

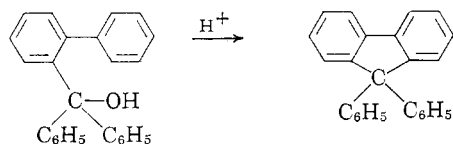
Mechanism of Cyclodehydration of 2-Phenyltriarylcarbinols

Harold Hart and Edward A. Sedor

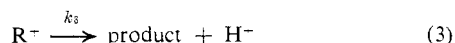
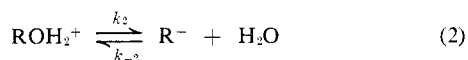
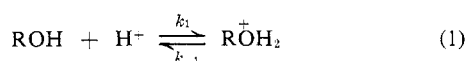
Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. Received January 19, 1966

Abstract: A kinetic study of substituent effects on the acid-catalyzed cyclodehydration of 2-phenyltriarylcarbinols to the corresponding 9,9-diarylfluorenes reveals that the rate-determining step depends on the nature of the substituents. A Hammett plot shows a sharp concave downward break. One group of carbinols have rates which correlate best with σ , have a large negative ρ (-2.51), and show a strong rate dependence on solvent acidity, a threefold rate enhancement in deuterated solvent, and an activation entropy near zero or slightly positive. The remaining carbinols have rates which correlate best with σ^+ , have a large positive ρ ($+2.77$), are insensitive to the solvent acidity, show no marked rate effect in deuterated solvent, and have a rather large negative activation entropy. These observations are rationalized by a three-step mechanism: (1) rapid and reversible protonation of the carbinol, (2) dissociation to the corresponding triarylcarbonium ion, and (3) intramolecular electrophilic substitution on the 2-phenyl ring. Step 2 is rate determining for carbinols on the negative ρ correlation line; step 3 is rate determining for carbinols on the positive ρ correlation line.

Attempts to convert triarylcarbinols with a 2-phenyl substituent in one of the aryl rings to the corresponding carbonium ion by dissolution in acid generally lead instead to a substituted fluorene, by cyclodehydration.¹ An analogous reaction has been observed with diaryl-² and monoaryldialkylcarbinols,³ as well as with 2-benzyl-,⁴ 2-phenoxy-,⁵ or 2-thiophenoxytriarylcarbinols.⁶ For example, Clarkson and Gomberg,¹ who were the first to isolate pure, crystalline 2-phenyltriphenylcarbinol, found that all attempts to convert it to the corresponding chloride gave instead a quantitative yield of 9,9-diphenylfluorene. Although this type of reaction has been known for over 60 years, its mecha-



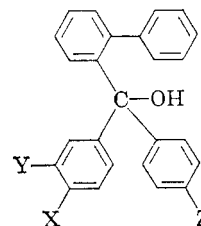
nism has not been examined in detail. Presumably a reaction sequence such as 1-3 is followed, but the



kinetics have not been studied. The reaction has interesting aspects. For example, if k_2 were rate

determining, the reaction would be analogous to an $\text{S}_{\text{N}}1$ solvolysis, with the aromatic ring serving as a built-in nucleophile. On the other hand, if k_3 were rate determining, the reaction would be comparable to other electrophilic aromatic substitutions, but with the electrophile and substrate built into the same reactive intermediate. Substituents might be expected to alter the relative rates of the various steps.

With a view to examining these alternatives, we synthesized a number of carbinols of the type shown (1-12) and found suitable conditions for carrying out



1-12
(for X, Y, and Z see Table I)

the cyclizations at measurable rates. The reaction rates were followed spectrophotometrically. A study of the effect of substituents on the reaction rates, of activation parameters, of effect of solvent acidity on the rates, and of solvent deuterium isotope effects allows a fairly complete mechanistic picture to be presented.

Results

The required carbinols were prepared either by reaction of a substituted phenyl Grignard reagent with 2-benzoylbiphenyl, or by reaction of the Grignard reagent from 2-bromobiphenyl with a disubstituted benzophenone. Formulas of the 12 carbinols studied and their relative rates of cyclodehydration are given in Table I listed in order of decreasing σ values of the substituents. Physical constants of the carbinols are given in Table VI and complete rate data are given in Table VIII in the Experimental Section.

Required samples of the cyclodehydration products were obtained by adding a few drops of strong acid to a refluxing solution of the carbinol in acetic acid. Upon cooling, nearly quantitative yields of the crystalline disubstituted fluorenes were obtained. They are

(1) F. Ullman and R. von Wursterberger, *Ber.*, **38**, 4105 (1905); E. Khotinsky and R. Patzewitch, *ibid.*, **42**, 3104 (1909); P. G. Sergeev, *J. Russ. Phys. Chem. Soc.*, **61**, 1421 (1929); R. G. Clarkson and M. Gomberg, *J. Am. Chem. Soc.*, **52**, 2881 (1930); E. P. Kohler and L. W. Blanchard, *ibid.*, **57**, 367 (1935); G. Wittig and G. Fuhrman, *Ber.*, **73B**, 1197 (1940); J. H. Weisberger, E. K. Weisberger, and F. B. Ray, *J. Am. Chem. Soc.*, **72**, 4250 (1950); H. Gilman and R. D. Gorsich, *ibid.*, **78**, 2218 (1956).

(2) E. Bergmann and A. Bondi, *Ber.*, **64**, 1477 (1931); J. R. Dice, T. E. Watkins, and H. L. Schuman, *J. Am. Chem. Soc.*, **72**, 1738 (1950); C. F. Koelsch, *ibid.*, **56**, 480 (1934); H. H. Hatt, *J. Chem. Soc.*, 478 (1941); H. Suzuki, *J. Chem. Soc. Japan*, **72**, 825 (1951).

(3) M. Anchel and A. H. Blatt, *J. Am. Chem. Soc.*, **63**, 1948 (1941).

(4) E. Barnett, J. W. Cook, and I. G. Nixon, *J. Chem. Soc.*, 504 (1927); F. F. Blicke and R. A. Patelski, *J. Am. Chem. Soc.*, **58**, 559 (1936); F. F. Blicke and R. J. Warzynski, *ibid.*, **62**, 3191 (1940); C. F. Koelsch, *J. Org. Chem.*, **3**, 456 (1938).

(5) Fourth reference in footnote 1.

(6) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2279 (1963).

Table I. Substituted 2-Phenyltriarylcarbinols, and Their Relative Cyclodehydration Rates^a

Compd	X	Y	Z	$k_{rel}^{25^\circ}$	σ^b	$\sigma^+{}^b$	E_a^c	$\Delta H^\ddagger{}^c$	$\Delta S^\ddagger{}^d$
1	Cl	H	Cl	0.096	0.454	0.228	23.7	22.8	1.60
2	H	CF ₃	H	0.052	0.42	0.52	21.3	22.8	4.4
3	H	Cl	H	0.100	0.373	0.399	22.8	21.7	2.7
4	Cl	H	H	0.30	0.227	0.114	21.3	20.1	-0.8
5	H	OCH ₃	H	0.74	0.115	0.047	25.3	21.1	4.3
6	H	H	H	1.00	0	0	19.2	18.9	-2.6
7	H	CH ₃	H	1.48	-0.069	-0.066	24.0	19.8	1.4
8	CH ₃	H	H	3.27	-0.170	-0.311	21.7	18.6	-1.0
9	OCH ₃	H	H	0.56	-0.268	-0.778	18.3	15.0	-16.7
10	CH ₃	H	CH ₃	5.80	-0.34	-0.622	15.4	14.9	-12.3
11	CH ₃	H	OCH ₃	1.76	-0.438	-1.089	18.3	15.0	-16.7
12	OCH ₃	H	OCH ₃	0.0090	-0.536	-1.556	21.8	20.7	-4.9

^a In 80% aqueous acetic acid containing 4% sulfuric acid. ^b Values are taken from H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). When two substituents are present, the sums of σ 's are used. ^c Kcal/mole. ^d Cal/mole^o.

listed, with their properties, in Table VII in the Experimental Section.

The cyclization rates of the carbinols were determined in 80% aqueous acetic acid containing 4 wt % of sulfuric acid. The choice of this rather unconventional medium was dictated by the need to strike a balance between measurable rates and solvents in which both the starting carbinol and the product hydrocarbon were soluble. For some carbinols, the amount of sulfuric acid was varied (4-6%). The reactions were studied at five temperatures between 15 and 35°. Progress of each reaction was followed by the appearance of a band in the vicinity of 308 m μ which was present in the fluorenes, but absent in the carbinols. In several cases (2, 6, and 10) a comparison of the product isolated from a kinetic run with that synthesized independently showed that the reaction proceeded quantitatively to completion, without formation of side products.

All of the reactions followed precise first-order kinetics through at least 88% reaction. The rate data are given in Table VIII in the Experimental Section, and the derived activation parameters are listed in Table I. The reaction rates were independent of initial carbinol concentration, tested with two different substrates (Table II).

Table II. Effect of Initial Carbinol Concentration on Cyclodehydration Rates^a

Compd	Initial concn, moles/l. $\times 10^6$	$k \times 10^4$, sec ⁻¹
4	7.05	7.96 \pm 0.04
	14.10	8.06 \pm 0.05
	25.00	7.78 \pm 0.02
8	3.30	87.6 \pm 0.2
	5.71	86.8 \pm 0.2
	9.53	86.6 \pm 0.2

^a In 80% aqueous acetic acid containing 4% sulfuric acid, at 25°.

Certain of the carbinols (9-12) gave colored solutions in the reaction medium. In these cases, it was possible to follow not only the appearance of product (at \sim 308 m μ) but also the disappearance of the visible peak (at \sim 470 m μ) due to the carbonium ion. The rates of the two processes were identical within experimental error (Table III).

Table III. Comparison of Cyclodehydration Rates Measured by Product Appearance and by Carbonium Ion Consumption^a

Compd	$k \times 10^4$, sec ⁻¹	$k' \times 10^4$, sec ⁻¹	λ_{max} , m μ (ϵ)
9	14.2	14.3	474 (53,000)
10	153	159	458 (53,000)
11	4.67	4.72	487 (79,000)

^a In 80% aqueous acetic acid containing 4% sulfuric acid, at 25°; k = rate constant measured by appearance of 308-m μ peak for the appropriate fluorene; k' = rate constant measured by disappearance of the peak in the visible region, at the wavelength shown in the last column.

Discussion

Hammett Correlations. It is clear from the data presented in Table I that substituents markedly affect the cyclodehydration rates, but that their effect does not follow a single Hammett plot. The fastest reaction occurred with two *p*-CH₃ substituents, and the slowest with two *p*-OCH₃ substituents, whereas compounds with one or two *p*-Cl substituents reacted at intermediate rates. The substituents in fact fall into two groups. One of these is best correlated by Hammett σ values, the value of ρ at 25° being -2.51. The correlation coefficient is 0.990, as contrasted with 0.955 if σ^+ values are used.⁷ A plot of $\log k$ vs. σ for these substituents is shown in the right portion of Figure 1. Those carbinols which have a *p*-OCH₃ substituent fall nowhere near the correlation line, and in fact fall into the second group of substituents, which are best correlated by σ^+ , with a value of ρ at 25° of +2.67 and a correlation coefficient of 0.976.⁸ Carbinol 10, with two *p*-methyl substituents, occupies an ambiguous position at the apex of Figure 1. The two points shown for this carbinol correspond to the use of σ or σ^+ constants, and the compound falls reasonably close to both correlation lines.

The activation parameters (Table I) also fall into two groups. For those substituents on the negative ρ correlation line, the activation enthalpies decrease as the electron-donating power of the substituents increases, and the activation entropy is on the whole near zero or slightly positive. Conversely, for those substituents on the positive ρ correlation line, the activation enthalpies increase as the electron-donating power of substituents increases, and the activation entropy is moderately

(7) Using σ^+ , ρ was -1.94.

(8) Using, σ , the correlation coefficient was 0.801 and ρ = +7.79.

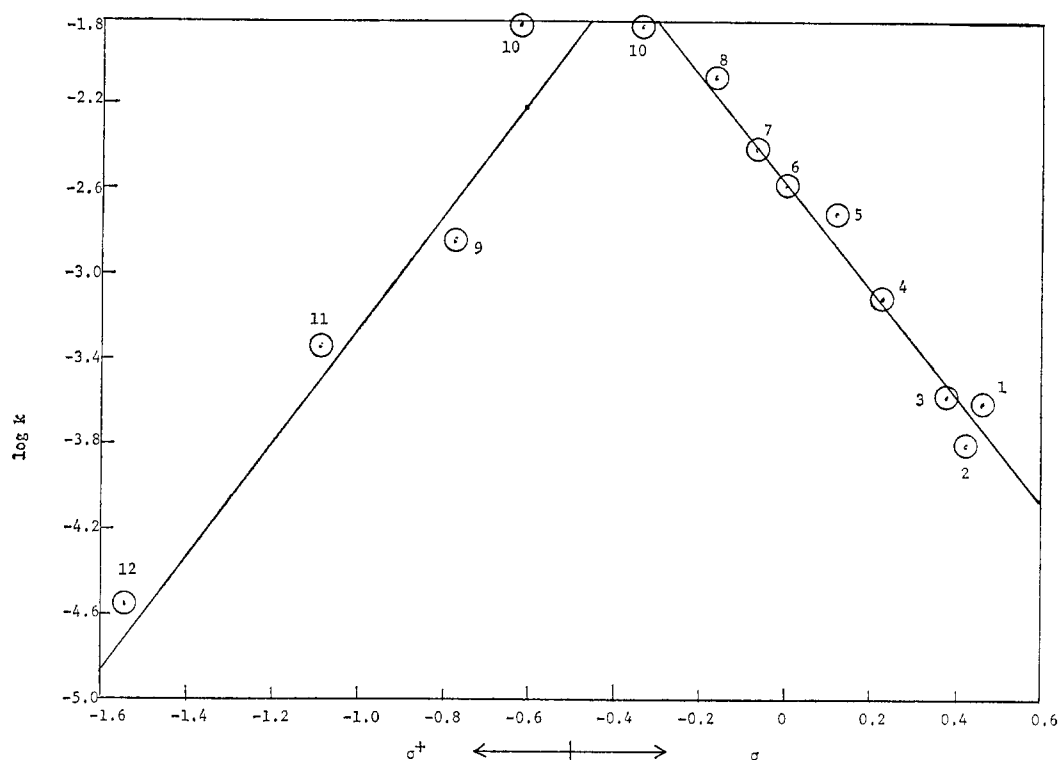


Figure 1. Hammett plot for the cyclodehydration of 2-phenyltriarylcarbinols in 80% aqueous acetic acid containing 4% sulfuric acid at 25°. Numbers refer to the formulas in the text.

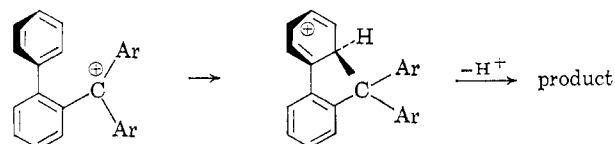
large and negative. A plot of ΔH^\ddagger vs. ΔS^\ddagger for either set of substituents shows a rather large degree of scatter. The best straight lines drawn through each set lead to isokinetic temperatures well above the temperatures of the kinetic measurements.

Mechanism. Leffler and Grunwald⁹ have pointed out that a Hammett plot which shows a concave downward break (Figure 1) is caused by a change in the rate-determining step of an otherwise constant mechanism. This is consistent with sequence 1–3, in which step 2 is rate determining for those substituents which appear on the right side of Figure 1, and step 3 is rate determining for those substituents which appear on the left side of Figure 1. Thus the ionization step is normally rate determining, but when the substituents stabilize the intermediate carbonium ion sufficiently, ring closure becomes rate determining.

The signs and magnitudes of the ρ values, the substituent correlations (*i.e.*, σ or σ^+), and the activation parameters are in accord with this interpretation. When step 2 is rate determining, the transition state will be electron deficient with respect to the ground state, and a negative ρ is expected. However, since formation of R^+ is undoubtedly not complete at the transition state, ρ should be less negative than -3.64 , the value observed¹⁰ for the equilibrium ionization of triarylcarbinols. The observed ρ of -2.51 is thus reasonable. The better agreement with σ rather than σ^+ indicates that direct resonance interaction of the substituents in 1–8 with the cationic center is small. Actually the correlation is not highly sensitive to the difference between σ and σ^+ (0.990 *vs.* 0.955), possibly because the sub-

stituents are mainly electron withdrawing on the right side of Figure 1. Also, because of the 2-phenyl substituent, the transition state may be sufficiently non-planar as to minimize the importance of a resonance effect. The small, slightly positive activation entropy is consistent with decreased crowding accompanying the change from sp^3 to sp^2 hybridization at the ionization site.

For those substituents on the left side of Figure 1, the reaction solutions became red almost instantly, and the red color disappeared as the reaction proceeded. Extrapolation to zero time gave the λ_{\max} (ϵ) values shown in the last column of Table III. These are nearly identical with reported values for the similarly substituted triphenylcarbinols¹¹ and support the conclusion that the corresponding carbonium ions of 9–12 form rapidly and undergo a slow, rate-determining ring closure (step 3). In accord with this interpretation and the expectation that positive charge is more dispersed in the transition state than in the ground state, one finds a rather large positive ρ value. The far better correlation with σ^+ than with σ is to be expected, since the ground state is in fact a carbonium ion. Finally, the large negative activation entropy is consistent with the requirement that the 2-phenyl group and the carbonium carbon atom be rather specifically oriented for the reaction



(9) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 189.

(10) N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957).

(11) W. N. White and C. A. Stout, *J. Org. Chem.*, **27**, 2915 (1962).

The consequent restriction in degrees of freedom should result in a large entropy effect.

Further Tests of the Mechanism. During any given kinetic experiment, acid consumed in step 1 is regenerated in step 3, so that good pseudo-first-order kinetics should be (and were) observed. However a difference in the effect of acidity on the observed rate constants is predicted, depending upon whether step 2 or 3 is rate determining. In the former instance, the rate depends on the concentration of ROH_2^+ which, in turn, depends on equilibrium 1. An increase in the acidity of the medium should increase the equilibrium concentration of ROH_2^+ and accordingly increase the observed cyclodehydration rate. On the other hand, if step 3 is rate determining, all of the carbinol will have been rapidly converted to carbonium ion, and there should be relatively little effect of acidity on the observed rate.

Accordingly, the cyclodehydration rates of several of the carbinols which follow each of the Hammett correlations were measured as a function of the per cent sulfuric acid in the reaction medium, with the results given in Table IV. The variation in per cent acid

Table IV. The Effect of Acid Strength on the Cyclodehydration Rates of 2-Phenyltriarylcarbinols

Compd	$k_r \times 10^4 \text{ sec}^{-1} \text{ }^a$		
	4%	5%	6%
1	2.53	4.16	6.58
3	2.64	4.53	6.75
4	7.88	14.40	21.88
5	19.5	31.3	
6	26.4	47.6	73.5
9	14.7	15.7	14.8
10	153	169	
11	4.64	4.88	

^a Measured in 80% aqueous acetic acid at 25°, with the indicated weight percentages of sulfuric acid.

was rather limited, in order to keep the rates in a measurable range; it was sufficient, however, to establish the essential correctness of the prediction. Cyclization rates for the carbinols on the right of Figure 1 showed a strong dependence on acidity, the rate ratios $k_{5\%}/k_{4\%}$ and $k_{6\%}/k_{4\%}$ being 1.72 ± 0.08 and 2.68 ± 0.10 , respectively. On the other hand, these ratios for the carbinols for which step 3 is thought to be rate determining are only 1.07 ± 0.02 and 1.01 (only one determination).

An alternative explanation for the increased rates with increased acidity for carbinols on the $-\rho$ correlation would be that step 1 rather than step 2 is rate determining. Although the protonation of oxygen is generally considered to be exceedingly rapid,¹² there was a remote possibility that the environment around the hydroxyl group in 2-phenyltriarylcarbinols was sufficiently crowded with hydrophobic groups that protonation might be slow. This possibility was subjected to experimental test. It is well known that many acid-catalyzed reactions proceed more rapidly in D_2O than in H_2O , and this effect has been used as a criterion for a pre-rate-determining equilibrium protonation.^{12,13}

(12) For a discussion, see F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 943 (1957).

(13) For a discussion, see K. Wiberg, *ibid.*, **55**, 718 (1955).

Accordingly, the cyclodehydration rates of several carbinols on both sides of Figure 1 were determined in 80% $\text{CH}_3\text{COOD}-\text{D}_2\text{O}$, with the results given in Table V. A nearly constant rate enhancement of about 3

Table V. Solvent Isotope Effect on Cyclodehydration Rates^a

Compd	k_D/k_H
4	2.91
6	3.10
8	2.88
9	0.94
10	1.55

^a Rates in deuterated solvent were measured in 80% $\text{CH}_3\text{COOD}-\text{D}_2\text{O}$ containing 4% H_2SO_4 , at 25°. Total deuterium enrichment of acidic hydrogen was 97.3%.

is observed for three carbinols (4, 6, and 8) on the $-\rho$ correlation line which vary by a factor of over 10 in their absolute cyclodehydration rates. On the other hand, carbinol 9 shows almost no solvent deuterium isotope effect, since step 3 is rate determining.

Carbinol 10, which is at the apex of Figure 1, occupies an ambiguous position. It seems likely that here k_2 and k_3 are of comparable magnitude, with the result that an intermediate solvent deuterium isotope effect is observed. Although the rates for cyclodehydration of 10 as measured by product appearance and by carbonium ion disappearance agree well (Table III), it must be pointed out that this carbinol dehydrates so rapidly that it was impossible to get initial rate readings until reaction was already 45% complete at 25°. Attempts to slow the reaction down by lowering the temperature were frustrated by limited solubility of the product, so it was not possible, as hoped, to observe both the appearance and decay of R^+ .

In summary, all of the data seem to substantiate schemes 1-3 as the correct cyclodehydration mechanism; step 1 is rapid in all cases, but step 2 or 3 may be rate determining, depending on the substituents.

Experimental Section¹⁴

Preparation of 2-Phenyltriarylcarbinols. One of three procedures was used, depending on the number and type of substituent. These procedures, designated A, B, and C, will be illustrated with examples, to indicate some of the ways in which the problem of isolating pure carbinols was overcome. The results of all the preparations are summarized in Table VI.

Procedure A. 3-Methoxy-2'-phenyltriphenylmethanol (5). To the Grignard reagent prepared from 0.643 g (0.0267 g-atom) of high purity magnesium and 5.0 g (0.0267 mole) of 3-bromoanisole in 90 ml of anhydrous tetrahydrofuran there was added (N_2 atmosphere) dropwise a solution of 3.0 g (0.0166 mole) of 2-phenylbenzophenone in 50 ml of the same solvent. The solution turned blue immediately, but became yellow after 30-hr reflux. After 48-hr reflux, 100 ml of distilled water was added dropwise. Extraction with ether (three 100-ml portions), drying over MgSO_4 , and evaporation of the solvent gave 6.1 g of a viscous oil. A sample (3.5 g) of the oil was chromatographed on 100 g of Woelm neutral alumina, activity 1, using 50% carbon tetrachloride-benzene as eluent. The major component (1.1 g, 31.1%) was an oil which showed one spot on tlc plates. Remaining fractions yielded 1.8 g of a complex mixture (tlc). The major product crystallized on standing, and was recrystallized from pentane, mp 104-105.5°. Its nmr spectrum (CCl_4) showed singlets at τ 7.28 (1 H) and 6.42 (3 H) and a multiplet at τ 3.50-2.68 (18 H).¹⁵

(14) Melting points are uncorrected. Analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

(15) Infrared and nmr spectra of all compounds are given in the appendix of the Ph.D. Thesis of E. A. S., Michigan State University, 1965.

Table VI. Preparation and Properties of 2-Phenyltriarylcarbinols

Compd	Conditions ^a	Yield, ^b %	Mp, ^c °C	Calcd, %		Found, %	
				C	H	C	H
1 ^d	B,EB,24	28	118–118.5(p)	74.08	4.48	74.24	4.52
2	A,T,24	52	Oil ^e	77.23	4.74	77.46	4.99
3 ^f	A,EB,5	14.5	101.5–102(p)	81.00	5.16	81.07	5.14
4 ^g	A,EB,2 ^h	5	105.0–106.5(b)	81.00	5.16	81.02	5.15
5	A,T,48	31.1	104–105.5(p)	85.22	6.05	85.07	6.09
6	B,E,4 ^h	28	91–92(p) ⁱ				
7	A,T,2	55.8	Oil ^j	89.11	6.33	88.68	6.41
8	C,E,1	37	72.5–74.5(h)	89.11	6.33	89.27	6.25
9	C, ^k E	16	87.5–89(h)	85.22	6.05	85.02	6.04
10	B,T,1	25	162–164(b)	88.97	6.64	88.97	6.56
11	B,T,48	28	126–127.5(p)	85.23	6.36	85.19	6.36
12	B,T,24	22	123–124(b)	81.79	6.10	81.62	6.01

^a The first letter refers to the procedure used: A, arylmagnesium bromide + 2-phenylbenzophenone; B, 2-biphenylmagnesium bromide + an appropriately substituted benzophenone; C, aryllithium + 2-phenylbenzophenone. The second letter refers to the solvent: E, ether; T, tetrahydrofuran; EB, ether for preparation of Grignard reagent, replaced by benzene for the subsequent reaction. The number refers to the reflux time in hours after addition of the reactants. Unless otherwise stated, work-up hydrolysis was with H₂O alone. ^b Purified product. ^c Uncorrected; recrystallization solvents are given in parentheses: p, pentane; h, hexane; b, benzene–petroleum ether. ^d Calculated for Cl: 17.50. Found: Cl, 17.56. ^e Purified by chromatography on basic alumina (50% benzene–CCl₄ eluent) and silica gel (benzene eluent) gave a single tlc spot. ^f Calculated for Cl: 9.56. Found: Cl, 9.44. ^g Calculated for Cl: 9.56. Found: Cl, 9.54. ^h Hydrolysis with ammonium chloride. ⁱ Lit. mp 87–88° (Clarkson and Gomberg, ref 1). ^j Purified by chromatography on basic alumina (benzene eluent) and Woelm neutral alumina, grade 1 (CCl₄ eluent); gave a single tlc spot. ^k Inverse addition at 0°.

Table VII. Preparation and Properties of 9,9-Diarylfluorenes

Compd ^a	Procedure ^b	Mp, ^c °C	Composition, ^d %		$\lambda_{\max}^{95\% \text{ EtOH}}$ (ε) ^e
			C	H	
1F ^f	A(5 min)100	165–166.5	77.53	4.17	308 (6780), 296 (4410), 284s (9160), 279.2s (11,500), 272.4 (15,000), 269.3s (14,300), 263.2s (13,400), 240 (31,500)
2F	B(3 days)60	127.5–129.5	80.81	4.44	307.2 (7870), 295.4 (5050), 282.3s (10,800), 278s (12,800), 271.0 (17,200), 267.0 (16,300), 263s (15,600), 236.7 (26,600), 228.2 (33,400)
3F ^g	A(1 min)100	154–155	85.09	4.86	307.2 (7730), 295.6 (4900), 283.2s (10,200), 278.7 (12,400), 271.7 (16,200), 85.13 4.85 267.3 (15,000), 261.5s (14,400), 238.5 (27,800), 229.6 (34,100)
4F ^h	A(5 min)100	142.5–144.0	85.09	4.86	307.9 (7470), 295.9 (7070), 284.2s (8710), 271.6 (15,100), 267.5s (21,140), 264.0s (13,680), 237.5 (28,400), 230.0 (34,700), 228s (33,700)
5F	A(10 min)95	150.5–151.5	89.62	5.79	307.8 (8380), 295.7 (5200), 283.7s (12,200), 270.0 (17,500), 267.5s (16,700), 263s (15,100), 237s (27,200), 228s (38,100)
6F	ⁱ		89.54	5.69	307.8 (8230), 296 (4970), 283s (8820), 279s (11,500), 271.5 (15,000), 267.5 (14,600), 263s (13,700), 238 (26,100), 230 (34,000), 224s (33,500)
7F	A(1 min)90	150.0–150.5	93.94	6.06	308 (8340), 296 (5200), 283s (9520), 278.5s (12,100), 271.6 (15,700), 267.5 (15,400), 263.3s (14,500), 238.2 (27,100), 230 (35,800)
8F	A(30 sec)100	134–134.5	93.94	6.06	308.1 (8310), 296.2 (5040), 284.1s (8140), 279s (11,500), 271.3 (15,120), 267.3 (14,960), 261.9s (13,910), 237.5s (27,400), 229.1 (36,050), 224.5s (35,900)
9F	B(50 min)100	165.5–166.0	89.62	5.79	308.6 (8780), 296.5 (5130), 279.5s (14,200), 273.0 (17,600), 268.2s (17,300), 264.1s (16,470), 236.9s (12,600), 230.0 (17,700)
10F	A(1 min)70	160.0–160.5	93.60	6.40	308.6 (8500), 296 (5090), 284s (8160), 279.6s (11,320), 271.8 (14,500), 267.5 (14,500), 263.5s (44,800), 238.8 (28,000), 228.3 (40,300)
11F	B(10 hr)96	129–130	89.47	6.12	308.8 (10,400), 297 (5970), 278.9s (16,300), 271.5 (22,600), 268 (21,800), 230 (50,300)
12F	B(4 days)85	120–122	85.69	5.86	309.8 (10,800), 297.5 (5620), 279.6s (19,000), 271 (24,400), 268 (24,800), 263 (24,800), 230 (79,800)

^a Compounds are numbered to correspond to the carbinols from which they were prepared (see Table I). ^b Although precise procedures varied, they can in general be grouped into two categories: A, 0.1–0.5 g of the carbinol was dissolved in 10–15 ml of glacial acetic acid, the solution brought to reflux, and three to five drops of concentrated HCl added; the reaction mixture became colored (yellow to red), then clear. On cooling, and addition of a few drops of water, crystals appeared; B, 0.1–0.3 g of the carbinol was dissolved in 15–20 ml of 80% aqueous acetic acid containing 4% H₂SO₄, allowed to stand at room temperature until the red color faded to yellow, warmed to 80°, then cooled, water added, and the crystals were collected. Reaction times are given in parentheses, and followed by the per cent yield. ^c Methanol was the recrystallization solvent in all cases. All products showed a single tlc spot. ^d Upper figures calculated, lower figures found. ^e In mμ; s, shoulder. ^f Calculated for Cl: 18.31. Found: Cl, 18.40. ^g Calculated for Cl: 10.05. Found: Cl, 10.00. ^h Calculated for Cl: 10.05. Found: Cl, 10.13. ⁱ Prepared according to Clarkson and Gomberg (ref 1).

Procedure B. 4,4'-Dichloro-2''-phenyltriphenylmethanol (1). Grignard reagent was prepared from 1.35 g (0.0563 g-atom of high purity magnesium and 13.1 g (0.0563 mole) of 2-bromobiphenyl in 50 ml of anhydrous ether. To the refluxing orange solution was added dropwise a solution of 5.5 g (0.0219 mole) of 4,4'-dichlorobenzophenone (Dow Chemical Co.) in 25 ml of anhydrous benzene and 10 ml of ether. After addition, the mixture was refluxed for 24 hr, then allowed to stand at room temperature for 48 hr. The white precipitated complex was filtered through glass wool and washed with anhydrous ether (two 20-ml portions). The complex and glass wool were stirred with 75 ml of ether and decomposed by dropwise addition of distilled water (20 ml). The ether layer

was separated and dried (MgSO₄) and the solvent removed on a rotary evaporator. The oily residue, when stirred with 20 ml of pentane, gave 2.48 g (28%) of the desired carbinol, mp 116.5–117.0°. Recrystallization from pentane raised the melting point to 118–118.5°. The mother liquors gave 4.8 g of a complex mixture (tlc) containing some of the desired carbinol. The nmr spectrum of 1 in CCl₄ had a singlet at τ 7.22 (1 H) and a complex multiplet at τ 4.42–2.67 (16.9 H).¹⁵

Procedure C. 4-Methyl-2'-phenyltriphenylmethanol (8). *p*-Tolylolithium was prepared (N₂ atmosphere) from 0.40 g (0.057 g-atom) of lithium and 10.0 g (0.0585 mole) of *p*-bromotoluene in 75 ml of anhydrous ether. To the gray solution was added drop-

Table VIII. Rate Constants ($\text{sec}^{-1} \times 10^4$) for Cyclization of 2-Phenyltriarylcarbinols in 80% Aqueous Acetic Acid Containing 4% Sulfuric Acid^a

Compd	15°	20°	25°	30°	35°
1	(0.295)	1.26 ± 0.03	2.53 ± 0.12	4.93 ± 0.03	8.89 ± 0.15
2	(0.257)	(0.631)	1.36 ± 0.01	2.25 ± 0.02	13.5 ± 0.1*
3	(0.646)	1.54 ± 0.02	2.64 ± 0.02*	5.06 ± 0.08	9.94 ± 0.27
4	1.87 ± 0.15	3.90 ± 0.09	7.88 ± 0.17	12.2 ± 0.1*	23.8 ± 0.9
5	6.39 ± 0.13	9.88 ± 0.02	19.5 ± 0.2	33.0 ± 0.3	(57.5)
6	9.66 ± 0.38	15.5 ± 0.1	26.4 ± 0.6	50.4 ± 1.6	76.2 ± 1.6
7	12.3 ± 0.1	21.8 ± 0.1	39.2 ± 0.1	66.2 ± 1.3	(148)
8	23.3 ± 0.3	44.5 ± 0.2	86.3 ± 0.5*	137 ± 1*	(283)
9	5.6 ± 0.05	8.82 ± 0.04	14.7 ± 0.1	24.4 ± 0.6	36.0 ± 0.7
10	53.4 ± 0.1	99.2 ± 0.7	153 ± 5	(282)	(363)
11	(2.04)	2.79 ± 0.01	4.64 ± 0.2	8.00 ± 0.05*	(12.3)
12		(0.12)	0.238 ± 0.003*	(0.417)	0.701 ± 0.007

^a Figures in parentheses are estimated from Arrhenius plots. All values are the average of three or more runs, except those marked with an asterisk, which are the average of only two runs.

wise over 15 min a solution of 4.0 g (0.0155 mole) of 2-phenylbenzophenone in 100 ml of anhydrous ether. The mixture was refluxed for 1 hr, then decomposed with 50 ml of water. Separation of the ether layer, drying, and evaporation afforded 6.0 g of light yellow oil which was chromatographed on silica gel (Baker's) using CCl_4 as eluent. The first three fractions (150 ml) yielded 3.0 g of impure alcohol; the remaining fractions (350 ml) gave 2.5 g of a clear oil which became a glass when final traces of solvent were removed. The glass resisted crystallization from pentane or benzene-pentane, but on standing for 2 months deposited a few crystals (mp 60–75°) which were used to seed a hexane solution of the glass. In this way, 2.0 g (37%) of 8, recrystallized from hexane, mp 72.5–74.5°, were obtained. The product gave a single tlc spot, $\lambda_{\text{max}}^{\text{EtOH}}$ 280 m μ (ϵ 790), and an nmr spectrum with singlets at τ 7.35 (1 H) and 7.70 (3 H) and a multiplet at τ 3.38–2.66 (18 H).¹⁵

Preparation of 9,9-Diarylfluorenes. Preparation of these compounds in pure form offered no difficulties, and the procedures sketched briefly in footnote b of Table VII should suffice for duplicating our results.

Kinetic Procedure. Reactions were carried out in 1-cm, 3-ml, stoppered, rectangular, silica cells in the thermostated cell compartment of a Beckman DB spectrophotometer, using a Tecam circulating unit to control the temperature to $\pm 0.1^\circ$. Most reactions were run in a solvent containing $4.000 \pm 0.001\%$ by weight sulfuric acid in 80% aqueous acetic acid. The solvent was prepared on a Mettler analytical balance by placing 5 g of $100 \pm 0.1\%$ sulfuric acid in a stoppered weighing flask and diluting with 80.0% by weight aqueous acetic acid until the desired percentage was obtained. This volume of solvent was usually sufficient to run the kinetics of all the compounds at a single temperature. To minimize errors due to deterioration of the acid solution¹⁶ the solvent was used within 5 days.

Stock solutions of the carbinols were prepared in 5-ml volumetric flasks using anhydrous benzene as the solvent. Aliquots (5 μ l) of such solutions (using a 10- μ l Hamilton syringe for measurement) were placed in 2-ml volumetric flasks and thermostated until use. When diluted to 2 ml with solvent, the solutions were about 9×10^{-5} M in carbinol.

(16) B. M. Tolbert and G. E. K. Branch, *J. Am. Chem. Soc.*, **69**, 1083 (1947).

A solution of each 9,9-diarylfluorene was prepared by diluting 5 μ l of a benzene stock solution of the hydrocarbon with the reaction solvent. This solution was then used to set the exact λ_{max} wavelength position of the "308-m μ " band on the instrument wavelength selector.

Aliquots of stock carbinol solution were diluted with thermostated sulfuric acid-acetic acid solution, mixed by six inversions, and poured into the thermostated silica cells, and the recorder was started. Elapsed time was 30 sec at most; time of mixing was taken as zero reaction time. The recorder was then allowed to record the appearance of product as a function of time, measured to an accuracy of 1 sec/hr.

Rate constants were obtained from the expression $kt = 2.303 \log [A_h^\infty / (A_h^\infty - A_h)]$ where A_h is the absorbance of the hydrocarbon at time t and A_h^∞ is its absorbance at infinite time. For those reactions in which carbonium ion was observable (9–12) the expression was modified to $kt = 2.303 \log [C_+^0(\epsilon_h - \epsilon_i) / (A_h^\infty - A_h)]$ where C_+^0 was the initial concentration of carbonium ion, ϵ_h and ϵ_i were the molar extinction coefficients of the product and the carbonium ion at 308 m μ , and other terms are as defined above, to correct for the finite absorbance of the carbonium ion at "308 m μ ." The rates were also followed, in these cases, by the decrease in absorbance at the λ_{max} of the carbonium ion (Table III). Plots of $\log [1 / (A_h^\infty - A_h)]$ were linear in all cases. Rate constants were checked with solvent and stock solutions prepared at different times, and gave excellent agreement. The data are summarized in Tables VIII, IV, and V.

Preparation of the Deuterated Solvent. For the results described in Table V, solvent was prepared as follows: to 16.1908 g (0.3202 mole) of D_2O (Merck, Canada) was added dropwise 2.0367 g of $100 \pm 0.1\%$ H_2SO_4 . The flask was fitted with a condenser, and 32.6937 g of acetic anhydride was added dropwise. Initial additions caused warming and slight sputtering at the surface. After complete addition, the system was closed and mixed well, then allowed to remain at 25° for 20 hr before use. The final percentage was 4.00% H_2SO_4 in 80.0% DOAc and 20.0% D_2O .

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