Benzene 1,4-(CH ₃) ₂ C ₆ H ₄ (also for 1,3-) Toluene Benzene and 24 homologs and isomers	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 2- [(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 3- [(CH ₃) ₃ Si]C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)- C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,3,6-(CH ₃ O) ₃ C ₆ H ₂ COCl 2-ClCO-furan, AlCl ₃ , CS ₂ 2-ClCO-furan 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene 4-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene 2-ClCO-5-CH ₃ -thiophene	$\begin{array}{l} 2\text{-}H_2NC_6H_4COC_6H_5\\ \\ 4\text{-}(4\text{-}CH_3C_6H_4CO)C_6H_4Si(CH_3)_8, \ 66\%\\ \\ \text{Resin}\\ 3\text{-}(4\text{-}CH_3C_6H_4CO)C_6H_4Si(CH_3)_8, \ 43\%\\ 1\text{-}[2,4,6\text{-}(CH_3)_3C_6H_2CO]\text{-}2,3,4,5,6\text{-}(CH_3)_5\text{-}C_5, \ 82\%\\ 5\text{-}[2,4,6\text{-}(CH_3)_3C_6H_2CO]\text{-}\text{acenaphthene, }71\%\\ 2\text{-}CH_3\text{-}4\text{-}CH_3\text{-}0\text{-}5\text{-}(i\text{-}C_3H_7)\text{-}C_6H_2\text{-}CO]\text{-}}\\ 2\text{-}CH_3\text{-}0\text{-}5\text{-}CH_3\text{-}-GH_3, \ 55\%\\ 1\text{-}[2\text{-}CH_3\text{-}4\text{-}CH_3\text{-}0\text{-}5\text{-}(i\text{-}C_3H_7)\text{-}C_6H_2\text{-}CO]\text{-}}\\ 2\text{-}4\text{-}(CH_3\text{-}0)_2\text{-}C_6H_3, \ 60\%\\ [2\text{-}CH_3\text{-}4\text{-}CH_3\text{-}0\text{-}5\text{-}(i\text{-}C_3H_7)\text{-}C_6H_2]\text{-}2\text{C}, \ 69\%\\ 1\text{-}[2,5\text{-}(CH_3\text{-}0)_2\text{-}C_6H_3\text{-}CO]\text{-}furan, \ 83\%\\ 2\text{-}(2\text{-}CH_3\text{-}0\text{-}5\text{-}Cl\text{-}C_6H_3\text{-}CO]\text{-}furan\\ 2\text{-}[2,4\text{-}6\text{-}(CH_3)_3\text{-}C_6H_3\text{-}CO)\text{-}furan\\ 2\text{-}(3\text{-}Br\text{-}4\text{-}CH_3\text{-}0\text{-}C_6H_3\text{-}CO)\text{-}furan\\ 2\text{-}(3\text{-}Br\text{-}4\text{-}CH_3\text{-}0\text{-}C_6H_3\text{-}CO)\text{-}furan\\ 2\text{-}(3\text{-}Br\text{-}4\text{-}CH_3\text{-}0\text{-}C_6H_3\text{-}CO)\text{-}furan\\ 2\text{-}[4\text{-}(CH_3)_2\text{-}C_6H_3\text{-}CO)\text{-}5\text{-}CH_3\text{-}thiophene\\ 2\text{-}[4\text{-}(CH_3)_2\text{-}C_6H_4\text{-}CO]\text{-}gH_4\text{-}CO]\text{-}pyridine}\\ 2\text{-}H\text{-}0\text{-}2\text{C}_6H_4\text{-}C\text{-}C_6H_3\text{-}C_6H_4\text{-}CO]\text{-}G_6H_3\text{-}phthalide}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}(4\text{-}CH_3\text{-}C_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}(4\text{-}CH_3\text{-}C_6H_4\text{-}CO)\text{-}G_6H_3\text{-}phthalide}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiophen}\\ 1\text{-}H\text{-}0\text{-}2\text{-}2\text{-}4\text{-}C\text{-}G_6H_4\text{-}CO)\text{-}G_6H_4\text{-}lhiop$	(54B) (11B) (11B) (11B) (161B) (64B) (156B) (156B) (156B) (156B) (30B) (30B) (30B) (30B) (30B) (43B) (177B) (185B) (43B) (102B) (110B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene 4-CH ₃ C ₆ H ₄ OCH ₃ 1,3-(CH ₃ O) ₂ C ₆ H ₄ 2-(i-C ₃ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₄ 1,4-(CH ₃ O) ₂ C ₆ H ₄ Mesitylene (also for durene 4-ClC ₆ H ₄ OCH ₃ (also for 2-Cl) 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) C ₆ H ₃ CH ₂ CH ₂ CH ₂ N(CH ₃) ₂ Benzene 1,4-(CH ₃) ₂ C ₆ H ₄ (also for 1,3-) Toluene Benzene and 24 homologs and isomers Phenanthrene Benzene and 27 homologs and	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 2- [(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₂ -4-CH ₃ O ₃ C ₆ H ₂ COCl 2-ClCO-furan, AlCl ₃ , CS ₂ 2-ClCO-furan 2-ClCO-furan 2-ClCO-5-CH ₃ -thiophene	2-H ₂ NC ₆ H ₄ COC ₆ H ₅ 4-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₈ , 66 ° _C Resin 3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₈ , 43% 1-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-2,3,4,5,6-(CH ₃) ₅ -C ₅ , 82% 5-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-acenaphthene, 71 ° _C 1-[2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ CO]-2-CH ₃ O-5-CH ₃ -S-C ₆ -G ₃ H ₃ , 35% 1-[2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ CO]-2,4-(CH ₃ O) ₂ -C ₆ H ₃ , 60% [2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂] ₂ CO, 69% 1-[2,5-(CH ₃) ₂ C ₆ H ₃ CO]-2,3,6-(CH ₃ O) ₃ -C ₆ H ₂ 2-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-furan, 83% 2-(2-CH ₃ O-5-Cl-C ₆ H ₃ CO)-furan 2-(3-Br-4-CH ₃ O-C ₆ H ₃ CO)-furan 2-(3-Br-4-CH ₃ O-C ₆ H ₃ CO)-5-CH ₃ -thiophene 2-[4-(CH ₃) ₂ NCH ₂ CH ₂ C ₆ H ₄ CO]-pyridine 2-HO ₂ CC ₆ H ₄ COC ₆ H ₃ , 96% 1,4-(CH ₃) ₂ -2-((2-HO ₂ CC ₆ H ₄ CO)C ₆ H ₃ and 74% 3,3-bis-[2,5-(CH ₃) ₂ -C ₆ H ₃] phthalide 1-HO ₂ C-2-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ 3,6-(2-HO ₂ CC ₆ H ₄ CO) ₂ -phenanthrene and isomers 1-HO ₂ C-2-ArCO-3,4,5,6-Cl ₄ -C ₆ 9,10-(4-CH ₃ OC ₆ H ₄ CO)-pyridine ClCH ₂ CH(C ₆ H ₄ CO)-pyridine ClCH ₂ CH(C ₆ H ₄ CO)-pyridine	(54B) (11B) (11B) (11B) (161B) (64B) (156B) (156B) (156B) (156B) (30B) (30B) (30B) (30B) (30B) (43B) (102B) (102B) (110B)
Benzene (also for toluene and anisole) Toluene (also for anisole) Toluene (also for anisole) Toluene 1,2,3,4,5-(CH ₃) ₅ C ₆ H Acenaphthene 4-CH ₃ C ₆ H ₄ OCH ₅ 1,3-(CH ₃ O) ₂ C ₆ H ₄ 2-(i-C ₈ H ₇)-5-CH ₃ -C ₆ H ₃ OCH ₄ 1,4-(CH ₃ O) ₂ C ₆ H ₄ Mesitylene (also for durene) 4-ClC ₆ H ₄ OCH ₃ 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) 2-BrC ₆ H ₄ OCH ₃ (also for 2-Cl) 2-BrC ₆ H ₄ OCH ₃ (also for 1,3-) Toluene Benzene 1,4-(CH ₃) ₂ C ₆ H ₄ (also for 1,3-) Toluene Benzene and 24 homologs and isomers Phenanthrene Benzene and 27 homologs and isomers Anisole C ₆ H ₅ Cl	2-(4-CH ₃ C ₆ H ₄ SO ₂ NH)-C ₆ H ₄ COCl 4- [(CH ₃) ₃ Si]C ₆ H ₄ COCl 2- [(CH ₃) ₃ Si]C ₆ H ₄ COCl, AlCl ₃ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2,4,6-(CH ₃) ₃ C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ COCl, AlCl ₃ , CS ₂ 2-ClCO-furan, AlCl ₃ , CS ₂ 2-ClCO-furan, AlCl ₃ , CS ₂ 2-ClCO-furan, AlCl ₃ , CS ₂ 2-ClCO-furan 2-ClCO-5-CH ₃ -thiophene 3-ClCO-byridine, AlCl ₃ , C ₆ H ₅ NO ₂ Phthalic acid, SiCl ₄ , AlCl ₃ 1,2-(ClCO) ₂ C ₆ H ₄ , AlCl ₃ 1,2-(ClCO) ₂ C ₆ H ₄ , AlCl ₃ 2-ClCO-furan 2-ClCO-furan 3-ClCO-furan 3-ClCO-furan	2-H ₂ NC ₆ H ₄ COC ₆ H ₅ 4-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 66 ° _C Resin 3-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ Si(CH ₃) ₃ , 43 % 1-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-2,3,4,5,6-(CH ₃) ₅ -C ₅ , 82 % 5-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-acenaphthene, 71 ° _C 1-[2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ CO]-2-CH ₃ O-5-CH ₃ -S-C ₆ H ₃ , 35 % 1-[2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂ CO]-2,4-(CH ₃ O) ₂ -C ₆ H ₃ , 60 % [2-CH ₃ -4-CH ₃ O-5-(<i>i</i> -C ₃ H ₇)-C ₆ H ₂] ₂ CO, 69 ° _C 1-[2,5-(CH ₃) ₂ C ₆ H ₃ CO]-2,3,6-(CH ₃ O) ₃ -C ₆ H ₂ 2-[2,4,6-(CH ₃) ₃ C ₆ H ₂ CO]-furan, 83 % 2-(2-CH ₃ O-5-Cl-C ₆ H ₃ CO)-furan 2-(3-Br-4-CH ₃ O-C ₆ H ₃ CO)-furan 2-(3-Br-4-CH ₃ O-C ₆ H ₃ CO)-5-CH ₃ -thiophene 2-[4-(CH ₃) ₂ C ₂ C ₂ H ₄ CO ₂ H ₄ CO]-pyridine 2-HO ₂ CC ₆ H ₄ COC ₆ H ₃ CO, 6H ₄ CO]-pyridine 2-HO ₂ CC ₆ H ₄ COC ₆ H ₅ , 96 % 1,4-(CH ₃) ₂ -2(2-HO ₂ CC ₆ H ₄ CO)C ₆ H ₃ and 74 % 3,3-bis-[2,5-(CH ₃) ₂ -C ₆ H ₄ CO]-gH ₄ 1-HO ₂ C-2-(4-CH ₃ C ₆ H ₄ CO)C ₆ H ₄ 3,6-(2-HO ₂ CC ₆ H ₄ CO) ₂ -phenanthrene and isomers 1-HO ₂ C-2-ArCO-3,4,5,6-Cl ₄ -C ₆ 9,10-(4-CH ₃ OC ₆ H ₄ CO) ₂ -anthracene 2-HO ₂ C-3-(4-ClC ₆ H ₄ CO) ₂ -pyridine	(54B) (11B) (11B) (11B) (11B) (161B) (64B) (156B) (156B) (156B) (156B) (30B) (30B) (30B) (30B) (177B) (185B) (43B) (102B) (110B) (42B) (111B) (153B) (184B)

OPEN-CHAIN ACYLATION (Pseudoaromatics)			
Pseudoaromatic	Reagent CH ₃ COCl, AlCl ₂ , CS ₂	Product 1,4-(CH ₃) ₂ -3-CH ₃ CO-7-(i-C ₃ H ₇)-azulene, 18%	Reference (23C)
1,4-(CH ₃) ₂ -7-(<i>i</i> -C ₃ H ₇)-azulenc Furan		$^{1,+(CH_3)/2-3-CH_3}$ 2-CH ₃ CO-furan 3-RCO-4-HO-coumarin (R = CH ₃ , n-C ₅ H ₁₁ , n-	(12C) (1C)
4-HO-coumarin	RCOCI	C_7H_{15} , n - C_9H_{19} , $ClCH_2$, $C_6H_5CH_2$, $C_6H_5CH_2$ -	(10)
Pyrrole (also for indole) Pyrrole	HCON(CH ₈) ₂ , POCl ₅ H ₂ NCOCl H ₂ NCOCl	CH ₂ , C ₆ C ₅ CH=CH, C ₆ H ₅) 2-HCO-pyrrole, 83% 2-H ₂ NCO-pyrrole Yields of 60-90%	(18C) (22C) (22C)
R_4 N R_1	R_1 R_2	R_3 R_4	
R_3 R_2	CH2 H2NCC CH3 C2H4O2 C2H2O2C CH3 CH3 H2NCC CH4 C2H6O2	CH ₃ H ₂ NCO CC CH ₃ H ₂ NCO H ₂ NCO CH ₃ C ₂ H ₃ O ₂ C	
1,2- $(C_6H_3)_2$ -3- CH_3 -pyrrole Pyridine Pyridine Indole (similarly for 2- CH_3 , 2- C_6H_6 , 5- CH_3CO_2 , 5- $C_6H_3CH_2O$, 5,6- $(CH_3O)_2$, 6- CH_3CO_2 -7- CH_3O ,	H ₂ NCOCl HCON(CH ₃) ₂ , POCl ₃ C ₆ H ₆ N(CH ₃)CHO, POCl ₃ (COCl) ₂	1,2-(C_6H_6) ₂ -3- CH_7 -5- H_2 NCO-pyrrole 2-HCO-pyridine, low yield 2-HCO-pyridine, low yield 3-ClCOCO-indole	(22C) (14C) (14C) (19C)
and 1-benz[g]) 2-CH ₃ -pyrrocoline 2,3-(CH ₃)-pyrrocoline 2-CH ₃ - 4-HO-quinoline Thiophene (also for 2-Cl, 2-CH ₃ , 3-CH ₃ , 2-(t-C ₄ H ₉), 2-CH ₂ CONH)	$\begin{array}{c} C_6H_5N(CH_3)CHO, POCl_5, (CH_2Cl)_2 \\ C_6H_5N(CH_3)CHO, POCl_4, (CH_2Cl)_2 \\ CH_3COCl or (CH_3CO)_2O, AlCl_3 \\ HCON(CH_3)_2 \ or \ C_6H_5N(CH_3)CHO, \\ POCl_3 \end{array}$	2-CH ₃ -3-HCO-pyrrocoline 1-HCO-2,3-(CH ₃) ₂ -pyrrocoline 2-CH ₃ -3-CH ₃ CO-4-HO-quinoline 2-HCO-thiophene, 72-77 7	(17C) (17C) (21C) (7C)
2-(t-C ₄ H ₉)-thiophene 2-C ₆ H ₅ -thiophene 2-(3-ClC ₆ H ₄)-thiophene	$\begin{array}{l} C_6\overline{H}_5N(CH_3)CHO,POCl_3\\ C_6\overline{H}_5N(CH_3)CHO,POCl_3,C_6\overline{H}_5CH_3 \end{array}$	2-HCO-5- $(t$ -C ₄ H ₉)-thiophene, 80^{C} 2-HCO-5-C ₆ H ₅ -thiophene 2-HCO-5-(3-ClC ₆ H ₄)-thiophene	(20C) (8C) (8C)
2- $(C_6H_5CH = CH)$ -thiophene 2,4- $(C_6H_5)_2$ -thiophene	$HCON(CH_3)_2$, $POCl_3$, 1,2- $Cl_2C_6H_4$ $HCON(CH_3)_2$, $POCl_3$	2-HCO-5-(C_6H_5CH —CH)-thiophene 2-HCO-3,5-(C_6H_5) ₂ -thiophene, 88%	(15C) (8C, 16C)
2,4- $(4-CH_sC_6H_4)_2$ -thiophene 2,5- $(C_6H_8)_2$ -1,4-dithiadiene 2,4- $(C_6H_8)_2$ -selenophene (also for	HCON(CH ₃) ₂ , POCl ₃	2-HCO-3,5-(4- CH_3 C ₆ H ₄) ₂ -thiophene 2-HCO-3,5-(C ₆ H ₅) ₂ -thiophene, above 32% 2-HCO-3,5-(C ₆ H ₅) ₂ -selenophene	(8C) (16C) (8C)
ditolyl and dianisyl) Thiophene 2-(t-C ₄ H ₉)-thiophene	CF ₃ CO ₂ COCH ₃ RCOCl, SnCl ₄ , CS ₂	2-CH ₃ CO-thiophene. $88^{C_{\ell}}$ 2-RCO-5- $(t$ -C ₄ H ₈)-thiophene (R = CH ₃ , C ₂ H ₅ , n -C ₃ H ₇)	(4C) (20C)
2-(C ₆ H ₅ CH=CH)-thiophene	RCOCl, SnCl ₄ , C_6H_6	2-RCO-5-($C_6H_5CH=CH$)-thiophene (R = CH_3 ,	(15C)
2-(3-ClC $_6$ H $_4$)-thiophene 9-(2-Thenylide)fluorene R $_4$ $_{\sim}$ S $_{\sim}$ R $_1$	CH ₈ COCl, SnCl ₄ , CS ₂ CH ₈ COCl CH ₈ COCl, SnCl ₅ , C ₆ H ₆	C ₂ H ₃ , C ₆ H ₅) C ₂ H ₃ CO-5-(3-ClC ₆ H ₅)-thiophene 9-(5-CH ₃ CO-2-thenylidene)-fluorene Yields of 45–99%	(8C) (15C) (9C)
	R_1	$egin{array}{cccccccccccccccccccccccccccccccccccc$	
R_3 R_2	CH₃ CH C₂H₅ CH	3CO H C₂H₅ 3CO H t-C₄H₅ 3CO H t-C₄H₅	
2,5-(CH ₅) ₂ -thiophene 2,5-(t -C ₄ H ₅) ₂ -thiophene 2,5-(C ₂ H ₅) ₂ -3-(n -C ₃ H ₇)-thiophene (also for n -C ₄ H ₉ and n -C ₅ H ₁₁)	CH ₃ COCl, AlCl ₃ , CS ₂ CH ₃ COCl CH ₃ COCl, AlCl ₃	placement of t -C ₄ H ₉) 2.5-(CH ₃) ₂ -3-CH ₃ CO-thiophene, 75% 2.5-(t -C ₄ H ₉) ₂ -3-CH ₃ CO-thiophene 2.5-(C ₂ H ₅) ₂ -3-CH ₃ CO-4-(n -C ₃ H ₇)-thiophene, 40-5%	(3C) (20C) (5C)
2,4-(C ₆ H ₅) ₂ -thiophene (also for ditolyl)		2-CH ₃ CO-3,5-(C ₆ H ₅) ₂ -thiophene	(8C)
2,4-(C ₆ H ₆) ₂ -selenophene (also for ditolyl and dianisyl)		2-CH ₃ CO-3.5-(C ₈ H ₃) ₂ -selenophene	(8C) (8C)
2,4-(C ₆ H ₅) ₂ -thiophene (also for ditolyl)		2-C ₂ H ₅ CO-3,5-(C ₆ H ₅) ₂ -thiophene	(8C)
2,4- $(4$ - $CH_3C_6H_4)_2$ -selenophene 2,4- $(C_6H_8)_2$ -selenophene 2,5- $(C_2H_8)_2$ -thiophene	RCOCl, AlCl ₃ , CS ₂	2-C ₂ H ₅ CO-3,5-(4-CH ₃ C ₆ H ₄) ₂ -selenophene 2-(n -C ₃ H ₇)-3,5-(C ₆ H ₅) ₂ -selenophene 2.5-(C ₂ H ₅) ₂ -3-RCO-thiophene, yields from 78–92 $\frac{r_c}{C}$ (R = C ₂ H ₅ , n -C ₃ H ₇ , n -C ₄ H ₉ , n -C ₅ H ₁₁ , n -C ₆ H ₁₃ , n -C ₇ H ₁₅ , n -C ₉ H ₁₉ , n -C ₁₅ H ₃₁ , C ₆ H ₅ , and C ₄ H ₅ CH ₂)	(8C) (5C)
$2-C_2H_5$ -thiophene 2,5-(CH ₃) ₂ -thiophene	n-C ₆ H ₁₈ COCl n-C ₆ H ₁₈ COCl, SnCl ₄ , C ₆ H ₆ ; or n-	$C_{8}H_{3}CH_{2}/C_{1}$ 2- $(n-C_{6}H_{13}CO)$ -5- $C_{2}H_{5}$ -thiophene, 90% 2,5- $(CH_{3})_{2}$ -3- $(n-C_{6}H_{13}CO)$ -thiophene, 60–84%	(3C) (3C)
Thiophene Thiophene	$C_6H_{18}CO_2H, P_2O_5$ $n-C_{10}H_{21}COCl$ $(n-C_8H_7)CH(C_2H_5)(CH_2)_3COCl$	2- $(n$ - $C_{10}H_{21}CO)$ -thiophene. $80\frac{C_C}{C}$ 2- $[(n$ - $C_3H_7)CH(C_2H_3)(CH_2)_5CO]$ -thiophene, $87\frac{C_C}{C}$	(3C) (3C)
Thiophene 2,5- $(C_2H_b)_2$ -thiophene 2,5- $(C_2H_b)_2$ -thiophene	$\begin{array}{l} \text{CH}_3\text{CH} \!\!=\!\!\!\!\!=\!$	2-(CH ₃ CH=CHCO)-thiophene. 71% 2.5-(C ₂ H ₅) ₂ -3-[CH ₂ O ₂ C(CH ₂) ₂ CO]-thiophene 2.5-(C ₂ H ₅) ₂ -3-[C ₂ H ₅ O ₂ C(CH ₂) ₃ CO]-thiophene, 67%	(11C) (5C) (5C)
4,5,6,7-H ₄ -thianaphthene Thiophene (also for 2-C ₂ H ₅ , 2,5-	$\begin{array}{l} C_2H_5O_2C(CH_2)_3COCl.\ AlCl_5,\ CS_2\\ Succinic \ anhydride,\ AlCl_3,\ C_6H_5NO_2 \end{array}$	$2-(C_2H_5O_2C(CH_2)_2CO)-4,5,6,7-H_4$ -thianaphthene $2-(HO_2CCH_2CH_2CO)$ -thiophene	(6C) (3C)
$(CH_3)_2$, 2,5- $(CH_3)_2$ -3- C_2H_5) 2- $(n$ - C_7H_{15})-thiophene [also for n - $C_{11}H_{23}$, $(n$ - $C_3H_7)CH(C_2H_5)$ - $(CH_2)_4$]	Succinic anhydride, AlCl ₃ , C ₆ H ₅ NO ₂	2-(HO ₂ CCH ₂ CH ₂ CO)-5-(n-C;H ₁₅)-thiophene	(3C)

	OPEN-CHAIN ACYLATION (Pseudo	paromatics) (Continued)	
${\it Pseudoaromatic}$	Reagent	Product	Reference
2-Br-thiophene 2,5-(CH ₂) ₂ -thiophene (also for diethyl)	Succinic anhydride, AlCl $_{\rm s}$, C $_6H_5NO_2$ Succinic anhydride	2-(HO ₂ CCH ₂ CH ₂ CO)-5-Br-thiophene 2.5-(C ₂ H ₃) ₂ -3-(HO ₂ CCH ₂ CH ₂ CO)-thiophene, $60\frac{C_{C}}{C}$	(3C) (2C, 5C)
$2,5-(C_2H_5)_2$ -thiophene $4,5,6,7-H_4$ -thianaphthene	Glutaric anhydride, AlCl ₂ , $C_8H_5NO_2$ Glutaric anhydride, AlCl ₅ , $C_8H_5NO_2$	2,5- $(C_2H_3)_2$ -3- $[HO_2C(CH_2)_3CO]$ -thiophene, 75% 2- $[HO_2C(CH_2)_3CO]$ -4,5,6,7- H_4 -thianaphthene,	(5C) (6C)
2-Cl-thiophene 2-CH ₃ -5-C ₈ H ₃ -thiophene Thiophene	$C_6H_5COCl,\ I_2\ (also\ 4-Cl)$ $C_6H_5COCl,\ AlCl_3$ $4-XC_6H_5COCl$	78%. 2-C ₆ H ₆ CO-5-Cl-thiophene, 34%. 2-CH ₃ -3-C ₆ H ₆ CO-5-C ₆ H ₆ -thiophene 2-(4-XC ₆ H ₄ CO)-thiophene ($X = CH_3$, CH ₃ O,	(13C) (8C) (13C, 15C)
Thiophene	$1-C_2H_5O_2C-2-ClCO-3-O_2N-C_6H_5, SnCl_4, C_6H_6$	and CI) $1-C_2H_6O_2C-2$ -thenoyl- $3-O_2N-C_6H_3$, 51%	(10C)
Thiophene	S_1C_14 , C_6H_6 1-ClCO-2-C ₂ H ₅ O ₂ C-3-O ₂ N-C ₆ H ₈ , SnCl ₄ , C ₆ H ₆	1-Thenoyl-2- $C_2H_5O_2C$ -3- O_2N - C_6H_3 , 45%	(10C)
Thiophene	2-CICO-naphthalene, SnCl ₊	2-Thenoylnaphthalene	(15C)
OF	PEN-CHAIN ACYLATION (Aromatics	, Gattermann-Koch-Hoesch)	
.4romatic	Reagent	Product	Reference
$\label{eq:Tetralin} \begin{split} & \text{Tetralin} \\ & \text{2-C_6H}_{5^-}6\text{-HO-chroman} \\ & \text{2-C_6H}_{5^-}5\text{-CH}_{5^-}7\text{-HO-chroman} \\ & \text{2-C_6H}_{5^-}6\text{-CH}_{5^-}7\text{-HO-chroman} \\ & \text{2-C_6H}_{5^-}5\text{-CH}_{5^-}07\text{-(C_6H}_{5^-}\text{CH}_{2^-}\text{O)-chroman} \\ & \text{2-C_6H}_{5^-}6\text{-CH}_{5^-}07\text{-(C_6H}_{5^-}\text{CH}_{2^-}\text{O)-chroman} \\ \end{split}$	CO, HCl, AlCl ₅ , CuCl, C ₆ H ₆ CO, HCl, AlCl ₃ CO, HCl, AlCl ₃ CO, HCl, AlCl ₃ CO, HCl, AlCl ₃	2-HCO-5,6,7,8-H ₄ -naphthalene 2-C ₆ H ₅ -6-HO-8-HCO-chroman 2-C ₆ H ₅ -5-CH ₃ -7-HO-8-HCO-chroman 2-C ₆ H ₆ -6-CH ₃ -7-HO-8-HCO-chroman 2-C ₆ H ₅ -5-CH ₃ O-7-(C ₆ H ₅ CH ₂ O)-8-HCO-chroman	(9D) (14D) (14D) (14D) (14D)
2-C ₆ H ₅ -5-CH ₃ O-7-HO-8-CH ₃ - chroman	CO, HCl, AlCl ₃	$2-C_6H_5-5-CH_3O-6-HCO-7-HO-8-CH_3-chroman$	(AAD)
2-(Cyclohexyl)-C ₆ H ₄ OCH ₃ 2-CH ₃ O-biphenyl 2-C ₆ H ₃ CH ₂ -C ₆ H ₄ OCH ₃ 3.5-(CH ₃) ₂ C ₆ H ₃ OH 3.4-(CH ₃ O) ₂ C ₆ H ₃ OH 3.4-(CH ₃ O) ₂ C ₆ H ₃ C ₂ H ₃ 2.6-(HO) ₂ C ₆ H ₃ CO ₂ H 2-C ₆ H ₃ -5-HO-7-CH ₃ O-chroman 2-C ₆ H ₃ -7-HO-4-chromanone 1.2,3-(HO) ₃ C ₆ H ₃ 2-C ₂ H ₃ -3.5-(CH ₃ O) ₂ -C ₆ H ₂ OH 2-C ₆ H ₃ -5-HO-7-CH ₃ O-chroman 1.3-(HO) ₂ C ₆ H ₂ OH 2-C ₆ H ₃ -5-CH ₃ O-7-HO-chroman 1.3-(HO) ₂ -2,4-(CH ₃) ₂ -C ₆ H ₂ 2.4-(6-(HO) ₃ C ₆ H ₂ CH ₂ CH-(CH ₃) ₂ 2.4,6-(HO) ₃ C ₆ H ₂ CH ₂	Zn(CN) ₂ , HCl, AlCl ₃ Zn(CN) ₂ , HCl, AlCl ₃ Zn(CN) ₂ , HCl, AlCl ₃ HCN, HCl, AlCl ₃ HCN, HCl, AlCl ₃ Zn(CN) ₂ , HCl, C ₂ H ₅) ₂ O Zn(CN) ₂ HCN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O HCN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O HCN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O CH ₃ CN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O CH ₃ CN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O CH ₃ CN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O CH ₃ CN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O CH ₃ CN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O CH ₃ CN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O n-C ₅ H ₁₁ CN, HCl, ZnCl ₂ , (C ₂ H ₅) ₂ O (CH ₃) ₂ CHCH ₂ CN, HCl, ZnCl ₂	3-(Cyclohexyl)-4-CH ₃ O-C ₆ H ₃ CHO 3-C ₆ H ₃ -4-CH ₃ O-C ₆ H ₃ CHO 3-C ₆ H ₃ CH ₂ -4-CH ₃ O-C ₆ H ₃ CHO 2.6-(CH ₃) ₂ -4-HO-C ₆ H ₂ CHO, 45% 2-C ₂ H ₃ -4,5-(CH ₃ O) ₂ -C ₆ H ₂ CHO 2.4-(HO) ₂ -3-Br-C ₆ H ₂ CHO 2.4-(HO) ₂ -3-HCO-C ₆ H ₂ CO ₂ H 2-C ₆ H ₅ -5-HO-6-HCO-7-CH ₃ O-chroman 2-C ₆ H ₅ -7-HO-8-HCO-4-chromanone 2.3,4-(HO) ₃ -3-4,6-(CH ₃ O) ₂ -C ₆ HCOCH ₃ 2-HO-3-C ₂ H ₃ -4,6-(CH ₃ O) ₂ -C ₆ HCOCH ₃ 2-C ₆ H ₅ -5-HO-7-CH ₃ O-8-CH ₃ CO-chroman 2-C ₆ H ₅ -5-CH ₂ O-7-HO-8-CH ₃ CO-chroman 2-C ₆ H ₅ -5-CH ₂ O-7-HO-8-CH ₃ CO-chroman 2-C ₆ H ₆ -5-(CH ₃ O) ₃ -5-(CH ₃ O) ₂ -C ₆ HCO-(n-C ₅ H ₁₁), 33% 2.4.6-(HO) ₃ -3,5-(CH ₃) ₂ -C ₆ HCO-(n-C ₅ H ₁₁), 33% 2.4.6-(HO) ₃ -3-[(CH ₃) ₂ -C ₆ HCO-(H ₂ CH ₂]-C ₆ HCOCH ₂ CH ₂ CH ₃ -C ₆ HCOCH ₂ CH ₄ CH ₅	(1D) (1D) (1D) (2D) (16D) (8D) (6D) (14D) (14D) (13D) (13D) (14D) (14D) (14D) (15D) (15D)
1.3-(HO) ₂ C ₆ H ₄ 1.3.5-(HO) ₃ C ₆ H ₃ 1.3-(HO) ₂ C ₆ H ₄ 2.4.6-(HO) ₃ C ₆ H ₂ CH ₃ (also for 4-C ₂ H ₃ O) 1.3,5-(HO) ₃ C ₆ H ₃ (also for 2-CH ₃)	4-HOC ₆ H ₄ CH ₂ CN (also for 4-CH ₃ O) 4-HOC ₆ H ₄ CH ₂ CN (also for 4-CH ₃ O) 2-CH ₃ OC ₆ H ₄ CH ₂ CN, HCl. ZnCl ₂ 2-CH ₃ OC ₆ H ₄ CH ₂ CN, HCl. ZnCl ₂ (also for 2-C ₂ H ₆ O) 2,3-(CH ₃ O) ₂ C ₆ H ₃ CH ₂ CN, HCl. ZnCl ₂		
2,4-(HO) ₂ C ₆ H ₃ C ₂ H ₅ 2,4-(CH ₃ O) ₂ C ₆ H ₃ C ₂ H ₅ 2.3,4-(HO) ₃ C ₆ H ₂ C ₂ H ₅ 1,3-(HO) ₂ -2,4-(CH ₃) ₂ C ₆ H ₂	ClCH ₂ CN, HCl, ZnCl ₂ , $(C_2H_{\delta})_2O$ ClCH ₂ CN, HCl, ZnCl ₂ , $(C_2H_{\delta})_2O$ ClCH ₂ CN, HCl, ZnCl ₂ , $(C_2H_{\delta})_2O$ ClCH ₂ CN, HCl, ZnCl ₂ , $(C_2H_{\delta})_2O$, (also for Cl ₂ CHCN)	2.4-(HO) ₂ -5-C ₂ H ₅ -C ₆ H ₂ COCH ₂ Cl, 88% 2.4-(CH ₃ O) ₂ -5-C ₂ H ₅ -C ₆ H ₂ COCH ₂ Cl, 83% 2,3.4-(HO) ₃ -5-C ₂ H ₅ -C ₆ H ₅ -C ₆ HCOCH ₂ Cl, 60% 2.4-(HO) ₂ -3,5-(CH ₂) ₂ -C ₆ HCOCH ₂ Cl, 93%	(13D) (13D) (13D) (1D)
Phenol and 28 derivatives Anisole	R ₁ R ₂ NCH ₂ CN, HCl, AlCl ₃ , C ₆ H ₅ NO ₂	90%	(11D, 12D)
Anisoic 1.3-(HO) ₂ C ₈ H ₄ [also for 1.2-(CH ₃ O) ₂ and 1.4-(CH ₃ O) ₂]	$(CH_3SO_2)_2C=C=N-CH_3, HCl, AlCl_3, C_6H_5NO_2 (CH_5SO_2)_2C=C=N-CH_3, HCl, AlCl_3, C_6H_5NO_2$	4-CH ₃ OC ₅ H ₄ COCH(SO ₂ CH ₃) ₂ , poor yield 2,4-(HO) ₂ C ₅ H ₃ COCH(SO ₂ CH ₃) ₂ , 27%	(AD) (AD)
OPEN	-CHAIN ACYLATION (Pseudoaromo	atics, Gattermann-Koch-Hoesch)	
Pseudoaromatic	Reagent	Product	Reference
R_6 R_6 R_1 R_2 R_3	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	arly 3 R4 R5 R6 HO HO	(5E)
	$\mathrm{CF_3CO}$	CH ₃ O CH ₃ O CH ₃ O CF ₃ CO CH ₃ O	

OPEN-CHAIN ACYLATION (Pseudoaromatics, Gattermann-Koch-Hoesch) (Continued)

Pseudoaromatic	Reagent	Product	Reference
2,3- $(CH_3)_2$ -4- $C_2H_4O_2C$ -pyrrole Indole 2- CH_3 -indole 2- $C_2H_4O_2C$ -5,6- $(CH_3O)_2$ -indole	$Zn(CN)_2$ $Zn(CN)_2$, HCl, $(C_2H_5)_2O$ $Zn(CN)_2$, HCl, CHCl ₃ , $(C_2H_6)_2O$	2-HCO-3-C ₂ H ₅ O ₂ C-4,5-(CH ₃) ₂ -pyrrole 3-CF ₃ CO-indole (similarly for 3-CCl ₃ CO) 2-CH ₃ -3-HCO-indole 2-C ₂ H ₅ O ₂ C-3-HCO-5,6-(CH ₃ O) ₂ -indole	(2E) (4E) (3E) (1E)

OPEN-CHAIN ACYLATION (Aromatic, Sulfonylation)

Aromatic	Reagent	Product	Reference
Benzene	CH ₃ SO ₃ H, CH ₃ SO ₂ Cl or (CH ₃ SO ₂) ₂ O, several catalysts and solvents	$C_6H_5SO_2CH_3$, 6–77%	(1F, 4F)
Toluene	CH ₃ SO ₂ Cl, AlCl ₃	52% x-CH ₈ C ₈ H ₄ SO ₂ CH ₈ x % of total 2 49 3 15 4 36	(JF)
C ₆ H ₈ Br (also for Cl and F) Mesitylene Benzene (also toluene) 1-CH ₃ O-naphthalene	CH3SO2Cl, AlCl3 CH3SO2Cl, AlCl3 C6H5CH=CHSO2Cl, AlCl3 C6H5SO2Cl, AlCl3	4-BrC ₆ H ₄ SO ₂ CH ₃ , 56% 2,4,6-(CH ₃) ₃ C ₆ H ₂ SO ₂ CH ₃ C ₆ H ₅ CH=CHSO ₂ C ₆ H ₅ , 55% 1-C ₆ H ₆ SO ₂ -4-CH ₃ O-naphthalene	$(4F) \ (4F) \ (3F) \ (2F)$

RING-CLOSURE ACYLATION (Aromatics)

acetonitriles gave the best yields when the AlCl₃ phenol ratio was 2.25. A review discussion of this reaction was published by Ebine (28A).

Methanesulfonvlations of toluene and chlorobenzene have been carefully studied (103A). Results indicate that a halogen is a more powerfully orienting substituent than a methyl group. In the case of toluene, the reaction is much less selective than with acetylation.

Cyclization of 1-benzyl-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid or the corresponding chloride gives a number of elimination and rearrangement products in addition to the expected spiroketone (106A).

Ring-closure acylation with ω -phenyl carboxylic acid chlorides shifts from the ortho to the para position as soon as sterically permitted (44A). The yield for the octamethylene chain derivative is very low because the carbonyl group is constrained to a position perpendicular to the plane of the ring and thus prevented from participating in resonance. High dilution techniques have given excellent yields of benzocycloöctanones (83A). Longer methylene chains gave dimeric and trimeric (large ring) products.

Fries rearrangements of salicylic acid derivatives indicate that the reaction is not hindered by ortho substituents (7A). Brändström (9A) has discussed the Fries rearrangement on the premise that Oacylation is fast and reversible while C-acylation is slow and irreversible. Nucleophilic solvents such as m-xylene and anisole can effectively compete for migrating acyl groups (58A). Maximum yields of ortho isomers are obtained at temperatures near 120° C.

Product and Reagent	Reference
3-CH ₃ -1-indanone, H ₃ PO ₄ , 87%	(42G)
$3-C_6H_5-1$ -indanone, AlCl ₃ , 74%	(19G)
3-CH ₃ O-1-indanone, PPA, 85-95% [also for 5-CH ₃ O, 6-CH ₃ O, and 4,5-	·
$(CH_3O)_2$	(75G)
(3-HO ₂ C-1-indanone), HF, little reaction	(7G)
$3-[4-(CH_3)_2NC_6H_4]-1-indanone, AlCl_3$	(26G)
$3-(C_6H_5CONHCH_2CH_2)-1$ -indanone, AlCl ₃	(53G)
$2-C_6H_5-3-CH_3-1$ -indanone, H_2SO_4	(47G)
$2-C_6H_6$ -3-benzylidine-1-indanone, H_2SO_4	(47G)
$2,2-(C_6H_5)_2-1$ -indanone, 70%	(<i>78G</i>)
3-HO ₂ C-5-CH ₃ O-1-indanone, HF or AlCl ₃ (also 7-CH ₃ O)	(<i>7G</i>)
3-HO ₂ C-6-C ₂ H ₅ -1-indanone, HF or AlCl ₃	(7G)
3-HO ₂ CCH ₂ -4-O ₂ N-1-indanone, AlCl ₈	(30G)
4,5-(CH ₃ O) ₂ -1-indanone, SnCl ₄	(43G)
2-R ₁ -x-R ₂ -1-indanone, PPA	(48G)

\mathbf{R}_1	x - K_2	
C_6H_5	5-CH ₃ O	40%
C ₆ H ₅	6-CH ₃ O	20%
C_6H_5	7-CH₃O	, 0
C_6H_5	5.6-(CH ₃ O) ₂	30%
3-CH ₃ OC ₆ H ₄	H	_
$4-CH_3OC_6H_4$	H	
$3,4-(CH_3O)_2C_6H_3$	H	
3.4-(CH ₃ O) ₂ C ₆ H ₃	$5.6-(CH_3O)_2$	

3,4-(CH ₃ O) ₂ C ₆ H ₃ H 3,4-(CH ₃ O) ₂ C ₆ H ₃ 5,6-(CH ₃ O) ₂	
Spiro[fluorene-9,2'-indan-1'-one], 60%	(78G, 79G)
$2,2,3-(C_6H_5)_3-1$ -indanone, 50%	(78G)
$4-C_2H_3-6,7-(CH_3O)_2-1-indanone, H_2SO_4, 84\%$	(71G)
$3-HO_2C-5.6-(CH_3O)_2-1-indanone$, HF or AlCl ₃ , $38-100\%$	(7G)
3-HO-thianaphthene, HF (enol form) [also for 5-CH ₃ , 4.7-(CH ₃) ₂ , and 5.6,7-	
Cl_3	(20G)
3-HO-9-Cl-naphtho[1,2-b]thiophene, HF, 89%	(20G)
9-Fluorenone, H ₂ SO ₄	(1G)
1-HO ₂ C-9a-ĆH ₃ -1,2,4a,9a-H ₄ -9-fluorenone, H ₂ SO ₄	$(\mathcal{I}G)$
cis-1,2,3,4,4a,9a-H ₅ -9-fluorenone	(11G)
2-CH ₃ O-8a-CH ₃ -4b,5,6,7,8,8a-H ₆ -9-fluorenone, SnCl ₄ , 15-81 %	(64G)
3-HO ₂ C-6,7-(CH ₂) ₄ -1-indanone	(57G)
2-R-4,5-benzindan-1-one, HF (R = CH ₃ , C ₂ H ₅ , n -C ₃ H ₇ , n -C ₄ H ₃	(5G)
3-R-4,5-benzindan-1-one, HF, low yield (R = CH_3 , C_2H_5 , n - C_3H_7 , n - C_4H_4)	(∂G)
3'-CH ₃ O-4,5-benzindan-1-one, PPA, AlCl ₃ or SnCl ₄	(33G)
3-HO ₂ C-6, ⁷ -benzindan-1-one, HF, FSO ₃ H or AlCl ₃	(57G)
5-Br-1-acenaphthenone, AlCl ₃ , 55%	(29G)
6-CH ₃ O-1-acenaphthenone, PPA or AlCl ₃	(33G)
8-CH ₃ O-1-acenaphthenone, PPA	(<i>33G</i>)
5-Aza-2a,3,4,5-H ₄ -1,4-dioxoacenaphthene	(30G)
1-Oxo-3,4-(CH ₂) ₄ -indan, PPA, AlCl ₃ or SnCl ₄ , 83-92%	(4G, 23G)
1'-Oxo-4,5-cyclopentenoacenaphthene, SnCl ₄	(22G)
1'-Oxo-4,5-cyclopenteno-6,7,8,8a-H ₄ -acenaphthene, SnCl ₄	(21G)
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RING-CLOSURE ACYLATION (Aromatics) (Continued)

Product and Reagent	Reference
15H-6,7,16,17-H ₄ -15-oxo-cyclopenta[a]phenanthrene 11H-10a-CH ₃ -11-oxo-6b,7,8,9,10,10a-H ₆ -benzo[a]fluorene, SnCl ₄ , 87% 13H-12-HO ₂ C-13-oxo-dibenzo[a,g]fluorene, AlCl ₃ 9H-8-HO ₂ C-9-oxo-naphtho[2,1-c]fluorene	(છેઇG) (64G) (12G) (12G)
7H-6-HO ₂ C-7-oxo-benzo[g]naphtho[1,2-c]fluorene, HF 7H-6-HO ₂ C-7-oxo-benzo[i]naphtho[1,2-c]fluorene, HF 9H-8-HO ₂ C-9-oxo-benzo[i]naphtho[2,1-c]fluorene, HF or AlCl ₃ 1-Tetralone, PPA or SnCl ₄ , 80-90%	(12G) (12G) (12G) (27G, 49G
4-CH ₃ -1-tetralone, AlCl ₃ , 87% 7-CH ₃ -1-tetralone, PPA, 88% 2-C ₆ H ₅ -1-tetralone, nearly quantitative 4-C ₆ H ₅ -1-tetralone, AlCl ₃ , 93%	(63G) (27G) (13G) (83G)
4-HO ₂ C-1-tetralone, PPA, 80% 2,7-(CH ₃) ₂ -1-tetralone, AlCl ₃ 4,6-(CH ₃) ₂ -1-tetralone, 92% 5,8-(CH ₃) ₂ -1-tetralone, PPA, 93%	(58G) (86G) (63G) (27G, 28G
3-HO ₂ C-4-CH ₃ -1-tetralone, H ₂ SO ₄ 2-(CH ₃ CCl=CHCH ₂)-5-CH ₃ O-1-tetralone, PCl ₃ , 61% 4-CH ₃ -7-CH ₃ O-1-tetralone, AlCl ₃ , 44% 5.8-(CH ₃ O) ₂ -1-tetralone, H ₂ SO ₄ , 68%	(77G) (73G) (80G) (60G)
[2,5,7-(CH ₃) ₃ -1-tetralone], H ₃ PO ₄ , I ₂ , P 4,5,7-(CH ₃) ₃ -1-tetralone, 88% 4,6,7-(CH ₃) ₃ -1-tetralone, 85% 5,7,8-(CH ₃) ₃ -1-tetralone, SnCl ₄ , 82%	(40G) (51G, 63G) (81G) (10G)
2,3-(CH ₃) ₂ -7-(i -C ₃ H ₇)-1-tetralone, AlCl ₃ 2.4-(CH ₃) ₂ -7-(i -C ₃ H ₇)-1-tetralone, AlCl ₃ or [H ₃ PO ₄ , I ₂ , P] 3.8-(CH ₃) ₂ -5-(i -C ₃ H ₇)-1-tetralone, AlCl ₃ 3-HO ₂ C-4,4-(CH ₃) ₂ -1-tetralone, H ₂ SO ₄	(39G) (38G) (56G) (77G)
2,5-(CH ₃) ₂ -7-CH ₃ O-1-tetralone, AlCl ₃ 4,7-(CH ₃) ₂ -5-CH ₃ O-1-tetralone, POCl ₃ 4,7-(CH ₃) ₂ -6-CH ₃ O-1-tetralone, H ₂ SO ₄ 2-C ₂ H ₃ -5,8-(CH ₃ O) ₂ -1-tetralone, SnCl ₄ , 94%	(56G) (56G) (56G) (10G)
5.8-(HO) ₂ -1.4-naphthoquinone, AlCl ₃ , NaCl 5-HO-8-Cl-1.4-naphthoquinone 2.4.5,7-(CH ₃) ₃ -1-tetralone, AlCl ₃ or HI, P 2.3,5-(CH ₃) ₃ -8-(i-C ₃ H ₇)-1-tetralone, AlCl ₃	(9G) (9G) (40G) (41G)
2,5,8-(CH ₃) ₃ -7-CH ₃ O-1-tetralone, H ₂ SO ₄ 3,5,8-(CH ₃) ₂ -7-CH ₃ O-1-tetralone, H ₂ SO ₄ 2,5-(CH ₃) ₂ -7-CH ₃ O-8-(i -C ₃ H ₇)-1-tetralone, AlCl ₃ 2-CH ₃ -3-C ₂ H ₄ O ₇ C-6,7-(CH ₃ O) ₂ -1-tetralone, PPA	(8G) (8G) (56G) (82G)
3-C ₂ H ₈ O ₂ C-5-Br-7,8-(CH ₃ O) ₂ -1-tetralone, PPA [2,3,4,5-(CH ₃) ₄ -8-(<i>i</i> -C ₃ H ₇)-1-tetralone], H ₃ PO ₄ , I ₂ , P 3-HO ₂ C-4-[3,4,5-(CH ₃ O) ₃ C ₆ H ₂]-6,7-(CH ₂ O ₂)-1-tetralone, AlCl ₃ 4-Chromanone, PPA	(82G) (37G) (31G) (59G)
6-C ₆ H ₃ -4-chromanone, PPA 7-CH ₃ O-4-chromanone, PPA 6-Cl-4-chromanone, H ₂ SO ₄ 6-O ₂ N-4-chromanone, H ₂ SO ₄ , PPA or POCl ₃	(59G) (59G) (46G) (46G)
4-Oxo-1,4-H ₂ -quinoline 1-C ₈ H ₅ -4-oxo-1,2,3,4-H ₄ -quinoline, PPA 1-(4-CH ₃ C ₆ H ₄ SO ₂)-4-oxo-6-Cl-1,2,3,4-H ₄ -quinoline, POCl ₃ , low yield (also for 6-Br)	(2G) (46G) (46G)
4-Oxo-thiachroman, PPA 8-CH ₃ -4-oxo-thiachroman, H ₂ SO ₄ 1-Oxo-trans-3,4-cyclopentano-1,2,3,4-H ₄ -naphthalene, AlCl ₃ 1-C ₆ H ₃ CO-5-oxo-1,2,2a,3,4,5-H ₆ -benz[cd]indole, AlCl ₃ (also for 1-CH ₃ CO)	(46G) (46G) (84G) (54G)
1-Oxo-1,2,3,4,5,6,7,8-H ₈ -anthracene, SnCl ₄ , 95% 4-CH ₃ -1-oxo-1,2,3,4,5,6,7,8-H ₈ -anthracene, 80% 1,4-(CH ₃) ₂ -9-[2,5-(CH ₃) ₂ C ₆ H ₃]-10-oxo-9,10-H ₂ -anthracene, ZnCl ₂ , NaCl 1,3-(CH ₃) ₂ -9-[2,4-(CH ₃) ₂ C ₆ H ₃]-10-oxo-9,10-H ₂ -anthracene, ZnCl ₂ , NaCl	(75G) (55G) (17G) (17G)
1.5-Dioxo-4,8,10-(CH ₈) ₃ -1,2,3,4,5,6,7,8-H ₈ -anthracene, PPA, 63% 9,10-Anthraquinone-9-Cl ⁴ , H ₂ SO ₄ 1-Oxo-1,2,3,4,5,6,7,8-H ₈ -phenanthrene 9-Oxo-1,2,3,4,4a,9,10, <i>trans</i> -10a-H ₈ -phenanthrene, HF or H ₂ SO ₄ 8-CH ₃ -1-oxo-1,2,3,4-H ₄ -phenanthrene	(62G) (72G) (75G) (11G)
10a-HO ₂ C-9-oxo-1,2,4a,9,10,10a-H ₆ -phenanthrene, H ₂ SO ₄ , 100% 9-CH ₃ O-1-oxo-1,2,3,4-H ₄ -phenanthrene, H ₂ SO ₄ 2,8-(CH ₃ O) ₂ -1-oxo-1,2,3,4-H ₄ -phenanthrene 3-(HO ₂ CCH ₂ CH ₂)-6-CH ₃ O-4-oxo-1,2,3,4-H ₄ -phenanthrene, H ₂ SO ₄ (also for	(85G) (1G) (33G) (25G) (33G)
7-CH ₃ O, 8-CH ₃ O and 9-CH ₃ O; using H ₂ SO ₄ , PPA or SnCl ₄) 2.8-(CH ₃) ₂ -5-CH ₃ O-1-oxo-1,2,3,4-H ₄ -phenanthrene, SnCl ₄ 2-CH ₃ -7-CH ₃ O-1,9-dioxo-1,2,3,4,4a,9,10,10a-H ₈ -phenanthrene, AlCl ₃ 1-CH ₃ O ₂ CCH ₂ -2-CH ₃ -2-CH ₃ O ₂ C-7-CH ₃ O-9-oxo-1,2,3,4,4a,9,10,10a-H ₅ -phenanthrene, AlCl ₃	(25G) (35G) (50G)
Perinaphthan-1-one, 83% 2-R-perinaphthan-1-one, HF (R = CH ₃ , C ₂ H ₅ , n-C ₃ H ₇ , n-C ₄ H ₉) 3-R-perinaphthan-1-one, HF (R = CH ₃ , C ₂ H ₅ , n-C ₃ H ₇ , n-C ₄ H ₉) (some dehydrogenation)	$^{(65G)}_{(5G)}_{(6G)}$
7-CH ₃ O-perinaphthan-1-one, PPA, H ₂ SO ₄ or SnCl ₄ (also for 9-CH ₃ O)	(33G)

(85A). The same investigators found that the presence or absence of solvent made little difference. Gerecs and coworkers (32A-34A) have accumulated evidence that hydrochloric acid plays an important role in the Fries rearrangement.

In lubricating oils rich in aromatics, the more reactive aromatics can be removed or rendered harmless by pretreatment with a liquid alkylating catalyst (62.4). The remaining aromatics can be alkylated using a solid catalyst with an olefin or alkyl halide.

Hydrogen transfer reactions with alkanes and olefins permit direct utilization of petroleum fractions to produce alkylbenzenes derived from the alkanes (50.4, 60.4, 70.4, 81.4).

Mixed cresols react with isobutylene to give di-tert-butyl derivatives (21A). Benzyl chloride and alcohol undergo polycondensation to give resins (52A). Dicarboxylic esters have been used as alkylating agents (26A). Benzene is alkylated in good yield with a complex boron trifluoride-phosphoric acid-water catalyst to give a mixture of mono- and dialkylation (100A). Dodecylbenzene is obtained from benzene and propylene tetramer in yields up to 73% (86A). Excess tetramer leads to side reactions involving fragmentation, hydrogen transfer, polymerization, cyclization, and polyalkylation. Propylene polymer reacts similarly (67.4). An attempted Friedel-Crafts reaction of anisole with ethyl chloromaleate was unsuccessful (93.4).

A liquid-liquid countercurrent system was used to effect continuous reaction between benzene and dodecyl chloride (75.4). The alkylation mixture is passed upward through a column of liquid catalyst. The product is removed at the top. The catalyst is gravity separated and recycled.

Zinc chloride supported on alumina gives fair yields of alkylbenzenes at 200° to 300° C. (88A, 89A). Silica-alumina catalysts at 200° to 500° C. have been used rather frequently (28A, 57A, 64A, 92A, 705A).

Alkyl halides with aluminum metal or alkylaluminum halides seem to give fair results (90.4, 91.4, 107.4, 108.4). Top-chiev and associates have made extensive study of the catalyst system, aluminum dichloride hydrogen sulfate (45.4, 97.4, 99.4). This catalyst appears to be deactivated by impurities in the reactants. Its failure to isomerize n-propyl chloride is taken as evidence that the isomerization actually occurs during the alkylation step.

Good yields in alkylations have been obtained using titanium tetrachloride (23A). Silicon tetrafluoride is relatively ineffective even at elevated temperatures with high pressures (98A). Of a series of

metal oxides in conjunction with phosphoric acid, only cupric oxide was an effective catalyst (104A). Molecular combinations of boron trifluoride with water and salts all show diminished catalytic activity (101A).

Octadecyl p-toluenesulfonate alkylates benzene without side-chain rearrangement (87A). 1-Dodecene gives a mixture of products with benzene with attachment of the phenyl group at the 2-, 3-, 4-, and 5-positions (2A). The last two are formed in smaller amounts than the others. Toluene can be alkylated with diisobutylene to give good yields without fragmentation of the side chain (76A). Schmerling and West (78A) have found that the major products from tert-alkyl chlorides are sec-alkylbenzenes which are presumed to be formed by isomerization of the initially formed tertalkylbenzene.

Polyhalogenated ethylenes and ethanes react with benzene in the presence of aluminum chloride to form polymeric resins with dihydroanthracene links which break up on dry distillation (48A). The final products include anthracene, diphenylmethane, triphenylmethane and. in one case p-xylene.

Styrene reacts with itself to form 1methyl-3-phenylindene, 1,3-diphenyl-1butene, a trimer and higher boiling material (20A). These products are also formed in reactions using styrene to alkylate benzene and ethylbenzene.

Toluene and xylenes react with acetylene to give diarylethanes from which can be prepared methyl- and dimethylstyrenes (25A). Acetaldehyde gives the same products but has a more desirable isomer distribution for polystyrene formation.

ω-Arvlalkane sulfonic acids can be prepared in good yield from sultones (102A).

Condensation products from 1.3- or 1,4-butanediol or 1,3,5-hexanetriol include the expected alkylation and cyclization products but these have also been acetylated in the aryl rings (51A).

Stereochemical evidence in the alkylation of phenols with α -phenylethyl chloride indicates that both ortho and para substitutions involve displacement (43.4). However, the retention of configuration for ortho substitution (in contrast to inversion for para substitution) suggests that a cyclic transition state with front-side displacement may be involved.

RING-CLOSURE ACYLATION (Aromatics) (Continued)

Product and Reagent	Reference
6-Oxo-5,6-H ₂ -benzo[c]quinoline, AlCl ₃ (also for 2-Br) 2,6-Dioxo-2,3,3a,4,5,6-H ₈ -naphtho[1,8-bc]pyran, P ₂ O ₅ , H ₃ PO ₄ 5H-2'-CH ₃ -5-oxo-7,8-H ₂ -spiro{benz[f]indan-6-1'-cyclopentane}, H ₂ SO ₄ 1H,6H-5-oxo-2,3,5,7,8,9,11-H ₃ -cyclopent[bg] naphthalene, H ₂ SO ₄ 1H-4-oxo-1,2,6,7-H ₄ -benz[fg]acenaphthylene, SnCl ₄ 8H-4-oxo-1,2,6,7-H ₄ -benz[fg]acenaphthylene, SnCl ₄ 6,11-Dioxo-6,11-H ₂ -benzo[b]naphtho[2,3-d]furan, AlCl ₃ 8-C ₂ H ₃ -4-oxo-1,2,3,4,5,6-H ₈ -chrysene, SnCl ₄ 5-HO-1,2,3,3a,4,5,9,10-H ₈ -pyrene, H ₃ PO ₄ , P ₂ O ₅ 5,10,15,18-Tetraoxo-5,10,15,18-H ₄ -dinaphtho[2,3-b, 2',3'-h]phenanthrene, H ₂ SO ₄ 4H,8H-4,8-dioxo-6,10-(HO ₂ C) ₂ -dibenzo[cd,mn]pyrene, H ₂ SO ₄ 4H,8H-4,8-dioxo-7,11-(HO ₂ C) ₂ -dibenzo[cd,mn]pyrene, H ₂ SO ₄ 5H-5-oxo-7,CH ₃ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ , 72% 5H-5-oxo-7-8-(CH ₂) ₃ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7-8-(CH ₂) ₃ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₃ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₃ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-oxo-7,8-(CH ₂) ₄ -6,7,8,9-H ₄ -cycloheptabenzene, AlCl ₃ 5H-5-o	(61G) (25G) (36G) (34G) (22G) (22G) (15G) (14G) (68G) (17G) (17G) (4G) (69G) (44G) (32G) (32G) (24G) (18G, 32G) (52G) (45G, 67G,
2,4-(CH $_3$) $_2$ -5-oxo-5,6,7.8,9,10-H $_6$ -cycloöctabenzene, AlCl $_3$, 54%	70G) (70G)
O=C (CH ₂) _n ($n = 6 \text{ to } 11$). AlCl ₃ , yields 1-36%	(45G)

RING-CLOSURE ACYLATION (Pseudoaromatics)

Product and Reagent	Reference
$1.3-(C_2H_b)_2-4-oxo-4.5,6.7-H_4-benzo[c]$ thiophene, SnCl ₄ , 91%	(1H)
5H-5-0x0-6,7,8,9-H ₄ -cyclohepta[b]furan, SnCl ₄ , 60%	(<i>3H</i>)
$4H-1,3-(C_2H_5)_2-4-oxo-5,6.7,8-H_4-cyclohepta[c]$ thiophene, SnCl ₄ , 71%	(1H)
$5H-5-oxo-1,2,3,4,6,7,8,9-H_s$ -cyclohepta[b]thianaphthene, $SnCl_4$, 80%	(2H)

RING-CLOSURE ACYLATION (Aromatics, Gattermann-Koch-Hoesch)

Product and Reagent	Reference
2-Thiono-1,2-H ₂ -benz [cd]indole, AlCl ₃ , 26% 4-Oxo-1,2,3,4-H ₄ -quinoline, AlCl ₃ , NaCl, 25% 1-(NCCH ₂ CH ₂)-4-oxo-7-CH ₃ -1,2,3,4-H ₄ -quinoline, HCl, AlCl ₃ 1-(NCCH ₂ CH ₂)-4-oxo-7-CH ₃ -1,2,3,4-H ₄ -quinoline, HCl, AlCl ₃ , 29% 1-(NCCH ₂ CH ₂)-4-oxo-6-Cl-1,2,3,4-H ₄ -quinoline, HCl, AlCl ₃ , 74% 1-(NCCH ₂ CH ₂)-4-oxo-7-Cl-1,2,3,4-H ₄ -quinoline, HCl, AlCl ₃ , low yield 1-(NCCH ₂ CH ₂)-4-oxo-6,7-(CH ₃) ₂ -1,2,3,4-H ₄ -quinoline, HCl, AlCl ₃ , 35%	(3i) $(1i)$ $(4i)$ $(2i)$ $(2i)$ $(4i)$ $(2i)$
8-CH ₃ -1.7-dioxo-1.2.3.5.6.7-H ₆ -benz [ij]quinolizine, HCl, AlCl ₃ , 19% 8-Cl-1.7-dioxo-1.2.3.5,6.7-H ₆ -benzo [ij]quinolizine, HCl, AlCl ₃ 9-Cl-1.7-dioxo-1.2.3.5,6.7-H ₆ -benzo [ij]quinolizine, HCl, AlCl ₃ , 7-50%	$egin{pmatrix} (2i) \ (4i) \ (2i) \end{pmatrix}$

RING-CLOSURE ACYLATION (Aromatics, Sulfonylation)

Product and Reagent	Reference
2,3-H ₂ -benzo[e]thianaphthene-1,1-dioxide, AlCl ₃ , 54% Benzo[f]thiachroman-1,1-dioxide, AlCl ₃ , 65%	$egin{pmatrix} (1J) \ (1J) \end{pmatrix}$
Benzo [g]homothiachroman-1,1-dioxide, AlCl ₃ , 16%	(1J)

RING-CLOSURE ACYLATION (Complex)

Product and Reagent	
4,5,8-(CH ₃) ₃ -1-tetralone, AlCl ₃ 4,6,7-(CH ₃) ₃ -1-tetralone, AlCl ₄ , PPA 9-Oxo-1,2,3,4,4a,9,10, trans-10a-H ₃ -phenanthrene, AlCl ₃ 1,8-Dioxo-4,5,9,10-(CH ₃) ₄ -1,2,3,4,5,6,7,8-H ₃ -phenanthrene, AlCl ₃ , PPA 3-C ₆ H ₃ -2,4-dithiono-1,2,3,4-H ₄ -quinazoline, AlCl ₂ , NaCl 2-C ₂ H ₃ -5-HO-6-CH ₃ O ₂ C-4-chromanone, AlCl ₃ 2,2-(CH ₃) ₂ -5-HO-6-CH ₄ O ₂ C-4-chromanone, AlCl ₄	(5K) (5K) (8K) (5K) (2K) (3K) (3K)

RING-CLOSURE ACYLATION (Complex) (Continued)

Product and Reagent	$R\epsilon ference$
1-HO-xanthone, $ZnCl_2$ (also for 3-HO; others mentioned) 11H-6-0x0-6,7,8,9-H ₄ -benzo [b] fluorene 5.8-(HO) ₂ -1,4-naphthoquinone, $AlCl_3$, $NaCl_2-C_2H_5-5$,8-(HO) ₂ -1,4-naphthoquinone, $AlCl_3$, $NaCl_3$	(6K) (1K) (4K) (4K)
O=C $-(CH_2)_n$ $-CH_2$ AlCl ₃ , small yield $(n = 6, 7, 10)$	(7K)

 $\dot{C}H_2$ — $(CH_2)_n$ —C=O

The rate of tert-butylation of phenol is inversely proportional to the concentration of dioxane or tetrahydropyran (40A). This rate inhibition provides good evidence for the formation of phenolether complexes. The reaction of phenols with triphenylmethyl chloride is autocatalytically affected by hydrochloric acid (39.4). The initial reaction in the absence of hydrochloric acid is second order. As the hydrochloric acid accumulates, a third-order term must be introduced into the kinetic expression.

OPEN-CHAIN ALKYLATION (Aromatics)

Anomatic	Propert	Product	Deference
Aromatic	Reagent		Reference
1-RO-naphthalene	BrCN, AlCl ₃ , CS ₂	1-RO-4-NC-naphthalene, $80\frac{C}{c}$, (R = C ₂ H ₅ , n-C ₅ H ₁₁ , n-C ₆ H ₁₃ , n-C ₇ H ₁₅ , n-C ₈ H ₁₇ , n-C ₉ H ₁₉ , n-C ₁₀ H ₂₁ , n-C ₁₂ H ₂₂ , n-C ₁₆ H ₃₃ , n-C ₁₆ H ₃₇)	(26N)
Benzene (also for C ₆ H ₅ Cl) 3,5-(CH ₃) ₂ C ₆ H ₃ -(t-C ₄ H ₉)	ClCH ₂ SiCl ₃ , AlCl ₃ H ₂ C=CH ₂ , HF	$C_6H_5CH_2SiCI_3$, 62% 3.5-(CH ₃) ₂ -4-C ₂ H ₅ -C ₆ H ₂ -(t-C ₄ H ₉) with some	$egin{array}{c} (60N) \\ (68N) \end{array}$
Phenol	HC≡CH, H ₂ PO ₄ -BF ₃ , HgO, C ₂ H ₃ OH	ethylated m -xylenes (4-HOC ₆ H ₄) ₂ CHCH ₃ and polymer	(79N)
Toluene (similarly for xylene) $(C_2H_5)_3C_6H_3$	$HC \stackrel{\frown}{=} CH$, $HgSO_4$, H_2SO_4 C_2H_5Br , $AlCl_3$	$(4-CH_5C_6H_4)_2CHCH_3 (C_2H_5)_4C_6H_2$	$(20N) \ (64N)$
Benzene Benzene (also for toluene) Benzene	Ethylene oxide, AlCl ₃ ClCH ₂ CH ₂ SiCl ₃ , AlCl ₃ ClCH(CH ₃)SiCl ₃ , AlCl ₃	C ₆ H ₅ CH ₂ CH ₂ OH C ₆ H ₅ CH ₂ CH ₂ SiCl ₃ . 65 ° _C C ₆ H ₅ CH(CH ₃)SiCl ₃ , 65 ° _C	$(70N) \\ (60N) \\ (60N)$
Benzene (also for toluene)	ClCH ₂ CH ₂ Cl, AlCl ₃	$C_6H_3CH_2CH_2C_6H_5$, $55\%_0$, and higher condensation	(21N)
Benzene C ₆ H ₅ Cl Anisole	CH ₃ CHClSCl, AlCl ₃ C ₃ H ₆ , H ₂ SO ₄ (also for C ₄ H ₅) i-C ₅ H ₇ OH	$CH_3CH(C_6H_5)SC_6H_5$ $CIC_6H_4-(i-C_3H_7), 75-85\%$ $(i-C_3H_7)C_6H_4OCH_3$	(5N) (50N, 51N) (25N)
Benzene Benzene (also for mesitylene) Phenol	(n-C ₃ H ₇) ₂ O, AlCl ₃ Trimethylene oxide, AlCl ₃ CH ₂ =CHCH ₂ OH, H ₂ SO ₄ or H ₃ PO ₄	i-C ₃ H ₇ , C ₆ H ₃ , n -C ₃ H ₇ C ₆ H ₅ , C ₂ H ₃ C ₆ H ₅ C ₆ H ₅ CH ₂ CH ₂ CH ₂ OH, 52-71 C_{ℓ} 2-HOC ₆ H ₄ C(CH ₃)=CH ₂ , 2-CH ₃ -coumaran,	(69N) (70N) (48N)
Phenol	CH ₂ =CHCH ₂ Br, ZnCl ₂	chroman, and usually a large proportion of resin HOC ₆ H ₄ CH ₂ CH=CH ₂	
Anisole Phenol (also for anisole and phenetole)	(CH₂=CHCH₂Cl is better) CH₂=CHCN, AlCl₃ CH₂COCH₂Cl, H₂SO₄ or AlCl₃	4-CH ₃ OC ₆ H ₄ CH ₂ CH ₂ CN 4-[4-HOC ₆ H ₄ C(CH ₄)=CH]C ₆ H ₄ OH, 67%	(22N) (88N)
Benzene 3,4-(CH ₃) ₂ C ₆ H ₈ OH Anisole (also for phenetole) Phenol (also for 2-CH ₃ , 2-Cl, and	CICH=CHCH ₂ Cl, AlCl ₃ CH ₃ CH=CH ₂ , H ₂ SO ₄ CH ₃ CH=CHCH ₃ , BF ₃ (CH ₂)=CHCH ₃ POC ₁ or POR ₂	$C_6H_6CH_2CH$ —CHCl, 47% $2-(t-C_4H_9)-3,4-(CH_3)_2-C_6H_2OH$ $CH_3OC_6H_4-(s-C_4H_9)$, up to 83% $t-C_4H_9C_6H_4OH$, isomers in various proportions	(69N) (2N) (85N, 87N) (7N)
2-C ₆ H̄ ₅) Phenol	$(CH_3)_2C=CH_2, H_2SO_4, C_6H_6$	2,4,6-(t-C ₄ H ₉) ₃ C ₆ H ₂ OH, 72° ₆	(16N, 74N)
Toluene Benzene 1,3-(CH ₃) ₂ C ₆ H ₄	$C_4H_9ClO_4$ $n-C_4H_9X$, AlCl ₃ or SbCl ₅ $n-C_4H_9Cl$, AlCl ₃ (also for $s-C_4H_9Cl$)	No reaction $n-C_4H_9C_6H_5$ and $i-C_4H_9C_6H_5$ 3,5- $(CH_3)_2C_6H_3$ - $(n-C_4H_9)$ and	$(13N) \ (59N) \ (57N)$
1,3-(CH ₃) ₂ C ₆ H ₄	s-C ₄ H ₉ OH, H ₂ SO ₄ (also for i- C ₄ H ₉ OH)	$\begin{array}{l} 3.5 \cdot (CH_3)_2 C_6 H_3 \cdot (s \cdot C_4 H_9) \\ 3.5 \cdot (CH_3)_2 C_6 H_3 \cdot (s \cdot C_4 H_9) \end{array}$	(57N, 65N)
Benzene	i-C ₄ H ₉ OH, H ₂ SO ₄ ; or i -C ₄ H ₉ Cl, AlCl ₃	t-C ₄ H ₉ C ₆ H ₅	(65N)
C₅H₅NHCOCH3 C₅H₅C2H5 Naphthalene	i-C ₄ H ₉ Br, AlCl ₈ t-C ₄ H ₉ OH, H ₂ SO ₄ t-C ₄ H ₉ OH, AlCl ₈	4-(t-C ₄ H ₉)C ₆ H ₄ NHCOCH ₃ 4-(t-C ₄ H ₉)C ₆ H ₄ C ₂ H ₅ 2-(t-C ₄ H ₉)-naphthalene, also 2,6- and 2,7- (t-C ₄ H ₉) ₂ -naphthalene	(J1N) (11N) (18N)
Toluene $C_6H_5C_2H_5$ (also for 3-CH ₃ and 3-C ₂ H ₅)	/-C ₄ H ₉ Cl, AgClO ₄ /-C ₄ H ₉ Cl, FeCl ₃ or AlCl ₃	t-C ₄ H ₉ C ₆ H ₄ CH ₃ , 56% para t -C ₄ H ₉ C ₆ H ₄ C ₂ H ₅	(13N) (11N)
Phenol Indan [also for 1,1-(CH ₃) ₂ -1,2,3,4- H ₄ -naphthalene]	t-C ₄ H ₉ Cl, AlCl ₈ or POCl ₈ t-C ₄ H ₉ Cl, AlCl ₃	t-C ₄ H ₉ C ₆ H ₄ OH and $(t$ -C ₄ H ₉) ₂ C ₆ H ₃ OH 5- t -C ₄ H ₉ -indan	$(7N, 11N) \ (11N)$
$1,4-(t-C_4H_9)_2C_6H_4$ $1,2-C_12C_6H_4$	t-C ₄ H ₉ Cl, AlCl ₃ t-C ₄ H ₉ Cl	1,3,5-(t-C ₄ H ₉) ₃ C ₆ H ₃ 3,4-Cl ₂ C ₆ H ₃ (t-C ₄ H ₉)	(4N) (82N)
2,2'-(HO) ₂ -biphenyl 9,10-H ₂ -phenanthrene	t-C ₄ H ₉ Cl, AlCl ₅ , CS ₂ CH ₂ =CHCH ₂ CO ₂ C ₂ H ₅ , AlCl ₅ , hexane	$2,2'-(HO)_2-3,3',5,5'-(t-C_4H_6)_4$ -biphenyl $2-[C_2H_5O_2CCH_2CH(CH_3)]-9,10-H_2$ - phenanthrene	(53N) (61N)
ArH (12 examples) Toluene	$CH_2 = C(CN)_2$, $AlCl_3$, $(CHCl_2)_2$ $CH_3CO_2CCH_2CH_2CO_2CH_3$, $AlCl_3$	$ArCH_2CH(CN)_2$, up to 89% 4- $CH_3C_6H_4(CH_2)_4O_2CCH_3$	(83N) (45N)
Benzene (also for toluene)	CH ₃ CH(O ₂ CCH ₃)CH ₂ CH ₂ O ₂ CCH ₃ , AlCl ₃	C ₆ H ₅ CH(CH ₃)CH ₂ CH ₂ O ₂ CCH ₃	(45N)

OPEN-CHAIN ALKYLATION (Aromatics) (Continued)

Aromatic	Reagent	Product	Referenc e
	CH ₃ COCH ₂ CH ₂ OH, HCl or AlCl ₃	4-HOC₀H₄CH₂CH2COCH₃, 28-45°€	(49N)
2-CH ₃ O) Phenol (also for anisole) Benzene	CH ₃ COCHClCH ₃ , AlCl ₃ or H ₂ SO ₄ CH ₃ CHBrCHBrCH ₃ , AlCl ₃	4-[4-HOC ₆ H ₄ C(CH ₃)=C(CH ₃)]C ₆ H ₄ OH C ₆ H ₅ CH(CH ₃)CH(CH ₃)C ₆ H ₆ , $9^{C_{Q}}$	(88N) (76N)
1,4-(CH ₃) ₂ C ₆ H ₄ (also for 1,4-Cl ₂) Benzene [also for C ₆ H ₅ Cl, toluene, 1,4-(CH ₃) ₂ C ₆ H ₄ , 1,4-Cl ₂ C ₆ H ₄ and anisole]	γ-Butyrolactone 4-HO-butane sulfonic acid sultone, AlCl ₃ or FeCl ₃	2,5-(CH₂)₂C₀H₃(CH₂)₂CO₂H, 24 [©] ; C₀H₅(CH₂)₄SO₂H, 63 [©] ;	(77N) (77N)
Anisole 2-ClC ₆ H ₄ OH (also for 4-) Phenol	$\begin{array}{l} CH_3CH_2CH &=\!$	CH ₃ OC ₆ H ₄ CH(C ₂ H ₅) ₂ , 62 C_C Mixture of ethers and phenols 2- and 4-HOC ₆ H ₄ C(CH ₃) ₂ CH ₂ CH ₃ with some dialkylation	(85N) (86N) (7N)
Benzene [also for toluene, anisole, 1,2-(CH ₃) ₂ C ₆ H ₄ , 1,3-(CH ₃) ₂ C ₅ H ₄ , tetralin, and 9,10-H ₂ -	CH ₂ =CHCH ₂ CH ₂ CO ₂ C ₂ H ₅ , AlCl ₅	$C_6H_3CH(CH_3)CH_2CH_2CO_2C_2H_3$, 93.2%	(43N, 56N, 80N, 81N)
phenanthrene] Naphthalene	(CH ₃) ₂ CHCH ₂ CH ₂ Cl, ZnCl ₂ , H ₃ PO ₄ , or BF ₃	1- and 2-[($\mathrm{CH_3}$) ₂ $\mathrm{CHCH_2CH_2}$]-naphthalene	(66N)
Toluene C ₆ H ₆ C ₂ H ₅ Benzene [also for 1,4-(CH ₃) ₂ C ₆ H ₄ and 9,10-H ₂ -phenanthrene]	(CH ₃) ₃ CCH ₂ Cl, H ₂ SO ₄ (CH ₃) ₃ CCH ₂ OH γ-Valerolactone	4-CH ₃ C ₆ H ₄ CH ₂ C(CH ₃) ₅ 4-CH ₃ C ₆ H ₄ CH ₂ C(CH ₃) ₃ C ₆ H ₅ CH(CH ₃)CH ₂ CH ₂ CO ₂ H, 70° ₀	(11N) (11N) (39N, 54N, 77N)
Benzene	4-HO-pentane sulfonic acid sultone, AlCl ₃	$C_6H_5CH(CH_8)CH_2CH_2CH_2SO_3H$, 88° $^{\circ}_{\mathcal{O}}$	(77N)
1,2-(CH ₃) ₂ C ₆ H ₄ (also for anisole and tetralin)	CH ₃ COCH ₂ CH ₂ CH=CH ₂ , AlCl ₃	$3,4-(CH_3)_2C_6H_3CH(CH_2)CH_2CH_2COCH_3,$ 52%	(43N, 80N, 81N)
Benzene (similarly for toluene) 4-CH ₃ C ₆ H ₄ (i-C ₃ H ₇) Toluene [also for benzene and similarly for 3,4-(CH ₃) ₂ C ₆ H ₃ OH]	n-C ₆ H ₁₃ CH=CH ₂ , H ₂ SO ₄ C ₈ H ₁₇ OH, AlCl ₃ , H ₂ SO ₄ or H ₃ PO ₄ Diisobutylene, AlCl ₃ , C ₆ H ₃ NO ₂ or CH ₃ NO ₂	$n-C_6H_{13}CH(CH_3)C_6H_5, 92\frac{c_0}{c_0}$ $2-C_3H_{17}-4-(i-C_3H_7)-C_6H_3CH_5$ $4-CH_3C_6H_4C(CH_3)_2CH_2C(CH_3)_3, 85\frac{c_0}{c_0}$	(19N, 47N) (40N) (67N)
Benzene	RCH=CH ₂ , H ₂ SO ₄	CH ₃ CHRC ₆ H ₅ , 70–90% (R = n -C ₅ H ₁₇ , n -C ₁₀ H ₂₁ , n -C ₁₂ H ₂₅ , n -C ₁₄ H ₂₉ , and n -C ₁₅ H ₃₃)	(47N)
Benzene 1,3-(CH ₃ O) ₂ C ₆ H ₄ Phenol (also for 4-CH ₃) Benzene 1,3-(CH ₃ O) ₂ C ₆ H ₄ (also for diethyl)	4-CH ₃ C ₆ H ₄ SO ₃ -(n-C ₁₃ H ₃₇), AlCl ₃ Cyclopentene, BF ₃ -(C ₂ H ₃) ₂ O Cyclopentadiene, H ₃ PO ₄ 3-CH ₃ -cyclopentanol, AlCl ₃ Cyclohexene, AlCl ₃ , C ₆ H ₅ Cl	n-C ₁₈ H ₃₇ C ₆ H ₅ 1-Cyclopentyl-2,4-(CH ₃ O) ₂ -C ₆ H ₅ 3-(4-HOC ₆ H ₄)-cyclopentene, 67°C ₀ 1-C ₆ H ₅ -3-CH ₃ -cyclopentane, 56°C ₀ 1-Cyclohexyl-2,4-(CH ₃ O) ₂ -C ₆ H ₃ and 1,5-(cyclohexyl) ₂ -2,4-(CH ₃ O) ₂ -C ₆ H ₂	(71N) (9N) (3N) (73N) (9N)
Indan Phenol (also for anisole) 1,3-(HO) ₂ C ₆ H ₄ 4-Cl-C ₆ H ₄ OH Toluene Benzene Benzene	Cyclohexene, AlCl ₃ Cyclohexanol, PPA Cyclohexanol, ZnCl ₂ Cyclohexanol, H ₂ SO ₄ Br-cyclohexane, AgClO ₄ 2-CH ₃ -cyclohexanol, AlCl ₃ 4-CH ₃ -cyclohexene, HF	5-Cyclohexyl-indan 2- and 4-cyclohexyl-C ₆ H ₄ OH 1-Cyclohexyl-2,4-(HO ₂)-C ₆ H ₃ Cyclohexylchlorophenol, 52% Cyclohexyl-C ₆ H ₄ CH ₃ , 93% 1-CH ₃ -1-C ₆ H ₅ -cyclohexane, 64% (also 1.2) 1-CH ₃ -1-C ₆ H ₅ -cyclohexane, 75% (some dialkylation)	(63N) (25N) (9N) (1N) (13N) (73N) (32N)
Phenol Biphenyl Benzene (also for toluene and C ₆ H ₅ Cl)	Dicyclopentadiene, H ₃ PO ₄ Cl-decalin, AlCl ₃ , CS ₂ C ₆ H ₆ CH ₂ Cl, AlCl ₃ or SbCl ₅	1-Cyclopentyl-2-HO-C ₆ H ₄ [(4-C ₆ H ₅)C ₆ H ₄]-decalin (C ₆ H ₅) ₂ CH ₂ , 35–55%	(3N) (30N) (39N, 59N)
Toluene (also C ₆ H ₅ Cl) Anisole 2-CH ₃ C ₆ H ₄ SCH ₃ [similarly for mesitylene, 1-CH ₃ -naphthalene, 2-CH ₃ -naphthalene, 2-CH ₃ -naphthalene, 2-CH ₃ -naphthalene, 2-HOC ₆ H ₄ -CO ₂ CH ₃ , 2-HOC ₆ H ₄ CO ₂ C ₂ H ₅ , 4-HOC ₆ H ₄ CO ₂ C ₂ H ₅ , 1,4-(C ₆ H ₅) ₂ C ₆ H ₄ , chrysene, and pyrene]	C ₆ H ₅ CH ₂ Cl, ZnCl ₂ C ₆ H ₅ CH ₂ Cl, I ₂ C ₆ H ₅ CH ₂ Cl, ZnCl ₂ , CHCl ₃	4-CH ₃ C ₆ H ₄ CH ₂ C ₆ H ₅ , 4-60 $\frac{c_7}{\ell}$ 4-CH ₃ OC ₆ H ₄ CH ₂ C ₆ H ₅ (some dialkylation) 2-CH ₃ -4-C ₆ H ₅ CH ₂ -C ₆ H ₃ SCH ₃ , 60 $\frac{c_7}{\ell}$	(39N) (36N) (10N)
1,3-(CH ₈ O) ₂ C ₆ H ₄ Naphthalene	C ₅ H ₅ CH ₂ Cl, Cu, heat C ₆ H ₅ CH ₂ Cl, P ₂ O ₅ , ZnCl ₂ , FeCl ₃ or AlCl ₃	2,4-(CH $_3$ O) $_2$ C $_6$ H $_3$ CH $_2$ C $_6$ H $_6$ (some dialkylation / 1- and 2-C $_6$ H $_5$ CH $_2$ -naphthalene, yields from 20-80%	$(9N) \ (38N)$
2-HOC ₆ H ₄ CO ₂ CH ₃ C ₆ H ₅ F Benzene [also for toluene, C ₆ H ₅ Cl,	4-ClC ₆ H ₄ CH ₂ Cl, ZnCl ₂ 4-FC ₆ H ₅ CH ₂ Cl, AlCl ₃ , CS ₂ 3,4-Cl ₂ C ₆ H ₅ CH ₂ Cl, AlCl ₃ (also for 4- O ₂ NC ₆ H ₄ CH ₂ Cl)	2-HO-5-(4-ClC ₆ H ₄ CH ₂)-C ₆ H ₃ CO ₂ CH; (4-FC ₆ H ₄) ₂ CH ₂ 3,4-Cl ₂ C ₆ H ₃ CH ₂ C ₆ H ₅ , 64° _C	(10N) (58N) (6N)
and 1,3-(CH_3) ₂ C_6H_4] ArOH (17 examples)	Ar'CH ₂ OH, HCl or 4-CH ₃ C ₆ H ₄ SO ₃ H	Phenolic resin intermediates	(12N, 62N, 75N)
ArOH (6 examples) Toluene [also for 1,2-(CH ₃) ₂ C ₆ H ₄ , 1,3-(CH ₃) ₂ C ₆ H ₄ , 1,4-(CH ₃) ₂ C ₆ H ₄ ,	Ar 'CH ₂ Br (C ₆ H ₅) ₂ CHOH, H ₂ SO ₄ , CH ₃ CO ₂ H	Phenolic diphenylmethanes 4-CH $_8$ C $_6$ H $_4$ CH(C $_6$ H $_5$) $_2$	(23N) (44N)
and mesitylene] Phenol (also for 2-CH ₃) Benzene Phenol [also for 4-CH ₃ , 4-Cl, and	$(C_6H_5)_3$ CCl, HCl, 1.2-Cl $_2$ C $_6$ H $_4$ Styrene, 71% H $_2$ SO $_4$ C_6 H $_5$ CHClCH $_3$	4-HOC ₆ H ₄ C(C_6H_5) ₈ (C_6H_5) ₂ CHCH ₃ and more complex products HOC ₆ H ₄ CH(CH ₃)C ₆ H ₅	(28N) (17N) (29N)
2,6-(CH₃)₂] 3,4-(CH₃)₂C₀H₃OH	$C_6H_5C(CH_3)=CH_2$, $SnCl_4$	$2-[C_6H_5C(CH_3)_2]-4,5-(CH_3)_2C_6H_2OH, 74\%$	(2N)

	OPEN-CHAIN ALKYLATION (Ar	omatics) (Continued)	
Aromatic	Reagent	Product	Reference
1,2,3-(HO) ₃ C ₆ H ₃	$C_6H_5C(CH_3)=CH_2$, H_2SO_4 , CH_3CO_2H [also for 4-CH ₃ OC ₆ H ₄ -	$1,2,3-(HO)_{\delta}-4,5-[C_{6}H_{\delta}C(CH_{\delta})_{2}]_{2}C_{6}H$	(35N)
Benzene (also for toluene, anisole,	C(CH ₃) ₂ OH J 4-CH ₃ C ₆ H ₄ SO ₃ CH(CN)C ₆ H ₅ , AlCl ₃	$(C_6H_5)_2$ CHCN, 60-82 $\%$	(72N)
C_6H_5Br , and C_6H_5Cl) C_6H_6Cl ArH	or H ₂ SO ₄ 4-ClC ₆ H ₄ CH(OH)CCl ₃ 2-HOC ₆ H ₄ CH ₂ CH ₂ SO ₃ H sultone,	(4-ClC₀H₄)₂CHCCl₃ No reaction	(8N) (77N)
Benzene Benzene (also for toluene) Toluene Benzene Benzene Benzene	AlCl ₃ C ₆ H ₅ CH=CHCO ₂ H, AlCl ₃ C ₆ H ₅ CH=CHSO ₂ CH ₃ , H ₂ SO ₄ 4-CH ₃ C ₆ H ₄ SO ₂ CH=CHC ₆ H ₅ , AlCl ₃ C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ Cl, AlCl ₃ C ₆ H ₅ CHBrCHBrCO ₂ H, AlBr ₃ trans-2-HO-cyclohexane-acetic acid lactone, AlCl ₃	(C ₆ H ₅) ₂ CHCH ₂ CO ₂ H, 87% (C ₆ H ₅) ₂ CHCH ₂ SO ₂ CH ₃ , 76% 4-[4-CH ₃ C ₆ H ₄ CH(C ₆ H ₅)CH ₂ SO ₂]C ₆ H ₄ CH ₃ C ₆ H ₅ COCH(C ₆ H ₅)CH ₂ C ₆ H ₅ (C ₆ H ₅) ₂ CHCH(C ₆ H ₅)CO ₂ H, 66-78% (2-C ₆ H ₅) ₂ cyclohexane-acetic acid	(17N) (78N) (78N) (52N) (42N) (84N)
$1,3\text{-}(\mathrm{CH_3})_2\mathrm{C_6H_4}$ (also for 1,4-) Anisole	1,2-(ClCO) ₂ C ₆ H ₄ , AlCl ₃ 1-CH ₃ -1-C ₂ H ₄ O ₂ C-2-oxo-3- C ₂ H ₅ O ₂ CCH ₂ -cyclohexene-3, AlCl ₃ (also for methyl ester)		(14N, 15N) (27N, 34N)
Benzene (also for toluene) Benzene [also for toluene and	2-(CH ₂ =CHCH ₂)-1-tetralone, AlCl ₃ 2-(CH ₂ =CHCH ₂)-4-CH ₃ -1-tetralone,	2-[C ₆ H ₅ CH(CH ₃)CH ₂]-1-tetralone, 82% 2-[C ₆ H ₅ CH(CH ₃)CH ₂]-4-CH ₃ -1-tetralone, 64%	(55N) (46N)
1,3-(CH ₃) ₂ C ₆ H ₄] 1,4-(HO) ₂ -2-CH ₃ -naphthalene	AlCl ₃ Phytol or isophytol, various catalysts		(31N, 33N
Benzene	5-Mesitoylacenaphthylene, HCl,	(vitamin K_1), 42% 1- C_6H_6 -5-mesitoylacenaphthene, 80%	(24N)
Benzene Anthracene	AlCl ₃ 1-Br-5-mesitoylacenaphthene, AlCl ₃ N-(ClCH ₂)-phthalimide, AlCl ₃ , CS ₂ or ZnCl ₂ , C ₆ H ₅ NO ₂	$1-C_6H_5$ -5-mesitoylacenaphthene 9,10-bis(phthalimido- CH_2)-anthracene	(24N) (37N)
	OPEN-CHAIN ALKYLATION	(Pseudoaromatics)	· · · · · · · · · · · · · · · · · · ·
Pseudoaromatic	Reagent	Product	Reference
Thiophene 2-CH ₃ -pyrrole [also for 2,4-(CH ₃) ₂ , 2-CH ₃ -3-C ₂ H ₆ O ₂ C, 2,4-(CH ₃) ₂ - 3-C ₂ H ₆ O ₂ C, 2,4-(CH ₃) ₂ - CH ₅ CO, and 2-C ₂ H ₅ O ₂ CH ₂ - 2, CH ₂ CO, and CH ₂ CH ₃ O ₂ CH ₂ -	H ₂ C=CH ₂ , SiO ₂ -Al ₂ O ₃ CH ₂ =CHCO ₂ H, BF ₃ -(C ₂ H _δ) ₂ O (similarly for corresponding lactone, nitrile, methyl and ethyl esters, and amide)	2-C ₂ H ₃ -thiophene 2-CH ₃ -5-HO ₂ CCH ₂ CH ₂ -pyrrole (corresponding nitrile was obtained only from 2,4-(CH ₃) ₂ - pyrrole; several failures occurred with the methyl ester)	(7Q) (6Q)
3-C ₂ H ₆ O ₂ C-4-CH ₃] 2-CH ₃ O ₂ C-furan Thiophene 2-CH ₃ O ₂ C-furan Thiophene	s-C ₄ H ₉ Br, AlCl ₃ , CS ₂ t-C ₄ H ₉ OH, SnCl ₄ , CS ₂ t-C ₄ H ₉ Br, AlCl ₃ , CS ₂ t-C ₄ H ₉ Cl, SnCl ₄ , CS ₂	2-CH ₃ -5-(s -C ₄ H ₉)-furan (also some t -C ₄ H ₉) 2,5-(t -C ₄ H ₉) ₂ -thiophene 2-CH ₃ O ₂ C-5- t -C ₄ H ₉ -furan 2- and 3- t -C ₄ H ₉ -thiophene (also some dialkylation	(3Q) (1Q) (3Q) (5Q)
2-CH ₃ -thiophene [also for 2-C ₆ H ₅ ,	t-C₄H₀Cl, FeCl₃, CS₂	and formation of biaryl type products) 2-CH ₂ -5- t -C ₄ H ₉ -thiophene, 25%, and 2-CH ₂ -3,5-	
2,5-(CH ₅) ₂ , and 2,5-(C ₂ H ₅) ₂] Thiophene Thiophene (also for 2-Cl) Thiophene	CH ₂ =C(CN) ₂ , AlCl ₃ , (CHCl ₂) ₂ C ₆ H ₅ CH ₂ Cl, I ₂ C ₆ H ₅ C(CH ₃) ₂ OH, SnCl ₄ , CS ₂ [also	$(t-C_4H_9)_2$ -thiophene, 60% 2- $[(NC)_2CHCH_2]$ -thiophene, 65% No reaction 2,5- $[C_6H_4C(CH_3)_2]$ -thiophene	(8Q) (4Q) (1Q)
Thiophene	for $(C_6H_5)_2C(CH_3)OH$] $(C_6H_5)_3COH$	No reaction	(1Q)
	OPEN-CHAIN PSEUDOALKYL	ATION (Aromatics)	-
Aromatic	Reagent	Product	Reference
^t -C ₄ H ₉ C ₆ H ₅ Tetralin (also for polystyrene) Benzene Benzene	PCl ₃ , AlCl ₃ PCl ₃ , AlCl ₃ CH ₃ SCl, AlCl ₃ (also for C ₂ H ₅ SCl) CH ₃ CHClSCl, AlCl ₃	$4-t-C_4H_9C_6H_4PCl_2$ (Cl_2P) -tetralin $C_6H_5SCH_3$ $CH_3CH(C_6H_5)SC_6H_5$	(7R) (1R) (3R, 4R (2R)

If the phenol is previously saturated with hydrochloric acid, the reaction exhibits simple third-order kinetics.

The rate of reaction of cyclohexene with benzene in the presence of aluminum chloride is independent of time or concentration of cyclohexene, but is directly proportional to the concentration of hydrochloric acid (53A). This is taken to indicate that the actual alkylating agent is RCl and not olefin. The rate dependence on hydrochloric acid is thus related to the rate of formation of RCl.

The rate of reaction between phenol and styrene in glacial acetic acid containing perchloric acid is proportional

to the concentration of perchloric acid and independent of initial styrene concentration, although there are batch variations in the effect of initial phenol concentration (29A). The acetoxonium ion is considered to be the effective catalyst.

The rates of reaction between 3,4-di-

chlorobenzyl chloride and benzene, chlorobenzene, toluene, and m-xylene are third order (10A). The substituents on the ring undergoing substitution have consistent but rather small influences on the relative rates. Dilution of the nitrobenzene solvent with methylcyclohexane has only a small diminishing effect on the rate. It is considered that the transition state involves a nucleophilic displacement by the aromatic on a complex between the benzyl halide and aluminum chloride.

Oda and Nomura (63A) have published a review which includes consideration of the Friedel-Crafts reactions of sulfenyl chlorides.

Chloromethylation followed by cyclization via amine displacement or, alternatively, formation of a Mannich base followed by ring-closure alkylation may be considered to be the intermediate steps in the synthesis of 3-aza-1-methyl-7ethyl - 1,2,3,4 - tetrahydrophenanthrene (6A).

Added sulfur to inhibit polymerization and the use of aqueous formaldehyde and hydrochloric acid permitted the successful chloromethylation of the sidechain double bond in styrene without affecting the benzene ring (109A). Further evidence is advanced in support of the claim that FCH2OH is the actual intermediate in fluoromethylation (66.4). Previously existing kinetic data on chloromethylations have been shown to be in error (11A). Chloromethylation is a highly selective reaction and heavily dependent upon the nature of substituents on the ring undergoing substitution and reaction conditions.

Migration of optically active allyl groups indicates steric control of asymmetric induction in the ortho-Claisen rearrangement (38A). Kinetic and stereochemical evidence suggests that nuclear alkylation of phenols may occur by direct displacement to give C-alkylation rather than through O-alkylation followed by rearrangement (41.4, 42.4).

Conclusive evidence from several approaches (19A, 22A, 24A, 59A, 71A, 79A, 80.4) has confirmed the view that the para-Claisen rearrangement is a twostep process involving an ortho-dienone intermediate with over-all retention of configuration and structure of the migrating group being due to two successive allylic rearrangements.

The literature covered by this period of review involves only a few reactions using C-14 (14A, 37A, 79A, 93A) in

RING-CLOSURE ALKYLATION (Aromatics)

Product and Reagent	Reference
2-Oxo-indoline, AlCl ₃ , NaCl	(1S)
$1,7-(CH_4)_2-2$ -oxo-indoline, AlCl ₃ , NaCl	(88)
1-Oxo-3-HO ₂ C-4-CH ₃ -7-HO-indan, AlCl ₃ , NaCl	(25)
1- $[4-(CH_3)_2NC_6H_4]$ -3- C_6H_5 -indene, CH_3CO_2H , H_2SO_4 [similarly for 5- $(CH_3)_2N$]	(9S)
1,3-[4-($\tilde{C}H_3$)2NC ₆ H ₄]2-indene. $\tilde{C}H_3CO_2H$. H ₂ SO ₄ [similarly for 5-($\tilde{C}H_3$)2N]	(9S)
Naphthalene, SnCl ₄ , 82 ⁶ ,	(10S)
1,4-(CH ₃) ₂ -6-CH ₃ O-1,2,3,4-H ₄ -naphthalene, H ₂ SO ₄ , 70°;	(188)
1,4,6,7-(CH ₃) ₄ -1,2,3,4-H ₄ -naphthalene, H ₂ SO ₄	(19S)
2-CH ₃ -6-CH ₃ O-4-chromanone. AlCl ₃	(.5.8)
2-HO ₂ C-5,7-(CH ₃) ₂ -4-chromanone, H ₂ SO ₄	(2S)
Chroman, SnCl ₄ , 85% (also for 6-CH ₃ , 6-Br, and 6-Cl)	(15S)
Isoquinoline, PPA, POCl ₃ (failed in 5 examples)	(11S)
2-Oxo-1,2,3,4-H ₄ -quinoline. AlCl ₃	(17S)
1H-5-CH ₃ -2,3,3a.4,5.9b-H ₆ -benz [e] indene, P_2O_3 , 60% [also for 5.8-(CH ₃) ₂ .	(78)
and 5,6,9-(CH ₃) ₃	(70)
$2.9-(CH_3)_2-1.2.3.4.4a.9.10.10a-H_s$ -phenanthrene, P_2O_5 , 60% [also for 2.6.9-	(<i>7S</i>)
$(CH_3)_3$ and $2.5.8.9 \cdot (CH_3)_4$	(=e)
4.9-(CH ₃) ₂ -1.4-endo-isopropylidine-1.2,3,4,4a,9,10,10a-H ₃ -phenanthrene, P ₂ O ₅ . 62% [also for 4.6.9-(CH ₃) ₃]	(78)
$1,4-(CH_3)_2-1,2,3,4,5,6,7,8-H_8$ -anthracene, H_2SO_4	(13S)
9-i-C ₄ H ₉ -phenanthrene, CH ₃ CO ₂ H, HBr	(.3S)
5-CH ₃ -5,6,6a,6b,7.8-H ₆ -benzo [c] phenanthrene, H ₂ SO ₄ , 70° [also for 2.5-(CH ₃) ₂ , 5.8-(CH ₃) ₂ , 2.5,8-(CH ₃) ₄ , and 2,4.5,8-(CH ₃) ₄]	(14S, 16S)
Naphtho [e] pyrene, AlCl ₃ , NaCl	(AS)
5,8-Dioxo-dibenzo [a.i]pyrene, AlCl ₃ , NaCl, 68%	(12S)
Benzo [a] benzonaphtheno [1,2,3-cd] perylene, AlCl ₃ , NaCl	(oS)

RING-CLOSURE ALKYLATION (Pseudoaromatics)

Starting Compound and Reagent Reference 2-[(C₀H₅O)₀CHCH₀N=CH|pvridine, no ring-closure with H₂SO₄-POCl₃, BF₃, HF, or PPA (similarly for 3- and 4-)
-[(C₂H₅O)₂CHCH₂N=CH|quinoline, no ring-closure with H₂SO₄-POCl₃, (IT)

RING-CLOSURE ALKYLATION (Complex)

Product and Reagent	Reference
1-CH ₃ -3-C ₈ H ₅ -indenc, silica gel 1-CH ₃ -7-CH ₃ CO-indenc, AlCl ₄ [also for 6-CH ₃ and 1,6-(CH ₃) ₂] 7-HO-1-indanone, AlCl ₄ (also for 4-C ₈ H ₅ and 4-HO) 2-CH ₃ -coumaran, H ₃ PO ₄ , 12 C_7	(10U) (16U) (18U) (17U)

distinct contrast to the greatly expanded application of all other aspects of the Friedel-Crafts reactions.

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RING-CLOSURE ALKYLATION (Complex) (Continued) Product and Reagent

3	3
1,2,3-(C ₆ H ₈) ₈ -azulene, AlCl ₈ , 25° ₆ 1-CH ₈ -6-CH ₈ O-1,2,3,4-H ₄ -naphthalene, HCl, Zn(Hg), 78° ₆	(2U) (25U)
1,4-(CH ₃) ₂ -6-CH ₃ O-1,2-H ₂ -naphthalene, AlCl ₃ , $52\frac{C}{6}$	(25U) (25U)
Chroman, H ₂ PO ₄ , 11%	(17U)
6-C ₂ H ₅ -7-HO-coumarin, H ₂ SO ₄	(22U)
6 -Br-7-HO-coumarin, H_2 SO $_4$	(22U)
5-HO-6-RNHCO-coumarin, AlCl ₃ , 30-60° (6 examples)	(7U)
4,7-(CH ₅) ₂ -5-HO-coumarin, H ₂ SO ₄	(14U)
4-CH ₃ -6-C ₂ H ₅ -7-CH ₃ O-coumarin, AlCl ₃ or H ₂ SO ₄ (also for 6- n -C ₃ H ₇)	(24U)
4-CH ₃ -6-RNHCO-7-HO-coumarin, H ₂ SO ₄ , 2-50% (5 examples)	(7U)
$4-CH_3-5-CH_3O-8-C_2H_3$ -coumarin, P_2O_3	$(\widetilde{24U})$
4H-2-Oxo-4-imino-5-CH ₃ -7-HO-2,3-H ₂ -1-benzopyran, HCl, ZnCl ₂	(14U)
4.8-(CH ₃) ₂ -5,7-(HO) ₂ -coumarin, HCl. CH ₃ CO ₂ H (similarly for 15 examples)	(11U)
4.5-(CH ₃) ₂ -7-HO-8-C ₂ H ₅ -coumarin, AlCl ₃ , H ₂ SO ₄ or P ₂ O ₅	(24U)
2-CH ₃ -6-CH ₃ O-quinoline, HCl	(4U)
1H-1-CH ₃ -7-CH ₃ CO-2,2a,3,4-H ₄ -cyclopent [cd] indene	$(\widetilde{1}6\widetilde{U})$
2.3-Cyclopentano-2,3-H ₂ -benzo [b] furan	(3U)
9-HO ₂ C-fluorene, AlCl ₃ , 71–81 \tilde{c}_{c}	(21U)
3-HO-2-acenaphthenone	(18U)
2-C ₆ H ₅ -naphtĥo[b]thiophene. AlCl ₃	(12U)
Anthracene, AlCl ₃	(5U, 23U)
9.10-(CH ₃) ₂ -anthracene, AlCl ₃	(1U)
9,9,10,10-(CH ₃) ₄ -9,10-H ₂ -anthracene. AlCl ₃	(5U)
2,3,6,7-(CH ₃ O) ₄ - $9,10$ -H ₂ -anthracene, HCl	(20U)
$9-H_2N-10-R$ -phenanthrene, H_2SO_4 (5 examples)	(6U)
9-HO-2,3-H ₂ -1-benzonaphthenone. AlCl ₃	(18U)
7.8-benzocoumarin, H_2SO_4	(15U)
4-Cl-benzanthrone, H ₂ SO ₄ (also for 9- and 10-)	(19U)
Naphtho[2,3-e]pyrene, AlCl ₃ , NaCl	(8U)
4,5,6,6a,6b,7,8,12b-H ₃ -benzo[j]fluoranthene, PPA	(13U)
Heptaphene. 400 °C. (other products are dibenzo [b,kl]picene and anthraceno-	(9U)
[2,1-a]naphthacene)	

MISCELLANEOUS

Aromatic	Reagent	Product	Reference
Ar ₄ Sn (3 examples)	CH3COCl, AlCl3	ArCOCH ₃ ,	(IY)
$(C_6H_5CH_2)_4Sn$	CH ₃ COCl, AlCl ₃ (similarly for C ₆ H ₅ COCl)	$C_6H_3CH_2COCH_3$, $78\frac{C}{C}$	(1Y)
Ar ₄ Sn	C ₆ H ₅ CH ₂ Cl, AlCl ₃	$ArCH_2C_6H_5$	(1Y)
4-CH ₃ C ₆ H ₄ OH (similarly for 3 analogs)	CCl ₄ , AlCl ₃ , CS ₂ (unsuccessful for a number of similar reagents)	1-Oxo-4-CĤ₃-4-Cl₃C-2,5-cyclohexadiene, 60 %	(2Y)
Phenol	C ₆ H ₅ CCl ₃ , AlCl ₃ , CS ₂	$4-HOC_6H_4COC_6H_5, 92\%$	(3Y)
4-CH ₃ C ₆ H ₄ OH (similarly for many examples)	ArCCl ₃ , AlCl ₃	$2-ArCO-4-CH_3-C_6\dot{H}_3O\dot{H}$ and $2,6-(ArCO)_2-4-CH_3-C_6H_2OH$	$(\overrightarrow{3}Y, 4Y, 5Y)$
4-CH ₃ C ₆ H ₄ OH (similarly for several examples)	C ₆ H ₅ CCl ₃ , AlCl ₃ , CS ₂	6,12- $(C_6H_5)_2$ -2,8- $(CH_3)_2$ -6,12-epoxy-6H,12H-dibenzo[b,f][1,5]dioxocin, 29%	(3Y)

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