Friedel–Crafts reactions of some conjugated epoxides

ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · FEBRUARY 1983

Impact Factor: 4.72 · DOI: 10.1021/jo00152a036

6 AUTHORS, INCLUDING:

Daniel L Clark
Indiana University School of Medicine
14 PUBLICATIONS **142** CITATIONS

SEE PROFILE

reduced pressure to give 2.20 g (6.9 mmol, 69%) of 2,4-dinitrophenyl diethyl phosphate as a light yellow oil. This was dissolved in 100 mL of dry acetone and refluxed for 3 h with 0.61 g (7 mmol) of dry LiBr. The solution was then allowed to stand at 25 °C overnight, and the precipitate of **6** was collected and washed several times with dry ether. We thus obtained 1.05 g (3.5 mmol, 35%) of purified **6** after recrystallization from methanol/ether: mp 110–120 °C dec; ^{1}H NMR (D_2O, DSS) δ 1.3 (t, J = 7 Hz, 3 H, CH_3), 4.1 ("quintet", J = 8 Hz, 2 H, CH_2),[24] 7.6–9.0 (m, 3 H, aryl). Anal. Calcd for $C_8H_8LiN_2O_8P$: C, 32.21; H, 2.71; N, 9.40. Found: C, 31.95; H, 2.97; N, 8.85.[25]

Kinetic Studies. Reactions were followed on a Gilford Model 250 spectrophotometer coupled to a Gilford Model 6051 recorder. A constant-temperature circulating bath maintained the reaction temperature at 25.0 ± 0.02 °C. Rate constants were obtained from computer-generated correlations of log ($A_\infty - A_t$) with time in the standard way. Micellar reactions were generally followed to >90% completion (70–80% in the case of vesicular reactions) and showed good first-order kinetics ($r > 0.999$).

Vesicular solutions were typically prepared at 60–65 °C by sonication with a Bransonic Model 221 bath-type sonifier, operated at maximum power (225 W) for 30 min, or by the injection method.[11] Further details appear in the Results section.

Acknowledgment. This work was supported in part by the U.S. Army Research Office and by the National Science Foundation. We are grateful to these agencies. We also thank Mr. George O. Bizzigotti for the illustrations.

Registry No. 1 (Z = O; $R_1 = R_2$ = OEt; X = Cl), 814-49-3; 1 (Z = O; $R_1 = R_2$ = OEt; X = 2,4-dinitrophenoxy), 54436-53-2; **2**, 10359-36-1; **3**, 83710-46-7; **4**, 20317-32-2; **5**, 77551-97-4; **6**, 84175-82-6; 16_2, 70755-47-4; CTABr, 57-09-0; MCB, 112-82-3; 2-(methylamino)ethanol, 109-83-1; *N*-methyl-*N*-(β-hydroxyethyl)-*n*-hexadecylamine, 7089-36-3; 2,4-dinitrophenol, 51-28-5.

Supplementary Material Available: Tables I–IV containing (respectively) rate constants for cleavage of PNPDPP by 16-OH and 16_2OH, rate constants for the cleavage of **6** by CTABr, 16-OH, 16_2, and 16_2OH, rate constants for the cleavage of PNPDPP by 16-PhOH and 16-OH, and rate constants for the cleavage of PNPDPP by 16-PhOH/16_2 and 16-PhOH/CTABr (4 pages). Ordering information is given on any current masthead.

(24) This signal is actually an overlapping doublet of quartets, with the additional splitting due to $^{31}POCH_2$ coupling. The quoted "J" value is apparent.

(25) Complete hydrolysis of **6**, followed by spectrophotometric determination of 2,4-dinitrophenol, gave a purity of 95 ± 2$_4$%.

Friedel–Crafts Reactions of Some Conjugated Epoxides[1]

Stephen K. Taylor,* Daniel L. Clark, Karl L. Heinz, Scott B. Schramm, Cindy D. Westermann, and Koleen K. Barnell

Department of Chemistry, Olivet Nazarene College, Kankakee, Illinois 60901

Received June 28, 1982

The Friedel–Crafts (FC) reactions of (1,2-epoxyethyl)benzene, 1,2-epoxy-1-*p*-tolylethane, 1,2-epoxy-1-(*p*-methoxyphenyl)ethane, 1,2-epoxy-3-butene, and 1,2-epoxy-2-methyl-3-butene were examined under various conditions. Reaction time, temperature, Lewis acid, Lewis acid concentration, and solvent were varied. For (1,2-epoxyethyl)benzene (**1**), aromatic nucleophilicity was shown to be an important factor in promoting good FC yields. It was also shown that para carbocation stabilizing substituents on **1** did not improve FC yields. Vinyloxirane yielded primary products from direct ring opening (2-aryl-3-buten-1-ols) and conjugate addition (4-aryl-2-buten-1-ols) and secondary products (1,4-diaryl-2-butenes). Increased reaction time or catalyst concentration increases the proportion of secondary products. The primary and secondary FC pathways gave an excellent opportunity for study of the effects on product distributions of the use of aluminum chloride, boron trifluoride etherate, and stannic chloride Lewis acids. A significant FC reaction yield was not obtained with 1,2-epoxy-2-methyl-3-butene and toluene under the same conditions used for 1,2-epoxy-3-butene. Presumably this results from steric effects. All products can be explained by attack of the aromatic nucleophile on the epoxide position (or positions) most capable of stabilizing incipient positive character. The epoxide is also less electrophilic than other alkylating agents under similar conditions. An explanation for this is given.

Despite the abundance of studies on other classes of Friedel–Crafts (FC) alkylation reactions,[2] comparatively few studies have been done on the FC reactions of epoxides.[3-9] As with many other reactions of this type, complex product mixtures have been observed, but, atypically, complex epoxide FC alkylation mixtures generally do not appear to be the result of isomerization and disproportionation processes.[2,5,8] Instead they apparently result from multiple ring-opening pathways and from the formation of halohydrins resulting from ring opening by the Lewis acid alkylation promoter (LAAP).[4-8]

Recently, Japanese workers demonstrated a 100% stereospecific epoxide FC alkylation,[5] and our group reported a highly stereoselective one involving the transannular cyclization of a medium-ring epoxide.[10] These reactions suggested further investigations on epoxide FC reactions were of significant interest. However, most work prior to ours, other than polyene cyclizations (which are not intermolecular FC reactions[11]) dealt mainly with simple

(1) Presented in part at the 179th National Meeting of the American Chemical Society, Houston, TX, Mar 1980.

(2) (a) Olah, G. A. *Aldrichimica Acta* **1979**, *12*, 45. (b) Olah, G. A. "Friedel–Crafts Chemistry"; Wiley-Interscience: New York, 1973.

(3) Colonge, J.; Rochas, P. *Bull. Soc. Chim. Fr.* **1948**, 818 and the following articles.

(4) Inoue, M.; Sugita, T.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 174.

(5) Nakajima, T.; Suga, S.; Sugita, T.; Ichikawa, K. *Tetrahedron* **1969**, *25*, 1807.

(6) Inoue, M.; Sugita, T.; Kiso, Y.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1063.

(7) Inoue, M.; Chano, K.; Itoh, O.; Sugita, T.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 458.

(8) Nakamoto, Y.; Nakajima, T.; Suga, S. *Kogyo Kagoku Zasshi* **1969**, *72*, 2594; *Chem. Abstr.* **1970**, *72*, 100192.

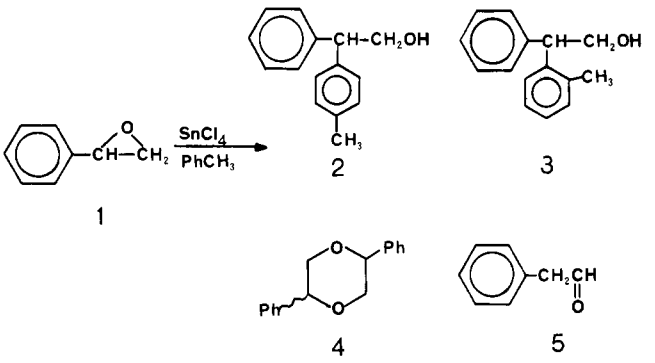
(9) Milstein, N. *J. Heterocycl. Chem.* **1968**, *5*, 337.

(10) Taylor, S. K.; Lilley, G. L.; Lilley, K. J.; McCoy, P. A. *J. Org. Chem.* **1981**, *46*, 2709.

(11) van Tamelen, E. E. *Acc. Chem. Res.* **1975**, *8*, 152.

0022-3263/83/1948-0592$01.50/0

Scheme I



epoxides.[3-9] Hence, there is a need for investigations on other more complex epoxides, particularly in light of the unusual selectivity of these recent reactions.

Also, most work has utilized aluminum chloride as an FC promoter, a strong Lewis acid and therefore possibly less selective than others. Also, it is insoluble in nonpolar solvents. Consequently, much previous work has been done under heterogeneous conditions.

The FC alkylation of benzene by phenyloxirane (1) with aluminum chloride as an LAAP has been reported[8] to give 2,2-diphenylethanol and phenylacetaldehyde as a major side product. On the other hand, other investigations under similar conditions, except with stannic chloride as a Lewis acid, report *cis*- and *trans*-2,5-diphenyldioxane and polymer as the sole products.[12,13] To understand this apparent discrepancy, we repeated the work.

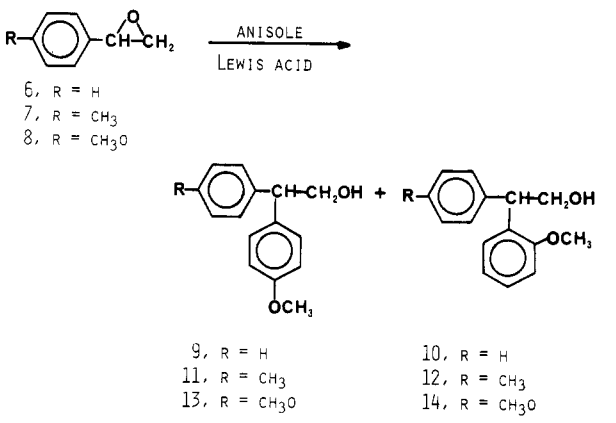
Results and Discussion

We observed essentially the same results as the latter report[12-14] with $SnCl_4$ as the LAAP. But in contrast to benzene, the more nucleophilic aromatic solvent toluene[15] is alkylated in 27% yield with $SnCl_4$ as an LAAP. The ortho/para ratio (3/2) is 28:72. However, several side products (Scheme I) also form. The product distribution of **2/3/4/5** is 31:12:13:33 by GC analysis, with three unidentified products accounting for 11% of the product mixture.

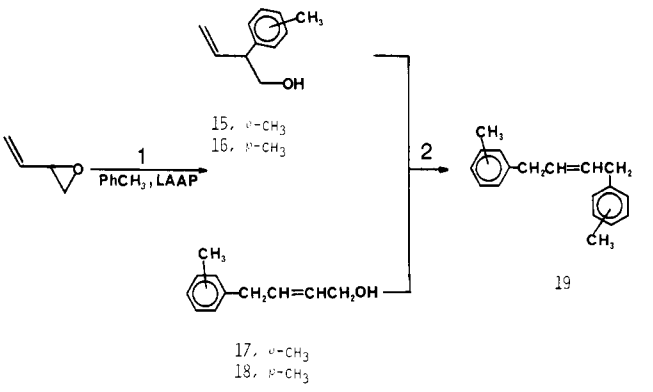
When anisole is the aromatic solvent, alkylation products result in at least 80% yield (ortho/para ratio of 16/84), and the reaction is free from significant side products.[16] Thus, an important factor in promoting FC alkylation is the aromatic molecule's nucleophilicity. Yields follow the order anisole > toluene > benzene. No alkylation product was detected when chlorobenzene was the solvent.

Anisyl- and tolylphenylethanols **2**, **3**, **9**, and **10** were independently synthesized by Kharash and Clapp's Grignard method[17] as described in the Experimental Section. The FC products were verified by NMR, IR, and GC comparison with the authentic compounds.

Scheme II



Scheme III



To test if aromatic activating groups on the epoxide would facilitate FC alkylation, we prepared *p*-methyl- and *p*-methoxy-substituted phenyloxiranes (7 and 8, respectively).[18] Such groups could stabilize a reactive species with positive character (at the ring-opening site). However, when toluene was the solvent, a low FC yield resulted with 7 and 8 on using stannic chloride as the LAAP. An NMR spectrum of both crude product mixtures suggested the reaction gave similar results to that of the FC reaction of phenyloxirane and toluene. However, when anisole was the reaction solvent, yields were 83% (12:88 ortho/para) and 94% (14:86 ortho/para for compounds 7 and 8, respectively (Scheme II).

In the above reactions, approximately 0.5 equiv of LAAP relative to epoxide was found to be the minimum quantity required to give the maximum yields. In the epoxide FC reactions we have investigated, dilute conditions have been necessary to minimize polymerization (see Experimental Section).

Most of our studies were done on 1,2-epoxy-3-butene. In these investigations we varied the LAAP, addition mode, LAAP concentration, and reaction temperature; toluene was always used as the aromatic substrate. This compound gave initial FC products (**15–18** in Scheme III), and then apparently all of these products were subject to rearrangement and/or further Friedel–Crafts reaction, depending on the reaction conditions, to more thermodynamically favorable products (isomers of **19**, Scheme III). This secondary pathway provides an excellent opportunity to study the influence of the above parameters on the reaction product distributions. The results of using stannic chloride (0.46 and 1.08 equiv relative to epoxide), 1,2-epoxy-3-butene, and toluene and varying the reaction time

(12) Summerbell, R. K.; Kland-English, M. J. *J. Am. Chem. Soc.* **1955**, *77*, 5095.
(13) Schaeffer, J. *J. Org. Chem.* **1968**, *33*, 4558.
(14) In repeating the work using $AlCl_3$, we were never able to get more than 2% alkylation using a freshly opened commercial bottle of aluminum chloride. However, the Japanese[8] workers used highly purified aluminum chloride, and this probably accounts for their better results. However, we also obtained 2,5-diphenylmethane in these reactions.
(15) We will refer to the aromatic compound as solvent even though it is also the substance being alkylated.
(16) Although the gas chromatogram showed only the two products, an NMR spectrum showed a doublet at δ 3.3 and a triplet at δ 4.6 which we tentatively attributed to 1-phenyl-2-anisylethanol (8% of the products by integration). The quantity of this product increases to 24% if the reaction temperature is held at 45 °C.
(17) Kharasch, M. S.; Clapp, H. G. *J. Org. Chem.* **1938**, *3*, 355.
(18) (a) Fuchs, R. *J. Am. Chem. Soc.* **1956**, 78, 5612. (b) Guss, C. O. *Ibid.* **1952**, *74*, 2561.

Table I. Products from the Stannic Chloride Promoted Friedel-Crafts Reactions of 1,2-Epoxy-3-butene

entry	equiv of LAAP	addn mode[d]	reaction time, min	product distribution,[c] % TB[a]	15 + 16[b]	17	18	19	unknowns	% yield
1	0.46	R	10	7	33	21	33	4	2	61
2	0.46	R	20	5	28	25	38	4		55
3	0.46	R	35	15	32	12	26	15		
4	0.46	R	60	12	23	8	16	41		57
5	1.08	R	10	11	20	8	16	45		50
6	1.08	R	60	5	0	0	0	92	3	51
7	0.46	I	10	12	8	27	47	3	3	58
8	0.46	I	20	12	9	24	44	11	<1	63
9	0.46	I	60	17	5	4	9	65	5	60
10	1.08	I	10	14	14	19	39	14	0	69
11	1.08	I	20	11	6	6	19	58	0	53
12	1.08	I	60	1	4	0	0	95	2	53

[a] TB is 1-tolylbutadiene, which results from alcohol dehydration (detected by GC/MS). [b] 15 and 16 were not separable on GC columns. However, an estimate of their ratio from IR analysis is 4:6. [c] Average values based on two or more reactions, accurate to ±5%. [d] R = regular; I = inverse.

Table II. Products from the Boron Trifluoride Etherate Promoted Friedel-Crafts Reactions of 1,2-Epoxy-3-butene

entry	equiv of LAAP	addn mode[d]	reaction time, min	product distribution,[c] % TB[a]	15 + 16[b]	17	18	19	unknowns	% yield
1	0.46	R	10	0	5	30	37	28	<1	54
2	0.46	R	20	0	1	20	27	52		43
3	0.46	R	60	<1	3	7	10	80	<1	46
4	1.08	R	10	0	<1	6	9	85	<1	47
5	1.08	R	60					100		46
6	0.46	I	10	8	1	36	43	12	<1	57
7	0.46	I	20	0	9	39	45	7	<1	41
8	0.46	I	60	<1	<1	20	27	53	<1	54
9	1.08	I	10	2	0	25	33	40	0	50
10	1.08	I	20	<1	1	11	16	72		45
11	1.08	I	60	3		5	6	86		39

[a] TB is 1-tolylbutadiene formed by alcohol dehydration. [b] 15 and 16 were not separable by GC. An estimate, by IR spectroscopy, of the 15/16 ratio is 4:6. [c] Average values based on two or more reactions, accurate to ±5%. [d] R = regular; I = inverse.

and addition mode are shown in Table I. We chose to call adding a Lewis acid solution to a dilute epoxide aromatic solvent solution "inverse addition". Adding the epoxide to a dilute LAAP promoter solution will be called "regular addition" since this mode is used most often.[3-9] The reaction temperature was controlled at 33 °C, and the addition time was 6–7 min. These conditions must be carefully reproduced or inconsistent product distributions are obtained.

From Table I data, several facts can be deduced. First, the proportion of isomeric, 1,4-ditolyl-2-butenes increases as the reaction time and LAAP concentration are increased. This suggests that the 2-tolyl-3-butenols **15** and **16** and the 4-tolyl-2-butenols **17** and **18** progressively are converted to **19**. Also, the proportion of **17** and **18** is seen to decrease faster than **15** and **16**. This is reasonable since **17** and **18** are allylic alcohols and therefore more prone to acidic elimination and electrophile formation than the primary alcohols **15** and **16**.

The inverse addition mode gave slightly higher proportions of **19** than the regular addition mode under the same conditions. However, this was not the case when boron trifluoride etherate was used as the LAAP (Table II). Also, unless very dilute solutions are used, the inverse addition mode is more susceptible to polymerization, as evidenced by more viscous products.

Separation of all the isomeric products, particularly those of **19**, proved very difficult. None of the 15 standard GC columns tried separated all the isomers. The ratio of **15**/**16** of 4:6 had to be estimated by preparative GC collection and infrared spectroscopic analysis. The cis/trans ratio of **17** and **18** averaged 9:1 as determined by NMR analysis (the trans CH_2O multiplet was centered at δ 3.9 whereas this cis multiplet appeared at δ 4.1[19]). Peaks from the cis isomers of **19** (8–11%) were not sufficiently resolved for quantitation. However, the trans isomers (89%) were resolved by capillary VPC: the *trans-o,o*-ditolyl-, *trans-o,p*-ditolyl, and *trans-p,p*-ditolyl-2-butene ratio was 16:45:39 to ±5%.

To add further suggestive evidence that the conversion of **15** and **16** to **19** occurs, we prepared **16** (vide supra) and treated it with 1.08 equiv of stannic chloride for 1 h in toluene. Surprisingly, very little rearrangement occurred (less than 5% **19** resulted). However, when the reaction described in Table I, entry 4, is repeated but the reaction mixture spiked with 0.53 g of 2-*p*-tolyl-3-buten-1-ol, 38% of it rearranged to **19**, as determined by product distribution analysis. Since the data in Table I are also suggestive of the disappearance of **15** and **16** with increasing reaction time, it appears that this rearrangement occurs under the FC conditions. However, the uncertainty introduced by the 50–60% yields and a ±5% reliability in product distributions make it impossible to eliminate completely other possibilities (e.g., under severe conditions the electrophile leading to **15** and **16** may suffer a different fate and not give **19**).

The simple treatment of the alcohol with stannic chloride did not mimic the FC reaction conditions, and such controls therefore should be interpreted with caution. Olah has pointed out that the acidic species in an FC reaction is not well-defined.[2] For example, a FC reaction eliminates

(19) Rose, C. B.; Taylor, S. K. *J. Org. Chem.* **1974**, *39*, 578.

a proton during rearomatization of the σ complex. It is well-known that a protonic acid is necessary for an alcohol FC reaction.[2] We suspect the simple control reaction is inadequate because the FC reaction generates an acidic species which is more effective at causing rearrangement.

Results with boron trifluoride etherate as an LAAP are given in Table II. This promoter is a slightly stronger Lewis acid[2] than stannic chloride, and hence it gives, expectedly, more **19** isomers under conditions equivalent to those where $SnCl_4$ was the LAAP. But it is highly surprising that very little of the 2-*p*-tolyl-3-butenols (**15** and **16**) result under any conditions.

It would be expected that these compounds would rearrange slower than **17** and **18**, which are present under most conditions. Therefore, the absence of **15** and **16** apparently is not due primarily to rearrangement. We have no explanation for this effect, but it does point out that more work needs to be done to explain such effects.

The use of aluminum chloride (freshly opened bottle) as an LAAP for 1,2-epoxy-3-butene resulted in highly viscous products indicative of polymer formation. Also, yields were low until a full 1 equiv of LAAP was used (perhaps due to LAAP insolubility). The only correlations drawn with this and the other LAAPs is that the same products are obtained. As an example, when 1.08 equiv of $AlCl_3$ was combined (regular addition) with the epoxide under typical conditions (reaction time 20 min), the product distrubution of **15**/**16**/**17**/**18**/**19** was 1:1:1:2:95 (1% tolylbutadiene).

Most of the compounds in this study were made by independent synthesis, and products were verified by GC, IR, and/or NMR analysis. The Grignard methods of Rose and Taylor[19] were used to make **15–18**.

Aryl Grignard reagent (2 equiv) was treated with 1,4-dichloro-2-butyne in an attempt, after hydrogenation, to make isomeric products of **19**. However, the dichlorobutyne promoted coupling of *p*-tolyl Grignards to bitolyl compounds.[20] However, treatment of *o*-tolylmagnesium bromide with 1,4-dibromo-2-butyne and subsequent reduction with sodium/ammonia gave 1,4-di-*o*-tolyl-*trans*-2-butene in reasonable yields.

When 1,2-epoxy-2-methyl-3-butene[21] was treated under our $SnCl_4$ FC conditions, little alkylation occurred. This lack of FC alkylation of tertiary epoxides has been noted for isobutylene oxide also and has been attributed to steric effects.[5,6] We did not conduct further investigations.

In conclusion, we have shown that (1) high epoxide FC yields are promoted by an activating group on the aromatic substrate, (2) an activating group on the epoxide substrate is less effective at promoting high epoxide FC yields (at least for phenyloxiranes), (3) changing reaction conditions can dramatically influence the product distributions of some epoxide FC reactions, and (4) the epoxide is apparently less electrophilic than other alkylating agents (e.g., R-X and R-OH which readily alkylate benzene[2]). We believe the latter point results because the positive character at the reactive site is reduced by interaction with the epoxide oxygen. This has been suggested before, particularly as a way to explain reaction stereospecificity.[5]

Experimental Section

The instruments used in this work are described elsewhere.[10] Reaction solvents were dried over sodium metal.

2-*p*-Tolyl-2-phenylethanol (2). To a Grignard reagent (0.02 mol) prepared in 20 mL of ether from *p*-bromotoluene and magnesium turnings was added dropwise 1.80 g (0.15 mol) of phenyloxirane in 10 mL of ether. After 1 h of reflux, the cooled solution was neutralized with 4% hydrochloric acid, washed with 5% sodium bicarbonate and water, and dried ($MgSO_4$). After distillation at 118–120 °C (0.2 mm), the product crystallized: mp 46–48 °C (lit.[22] mp 45–46 °C; NMR (CCl_4) δ 2.3, (s, 3 H), 4.1 (pseudo s, 3 H), 7.2 (s, 5 H), 7.1 (s, 4 H), 2.0 (br s, OH): IR (AgCl disks) 3100–3600 (br OH), 800 (para-disubstituted benzene), 730 and 690 (monosubstituted benzene) cm^{-1}.

2-*o*-Tolyl-2-phenylethanol (3).[23] The procedure above was repeated except with *o*-bromotoluene instead of *p*-bromotoluene: bp 123–124 °C (0.4 mm); n^{25}_D 1.5866; NMR (CCl_4) δ 2.2 (s, 3 H), 2.1 (s, 1 H), 3.9–4.5 (multiplets, 3 H), 7.1–7.4 (s and m overlapping, 9 H); IR (AgCl disks) 3100–3600 (br, OH), 750, 740, and 690 (ortho- and monosubstituted benzene) cm^{-1}.

2-(*p*-Methoxyphenyl)-2-phenylethanol (9).[23] Distillation of **9** (from a Grignard of *p*-bromoanisole) was hampered by concurrent sublimation of bianisyl, bp 160–170 °C (0.4 mm). The next day it formed a waxy solid. Trituration (ether/pentane) failed to increase the melting point (20–22 °C): NMR (CCl_4) δ 3.7 (s, 3 H); 3.9 (pseudo s, 3 H), 6.6–7.1 (AB, 4 H), 7.1 (s, 5 H); IR (AgCl disks) 3100–3600 (br, OH), 1230 (strong, ether), 810 (para) cm^{-1}. A 3,5-dinitrobenzoate derivative melted at 109–111 °C (ethanol).

2-(*o*-Methoxyphenyl)-2-phenylethanol (10). The above reaction was repeated with *o*-bromoanisole. The product was slightly contaminated with an impurity): bp 126–127 °C (0.3 mm) [lit.[24] mp 220 °C (30 mm)]; NMR (CCl_4) δ 2.1 (br s, 1 H), 3.6 (s, 3 H), 3.8–4.0 (m, 3 H), 6.6–7.1 (AB, 4 H), 7.1 (s, 5 H); IR (AgCl disks) 3100–3600 (OH), 1240 (ether), 740 and 690 (ortho- and monosubstituted benzene) cm^{-1}.

General FC Procedure of Phenyloxiranes (1, 7, 8). In a dry box, under a nitrogen atmosphere, was combined 1.7 mmol of Lewis acid with 25 mL of aromatic solvent. To this ice-cooled solution was added dropwise over 6 min a solution of 4.2 mmol of the phenyloxirane in 2.5 mL of the same aromatic solvent. After 1.5 h, the mixture was poured into 15 mL of 4% hydrochloric acid/ice, and the organic layer was washed with 5% sodium bicarbonate and water and dried ($MgSO_4$). GC,[25a] IR, and NMR analysis verified the product identifications.

2-*o*-Tolyl-3-buten-1-ol (15).[23] Compound **15** was prepared from *o*-tolylmagnesium bromide and 1,2-epoxy-3-butene by Rose and Taylor's general Grignard method:[19] bp 63–64 °C (0.05 mm), n^{25}_D 1.5356; NMR (CCl_4) δ 1.9 (s, OH), 2.3 (s, 3 H), 3.3–3.7 (multiplets, 3 H), 4.8–6.2 (vinyl, 3 H), 7.0 (s, 4 aromatic H); IR (AgCl disks) 3100–3600 (OH), 1050 (OH), 750 cm^{-1} (ortho) cm^{-1}. A 3,5-dinitrobenzoate derivative melted at 134–136 °C.

2-*p*-Tolyl-3-buten-1-ol (16).[23] Compound **16** was prepared from *p*-tolylmagnesium bromide and 1,2-epoxy-3-butene: bp 59–61 °C (0.05 mm); n^{25}_D 1.5342; NMR (CCl_4) δ 1.8 (OH), 2.3 (s, 3 H), 3.2–3.7 (multiplets, 3 H), 4.8–6.2 (vinyl, 3 H), 7.0 (s, 4 aromatic H); IR (AgCl disks) 3100–3600 (OH), 1050 (OH), 810 (para-disubstituted benzene) cm^{-1}. A 3,5-dinitrobenzoate derivative melted at 122–124 °C.

4-*o*-Tolyl-2-buten-1-ol (17). Compound **17** (cis) was prepared from *o*-tolylmagnesium bromide and 4-chloro-2-butynol and subsequent reduction over a poisoned catalyst.[19] The product, which distilled at 82–84 °C (0.1 mm), was 70% pure. However, when we began to repeat the reaction, the *chlorobutynol exploded during distillation*, and hence we did not prepare analytically pure material. Instead, the compound was used for a GC retention time reference.[25b]

4-*p*-Tolyl-2-buten-1-ol (18). Compound **18** was prepared from *p*-tolylmagnesium bromide, 1,2-epoxy-3-butene, and the conjugate

(20) Taylor, S. K.; Bennett, S. G.; Heinz, K. J.; Lashley, L. K. *J. Org. Chem.* **1981**, *46*, 2194.

(21) Reist, E. J.; Junga, I. G.; Baker, B. R. *J. Org. Chem.* **1960**, *25*, 1673.

(22) Ramart, P.; Amagat, M. *C. R. Hebd. Seances Acad. Sci.* **1924**, *179*, 901.

(23) Satisfactory combustion analyses (±0.3%) were obtained for these compounds.

(24) Stermer, O.; Frick, H. *Ber.* **1924**, *57*, 28.

(25) (a) GC retention times (in minutes) for toluene + 1 (10 ft Carbowax 20M column, 200 °C: **2** (28), 3 (25.5), **4** (24), **5** (2.5). For anisole + 1 (4 ft, OV1, 200 °C: **9** (7.5), **10** (5.0). For anisole + **7** (6 ft, OV17, 232 °C): 11 (12), **12** (8). For anisole + 8 (6 ft, OV1, 232 °C): **13** (28), **14** (22). (b) GC retention times for toluene + vinyloxirane (minutes):: **15** (14), **16** (14), **17** (27), **18** (30), **19** (58).

addition promoter cupric acetate monohydrate.[19] The trans/cis ratio was 83:17 by NMR integration (doublets at δ 3.9 and 4.1, respectively). HPLC purification (10-μm silica gel column; 20% CH_2Cl_2; 0.1% ethanol, 80% hexane; retention time 13.5 min at a 5-mL/min flow rate) gave **18**: 99.8% pure; n^{21}_D 1.5532; NMR (CCl_4) δ 2.3 (s, 3 H) 3.2 (d, 2 H, J = 4 Hz) 3.6 (s, OH), 3.9 (d, 2 H, J = 4 Hz), 5.6 (m, 2 vinyl H), 7.0 (s, 4 aromatic H); IR (AgCl disks) 3200–3600 (OH), 960 (trans C=C), 800 (para) cm^{-1}; mass spectrum, calcd for $C_{11}H_{14}O$ (M^+) 162.1044, m/e found 162.1048.

1,4-Di-*o*-tolyl-*trans*-2-butene (Isomer of 19). The Grignard of *o*-bromotoluene (2 equiv) was combined with 1,4-dibromo-2-butyne. After a typical workup, 0.95 g of the alkyne was forced under a mixture of 0.28 g of sodium and 20 mL of anhydrous ammonia. A normal reaction time and workup gave 0.5 g of product, which was purified by preparative GC (6 ft OV17 column, 180 °C): NMR (CCl_4) δ 2.3 (s, 6 H), 3.3 (d, 4 H), J = 4 Hz), 5.6 (m, 2 H), 7.0 (s, 4 H); IR (AgCl disks) 965 (m, trans C=C), 740 (ortho) cm^{-1}.[26] The GC retention time and spectra agreed with those of the sample from the Friedel–Crafts reaction (see below).

General Friedel–Crafts Procedure for 1,2-Epoxy-3-butene (Regular Addition). A solution of 1.0 g of the epoxide (14 mmol) in 9 mL of toluene was added dropwise over 6–8 min to a solution of 0.46 or 1.08 equiv of Lewis acid in 50 mL of dry toluene (initially at 27 °C; the temperature increased to 33 °C after the addition began). The addition time was varied only slightly to control the temperature at 33 °C. The solution was stirred at 33 °C for the time described in Tables I–III, washed with 10% sodium hydroxide and water, and dried ($MgSO_4$). The organic layer was evaporated overnight in an evaporating dish. The concentrate (1.2–1.5 g) was analyzed by GC, IR, and NMR. The NMR and IR data for these compounds are given above; GC data are footnoted.[25b]

(26) The 1,4-di-*m*-tolyl-*trans*-2-butene has been reported: bp 168–170 °C (2 mm); n^{20} 1.5788. See: Askerov, A. K.; Mustafaeva, P. R.; Sadyleh-Zade, S. I. *Soobshch. Akad. Nauk. Gruz. SSR* **1966**, *42*, 589.

Inverse Addition Procedure. A solution of 0.46 or 1.08 equiv of Lewis acid in 9 mL of toluene was added dropwise over 6–8 min to a mixture of 50 mL of toluene and 1.0 g of 1,2-epoxy-3-butene, controlling the reaction temperature at 33 °C (see above). After the addition was complete and the reaction was stirred at 33 °C for the time specified in the tables, the workup procedure above was followed.

Procedure for Isolating 19 Isomers. The procedure described in entry 12 of Table I was repeated on a larger (7 times) scale. The product was distilled: bp 120–126 (0.2 mm);[25] NMR ($CDCl_3$) δ 2.3 (at least 2 s, 6 H), 3.3 (at least 2 d, 4 H), 5.6 (vinyl, 2 H), 7.1 (2 s, 8 H) IR (AgCl disks) 960 (trans C=C), 800 (m, para), 740 (s, ortho) cm^{-1}; mass spectrum, m/e (relative intensity) 236 (21, M^+) 131 (100), 105 (45), 91 (32). A 60-m DB-1 capillary column (J&W Scientific) separated the isomers of **19** (temperature programmed from 100 to 240 °C at 2 °C/min). Retention times: cis isomers overlapping peaks centered at 53.2 min; *o,o* isomer, 53.6 min; *o,p* isomer, 53.8 min; *p,p* isomer, 54.1 min (16:45:39 ratio).

Acknowledgment. We thank M. Beeny, C. E. McEwen, Sidney Bourne, and John Schneider (Argonne National Labs) for instrumental assistance. Also, we thank Olivet Research Associates, Research Corp. (Grant No. C1108), and the National Science Foundation (Grant No. CDP-8006131) for financial support. Encouragement and discussions with John Hanson were also helpful.

Registry No. 1, 96-09-3; **2**, 84174-30-1; **3**, 84174-31-2; **7**, 13107-39-6; **8**, 6388-72-3; **9**, 84192-53-0; **9** 3,5-dinitrobenzoate, 84174-32-3; **10**, 84174-33-4; **15**, 84174-34-5; **15** 3,5-dinitrobenzoate, 84174-35-6; **16**, 84174-36-7; **16** 3,5-dinitrobenzoate, 84174-37-8; *cis*-**17**, 84174-38-9; *trans*-**17**, 84174-39-0; *cis*-**18**, 84174-40-3; *trans*-**18**, 84174-41-4; *trans*-**19** (*o,o* isomer), 84174-42-5; *trans*-**19** (*o,p* isomer), 84174-43-6; *trans*-**19** (*p,p* isomer), 60155-90-0; 4-chloro-2-butynol, 13280-07-4; *p*-bromotoluene, 106-38-7; *o*-bromotoluene, 95-46-5; 1,2-epoxy-3-butene, 930-22-3; 1,4-dibromo-2-butyne, 2219-66-1.

Preparation and Properties of Annelated Tropylium Salts

Randolph P. Thummel* and Paochai Chayangkoon

Department of Chemistry, University of Houston, Houston, Texas 77004

Received February 16, 1982

The insertion of methylene into the aromatic ring of benzocyclobutene leads to a mixture of cyclobutane-fused cycloheptatrienes. Treatment of this mixture with a trityl salt affords the cyclobutane-fused tropylium salt in essentially pure form. If this same synthetic approach is applied to other annelated benzenes, bis- and tris-annelated salts can be prepared. The proton and carbon-13 NMR spectra of a series of annelated tropylium salts have been analyzed and interpreted in terms of a rehybridization theory. Small but meaningful trends have been observed in the ultraviolet absorption spectra and pK_{R^+} values.

The synthesis and properties of benzocyclobutene have been thoroughly studied.[1] The properties of this molecule represent a unique compromise between the thermodynamic stability associated with a benzenoid aromatic system and the kinetic reactivity of a strained cyclobutene. The effects of further strain on benzene have been probed by the fusion of additional small rings to the aromatic nucleus.[2] The effect of ring strain on several polynuclear hydrocarbons[3] as well as on certain heteroaromatic rings[4] has recently been given increased attention. Thus far, however, there have been relatively few accounts of small ring-fused charged aromatic systems. It is the purpose of this paper to present some initial investigations in this area.

The two simplest cyclobutene-fused aromatic hydrocarbons which would be isoelectronic with benzocyclo-

(1) (a) Thummel, R. P. *Acc. Chem. Res.* **1980**, *13*, 70. (b) Klundt, I. L. *Chem. Rev.* **1970**, 471.

(2) (a) Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1977**, *42*, 300. (b) Davalian, D.; Garratt, P. J.; Koller, W.; Mansuri, M. M. *Ibid.* **1980**, *45*, 4183. (c) Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1976**, *98*, 3579. (d) Saward, C. J.; Vollhardt, K. P. *Tetrahedron Lett.* **1975**, 4539. (e) Heilbronner, E.; Kovac, B.; Nutakul, W.; Taggart, A. D.; Thummel, R. P. *J. Org. Chem.* **1981**, *46*, 5279.

(3) (a) Bilyard, K. G.; Garratt, P. J.; Underwood, A. J.; Zahler, R. *Tetrahedron Lett.* **1979**, 1815. (b) Doecke, C. W.; Garratt, P. J. *J. Chem. Soc., Chem. Commun.* **1981**, 873. (c) Hart, H.; Teuerstein, A.; Jeffares, M.; Kurg, W.-J. H.; Ward, D. L. *J. Org. Chem.* **1980**, *45*, 3731. (d) Thummel, R. P.; Nutakul, W. *J. Am. Chem. Soc.* **1978**, *100*, 6171.

(4) (a) Garratt, P. J.; Nicolaides, D. N. *J. Org. Chem.* **1974**, *39*, 2222. (b) Thummel, R. P.; Kohli, D. K. *Ibid.* **1978**, *43*, 4882. (c) Thummel, R. P.; Kohli, D. K. *Tetrahedron Lett.* **1979**, 143.

0022-3263/83/1948-0596$01.50/0