This rotation was taken of a mixture that consisted of 0.037 g. of the product diluted with racemic 2-phenylbutane to 0.101 g.

Reductive Cleavage of (−)-2-Phenyl-2-butanol (IV) in *t*-Butyl alcohol with Potassium Metal (Run 1).—A solution of 1.00 g. (0.00667 mole) of alcohol IV, $\alpha^{25}D$ −9.72° (neat, *l* 1 dm.), in 67 ml. of dry *t*-butyl alcohol under dry nitrogen was heated to 70° and stirred. To this solution over a period of 45 minutes was added in small pieces 1.305 g. (0.0033 mole) of clean potassium metal.

The reaction mixture was cooled and shaken with a mixture of 200 ml. of ether and 200 ml. of water. The aqueous layer was extracted with 100 ml. of pure pentane, and the combined organic layers were washed with water. The 2-phenylbutane product was isolated as in run 8, except that no olefin was present. The 2-phenylbutane product amounted to 0.317 g. (35% yield), $n^{25}D$ 1.4879, $\alpha^{24}D$ +2.78° (*l* 1 dm., neat) (21% stereospecificity).

Reductive Cleavage of (+)-2-Methoxy-2-phenylbutane (V) in N-Methylaniline with Potassium (Run 12).—A solution of 1.00 g. (0.00609 mole), $\alpha^{24}D$ +37.1° (neat, *l* 1 dm.), of ether V in 61 ml. of pure N-methylaniline was heated to 90° under nitrogen and stirred. To this solution was added 1.190 g. (0.0305 gram atom) of potassium metal. The mixture was stirred vigorously, and it turned black very quickly although the potassium reacted slowly. After 8 hours, the mixture was cooled, and the excess potassium was decomposed with methanol. The reaction mixture was shaken with a mixture of 200 ml. of pure pentane–200 ml. of water. The organic layer was extracted with four 100-ml. portions of 6 *N* sulfuric acid, washed with water, dried and evaporated through a fractionating column. The residue was chromatographed, and the 2-phenylbutane product isolated as in the other runs (no olefin was present) to give 0.270 g. (28% yield) of material, $n^{25}D$ 1.4878, $\alpha^{26}D$ +0.06° (neat, *l* 1 dm.).

LOS ANGELES 24, CALIF.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Carbonium Ions. VIII. Diarylolefin–Diarylalkyl Cation Equilibria[1]

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The equilibria between diarylalkyl cations and their corresponding olefins and alcohols were studied as a function of sulfuric acid concentration. It was found that the protonation of diarylolefins, although an equilibrium of the $BH^+ = B + H^+$ type, widely deviates from the well-known eq., $H_0 = pK_{BH^+} + \log (c_B/c_{BH^+})$. The manner of the deviation can be quantitatively predicted from a consideration of activity coefficient data. The diarylolefins are usually, but not always, stable in respect to their corresponding alcohols in sulfuric acid concentrations where half of the olefin is converted into the diarylalkyl cation. Deuterium experiments showed that *t*-alkyl cations are present in small amounts in equilibrium with diarylalkyl cations. The hexamethylbenzene-protonated hexamethylbenzene equilibrium was examined. The spectra and structure–stability relationships of arylmethyl cations were re-examined with the aid of simple LCAO MO theory.

Diarylolefin–Diarylalkyl Cation Equilibria.—In earlier papers in this series, it was established that in aqueous mineral acids, arylmethanols were in equilibrium with their corresponding arylmethyl cations and that the equilibria shifted with acidity according to eq. 1.[2,3]

$$H_R = pK_{R^+} + \log (c_{ROH}/c_{R^+}) \qquad (1)$$

These equilibria studies led to the evaluation of the H_R acidity function[4] in aqueous sulfuric acid,[2] perchloric acid[3] and nitric acid.[3] In all of this previous work, arylolefins were eliminated from consideration by choosing arylmethanols which were structurally prevented from directly dehydrating to olefins. It now seemed appropriate to extend these studies to arylolefins. The present study was restricted to 1,1-diarylolefins.

The addition of sulfuric acid solutions of 1,1-diphenylethyl, 1,1-diphenylpropyl, 1,1-diphenyl-2-methylpropyl, 1,1-bis-(4′-methylphenyl)-ethyl, 1,1-bis-(4′-methoxyphenyl)-ethyl and 1,1-bis-(4′-chlorophenyl)-ethyl cations to water led to the recovery of olefin and/or olefin dimer (*cf.* Experimental). It was thus concluded that in general the diarylolefins were stable in respect to the diarylalkanols in sulfuric acid solutions. This result permitted the treatment of diarylolefin–diarylalkyl cation equilibria to be simplified by neglecting the diarylalkanol concentration.

A complete exception to the above generalization was the 9-isopropylxanthyl cation. This cation quantitatively gave 9-isopropyl-9-xanthenol on addition of water to a solution of the cation in 25% sulfuric acid.

The equilibria between arylolefins (ol) and arylmethyl cations (R^+) can be predicted to follow eq. 4 on the basis of the following derivation. The definition of the H_R acidity function is eq. 2,[2] and the *pK* expression for arylolefin–arylmethyl cation equilibria is eq. 3. Previous work on activity coefficient behavior in sulfuric acid solutions[5] would indicate that $f_{ROH} = f_{ol}$. Also, since f_{R^+} was the same for $R = Ar_3C^+$ or Ar_2CH^+, it is reasonable to assume that f_{R^+} is the same for Ar_2CH^+ and $Ar_2C(alkyl)^+$. Combining these relations with eqs. 2 and 3 gives eq. 4. The significance of the prime on $pK_{R}{'}_{+}$ is to distinguish this *pK* for arylolefin–arylmethyl cation equilibria from pK_{R^+} which had been used for the arylmethanol–arylmethyl cation equilibria.

$$H_R = -\log (a_{H^+}) + \log (a_{H_2O}) + \log (f_{R^+}/f_{ROH}) \qquad (2)$$

$$pK'_{R^+} = -\log (a_{H^+}) + \log (c_R/c_{ol}) + \log (f_{R^+}/f_{ol}) \qquad (3)$$

$$H_R - \log (a_{H_2O}) = pK'_{R^+} + \log (c_{ol}/c_{R^+}) \qquad (4)$$

Data on the diarylolefin–diarylalkyl cation equilibria are summarized in Table I. As predicted, the data satisfactorily fit eq. 4. It might have been thought that since these equilibria are of the $BH^+ = B + H^+$ type, the data would have

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[2] N. Deno, J. J. Jaruzelski and A. Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

[3] N. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

[4] The decision to use the symbol H_R rather than C_0 and J_0, which were previously employed, is explained in ref. 3.

[5] N. Deno and C. Perizzolo, THIS JOURNAL, **79**, 1345 (1957).

fit eq. 5. Besides the arguments inherent in the above derivation, the data in Table I show that where eqs. 4 and 5 are distinguishable (principally compounds 1,2 and 7 in Table I), the data fit eq. 4 better. The failure to fit eq. 1 confirms that R^+ is in equilibrium with olefin and not the alcohol.

$$H_0 = pK_{BH^+} + \log (c_H/c_{BH^+}) \qquad (5)$$

The 9-isopropylxanthyl cation is in equilibrium with the alcohol. Equation 1 is followed (Table I) as expected for an ROH–R^+ equilibria although in this 10–25% sulfuric acid, it is not possible to distinguish between eqs. 1 and 4 because log (a_{H_2O}) makes so little contribution.

Chemical Instability of Diarylalkyl Cations.—Except for members of the xanthyl series, all of the solutions of diarylalkyl cations in sulfuric acid were more or less unstable. A common cause of instability is the reaction of the diarylolefin and diarylalkyl cation to produce a dimer of the olefin. It is evident that this dimer formation is favored by longer reaction times, larger stoichiometric concentrations of diarylolefins since the dimerization kinetics are second order, less alkyl substitution on the olefin, and sulfuric acid concentrations where olefin and cation are in equal concentration since this maximizes the product $(c_{ol})(c_{R^+})$ and this maximizes the rate of self-alkylation.

This last factor is responsible for the fact that 97% sulfuric acid solutions of the diarylalkyl cations in Table I were relatively stable, although in more dilute acids, the cations disappeared at moderate rates.

Attempts to block the dimerization by employing 1,1-diphenyl-2,2-dimethylpropyl cations were surprisingly ineffectual. The 1,1-bis-(4′-methoxyphenyl)-2,2-dimethylpropyl cation was the least stable cation of any studied in this paper.

Thermodynamic Stability of Diarlylalkyl Cations.—The stability of the diarlylalkyl cation is affected by substituents on the aryl rings in the same way as triarylmethyl and diarylmethyl cations.[6] For the 1,1-diarylethyl cations substituted in the *p*-position, the four substituents studied (methoxy, methyl, hydrogen and chloro) give a

TABLE I

EQUILIBRIA INVOLVING 1,1-DIARYLALKYL CATIONS

		pK^a		
H_2SO_4, %	log (c_{R^+}/c_{ol}) (*I*)	$I + H_R - \log a_{H_2O}$ (eq. 4)	$I + H_0$ (eq. 5)	$I + H_R$ (eq. 2)
1,1-Bis-(4′-methoxyphenyl)-ethyl cation, λ_{max} 495 mμ[b] log ε 4.87[b]				
42	−0.80	−5.64	−3.24	−5.92
46	+ .11	−5.37	−2.72	−5.72
50	+ .63	−5.51	−2.60	−5.97
54	+1.28	−5.58	−2.39	−6.16
	Best value	−5.5		
1,1-Bis-(4′-methylphenyl)-ethyl cation, λ_{max} 458 mμ, log ε 4.80				
61	−0.90	−9.25	−5.34	−10.08
65	+ .21	−9.00	−4.69	−10.01
69	+ .83	−9.16	−4.56	−10.43
71	+1.30	−9.07	−4.33	−10.48
	Best value	−9.1		
1,1-Diphenylethyl cation, λ_{max} 430 mμ, log ε 4.35				
72	+0.12	−10.44	−5.63	−11.92
75	+ .66	−10.41	−5.46	−12.16
78	+1.06	−10.44	−5.48	−12.46
	Best value	−10.4		
1,1-Bis-(4′-chlorophenyl)-ethyl cation, λ_{max} 466 mμ, log ε 4.66				
76	−0.35	−11.59	−6.60	−13.43
79	+ .25	−11.45	−6.42	−13.59
82	+ .85	−11.29	−6.28	−13.79
	Best value	−11.4		
1,1-Diphenylpropyl cation, λ_{max} 432 mμ, log ε 4.42				
78	−0.13	−11.71	−6.68	−13.73
81	+ .45	−11.55	−6.53	−13.93
84	+ .83	−11.50	−6.63	−14.33
	Best value	−11.5		
1,1-Diphenyl-2-methylpropyl cation, λ_{max} 432 mμ, log ε 4.11				
90	+0.19	−12.92	−7.99	−16.53
92	+ .51	−12.82	−7.90	−16.73
94	+ .82	−12.73	−7.82	−16.96
	Best value	−12.8		
1-Phenylindanyl cation, λ_{max} 418 mμ, log ε 4.32				
63	−1.18	− 9.97	−5.84	−10.88
67	−0.41	−10.02	−5.56	−11.15
71	+ .29	−10.07	−5.27	−11.48
75	+ .91	−10.16	−5.21	−11.91
	Best value	−10.1		
1-Phenyl-3,4-dihydronaphthyl cation, λ_{max} 420 mμ, log ε 4.33				
72	−0.90	−11.46	−6.65	−12.94
77	+ .17	−11.24	−6.20	−13.17
82	+ .76	−11.38	−6.38	−13.88
	Best value	−11.3		
9-Isopropylxanthyl cation,[c] λ_{max} 370 and 438 mμ, log ε 4.54 and 3.53				
	log (c_{R^+}/c_{ROH})			
10	−1.31			−2.03
15	−0.62			−1.94
20	− .01			−1.93
25	+ .52			−2.03
			Best value	−1.98
Hexamethylbenzene·H^+, λ_{max} 395 mμ, log ε 3.86				
	log (c_B/c_{BH^+})			
84	−1.03	−13.36		
86	−0.72	−13.31		
88	− .40	−13.36		
90	− .23	−13.34		
92	+ .43	−12.90		
	Best value	−13.3		

[a] Tables of H_R and log a_{H_2O} appear in ref. 2. Tables of H_0 appear in L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 268. [b] Values at 60% sulfuric acid. At 97% acid, λ_{max} was 488 mμ and log ε was 4.68. This shift is probably due to protonation of one of the methoxy substituents since in general extinction coefficients of arylmethyl cations are insensitive to acid concentration. [c] This ion is in equilibrium with the alcohol.

TABLE II

VISUAL ESTIMATES OF THE % SULFURIC ACID WHERE DIARYLMETHANOL AND/OR DIARYLOLEFIN IS HALF CONVERTED TO DIARYLALKYL CATION

Diarylalkyl cation	λmax, mμ and log ε (or color)		% H_2SO_4 where half-ionized	Approximate half-life of cation, sec., at[a] % H_2SO_4 in previous column	97% H_2SO_4
1,1,3-Triphenylpropynyl	Orange-red		50	<1	<1
1,1-Bis-(2′,4′,6′-trimethylphenyl)-ethyl[b]	528	4.20	85	>60	>60
1,1-Bis-(2′,4′,6′-trimethylphenyl)-propyl[b]	Purple		87	30	30
1,1-Bis-(2′,4′,6′-trimethylphenyl)-butyl[b]	Purple		93	2	2
1,1-Bis-(4′-methylphenyl)-2,2-dimethylpropyl[c]	Yellow		83	>60	>60
1,1-Bis-(4′-methoxyphenyl)-2,2-dimethylpropyl[c,d]	Rose-red		50	1	1
9-Methylxanthyl	433	3.44	5	Stable	
	366	4.52			
9-Ethylxanthyl	430	3.45	8.5	Stable	
3,3′-Dinitrodiphenylmethyl	367	4.52	>97		
4,4′-Dinitrodiphenylmethyl			>97		

[a] The disappearance reaction may be second order so that these values have significance only in view of the stoichiometric concentrations employed which were about 10^{-5} molar. [b] Kindly supplied by Dr. H. R. Snyder (*cf.* H. R. Snyder and R. W. Roeske, THIS JOURNAL, **74**, 5820 (1952)). [c] Kindly supplied by Dr. E. F. Rogers of Merck and Co. (*cf.* E. F. Rogers, H. D. Brown, I. M. Rasmussen and R. E. Heal, *ibid.*, **75**, 2991 (1953)). [d] The pink color of the cation fades within 2 sec. to a yellow color. This yellow species is also an indicator whose color is half-developed at 67% sulfuric acid.

linear plot when pK is plotted against σ^+-values.[6] The value of ρ is 8.0. This corresponds to $\rho = 4.0$ per aryl ring which is exactly the same value as found for the triarylmethyl cations and somewhat less than the value 5.63 found for the diarylmethyl cations[7] where there is less steric inhibition of resonance.

In the equilibria between Ar_3C^+ (or Ar_2CH^+) and alcohols, steric crowding favored the formation of the cation since the cation carbon was trigonal whereas the same carbon in the alcohol was tetrahedral. With diarylolefins–diarylalkyl cation equilibria, both olefin and cation are trigonal and the steric repulsion energies will be similar. Thus the main effect of steric crowding in olefin–cation equilibria is to reduce the solvation energy of the ion. Thus increased steric requirements will make the cation *less stable* relative to the olefin. This effect can be seen both in the three 1,1-diphenylalkenes (Table I) and in the three 1,1-bis-(2′,4′,6′-trimethylphenyl)-alkenes (Table II).

The above effect is responsible for the tremendous difference in apparent stability between the bis-(2,4,6-trimethylphenyl)-methyl (half-ionized in 50% H_2SO_4) and the 1,1-bis-(2′,4′,6′-trimethylphenyl)-ethyl cation (half-ionized in 85% acid).[8]

Hydrogen–Deuterium Exchange in Diarylalkyl Cations.—1,1-Diphenylethylene, 1,1-diphenylpropene and 1,1-diphenyl-2-methylpropene were shaken with ten times their wt. of 97% D_2SO_4–D_2O for 5 min. Although 40–90% of the olefin had dimerized, pure monomeric olefin was isolated by distillation at 10 mm., and the infrared absorption spectra studied.

The most interesting result occurred with 1,1-diphenyl-2-methylpropene. The spectra of the recovered olefin had a sharp maxima at 4.48 μ, several lesser peaks and shoulders extending from 4.48 to 4.72 μ, and a small peak at 4.84 μ. This is interpreted to mean that the methyl groups were substantially deuterated and that the hydrogens on the two phenyl rings were unaffected. This interpretation is based on the fact that the $-CD_3$ group in ethane absorbs at 4.47 and 4.74 μ whereas the C–D on aryl rings such as benzene absorbs at a lower wave length, 4.36 μ,[9] a region where our deuterated sample showed no absorption.

The ratio of optical densities of the 3.43 μ (C–H) to the 4.48 μ (C–D) band was 9.7/1. The rest of the infrared spectra from 2–15 μ was virtually identical for the deuterated and undeuterated samples except for a moderate peak at 12.35 μ which occurred only in the deuterated sample. The rapid dimerization of the 1,1-diphenyl-2-methylpropene prevented longer reaction times and more extensive deuteration.

The interpretation that only the methyl groups were deuterated was supported by three additional observations. In both the deuterated and undeuterated samples, there is strong absorption at 3.29 and 3.43 μ. These are believed to be due to the phenyl ring hydrogens and the methyl hydrogens, respectively. In the undeuterated sample, the ratio of optical densities of the 3.43 to the 3.29 band was 1.17/1. In the above deuterated sample, this ratio had decreased to 1.02/1. Secondly, oxidation of the deuterated sample to benzophenone gave product with no absorption in the C–D stretching region.

Finally, the nuclear magnetic resonance (n.m.r.) spectra showed two intense narrow bands. The ratio of the area (or heights since both bands had the same shape) of the two peaks were 10/6 corresponding to the 10 phenyl hydrogens and the 6 methyl hydrogens. In a deuterated sample (about 40% as much deuterated as the sample described in the previous paragraph), this ratio increased to 10/5.1.

The H–D exchange observed in 1,1-diphenyl-2-methylpropene is interpreted as occurring *via* $(C_6H_5)_2CHC^+(CH_3)_2$ and $(C_6H_5)_2CHC(CH_3){=}CH_2$ which exist in small amounts. This H–D exchange cannot occur by simple reversible dimerization.

In 1,1-diphenylethylene, the two exocyclic hy-

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(6) N. Deno and W. L. Evans, THIS JOURNAL, **79**, 5804 (1957).

(7) N. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955).

(8) Ph.D. Thesis of Paul T. Groves, Pennsylvania State Univ., 1959.

(9) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangle, "Infra-red Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

drogens would exchange virtually instantly. Surprisingly, the infrared spectra failed to show absorption in the C–D stretching region. Perhaps the deuterium were exchanged back to hydrogen during the process of dilution with water, or perhaps the symmetry of the molecule is such as to weaken the absorption resulting from stretching of the two symmetrically placed exocyclic hydrogens. In any event, this result supports the previous conclusion that the phenyl rings were not undergoing H–D exchange.

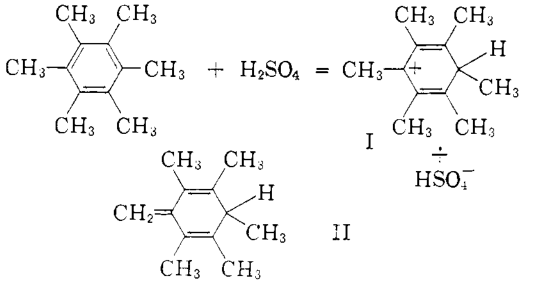
1,1-Diphenylpropene recovered after 5 min. from 97% D_2SO_4–D_2O had absorption at 4.55 μ, but no other place in the 4 to 5 μ region. Although it would seem that the methyl group had undergone H–D exchange, the interpretation is clouded by the presence of the ethylenic hydrogen. Also the spectra differed in several other respects relative to the original olefin despite the fact that the recrystallized recovered olefin had a satisfactory m.p.

Protonated Hexamethylbenzene.—An unusual type of $BH^+ = B + H^+$ equilibria is that involving hexamethylbenzene as the base B. Kilpatrick and Hyman[10] and Reid[11] both reported that protonated hexamethylbenzene has a strong absorption maxima at 395 mμ. We have confirmed this result and have measured the shift in BH^+/B equilibrium with changing concentration of sulfuric acid. The data, which appear in Table I, are within experimental error of fitting either eq. 4 or 5.

Hexamethylbenzene irreversibly disappears in 97% sulfuric acid. The percentage recovery from solution at 25° at the end of 0.5, 1 and 4 hr. were 92, 87 and 69%, respectively, using an initial concentration of 0.061 molar. A 4-hr. run using an initial concentration of 0.012 molar gave a 58% recovery. Recognizing that the recovery from the more dilute run was somewhat less quantitative, it is apparent that the hexamethylbenzene is disappearing by a first-order process.[12] If it had been a second-order process, 92% recovery would have been anticipated based on the data from the 0.061 molar runs. Also the recovery from the 0.061 molar runs approximately fit a first-order rate law. The rate of irreversible decomposition increases with increasing SO_3 content so that in a 20% solution of SO_3 in H_2SO_4, only 8% of hexamethylbenzene of questionable identity was recovered after 2 hr.

The i-factor of hexamethylbenzene in sulfuric acid was found to be 2.70 after 16 min., 3.26 after 50 min. and about 6 after 2 hr. The value extrapolated to zero time was 2.5 in reasonable agreement with the interpretation that the hexamethylbenzene is initially undergoing simple protonation as shown in eq. 7.

The principal reason for writing I as the structure for protonated hexamethylbenzene is that the simplest LCAO MO calculation for I indicates that its longest wave length absorption should occur at the same place as the arylmethyl cations, which is in reasonable agreement with experiment. A π- bonded structure would have an absorption spectrum more closely related to hexamethylbenzene itself.


(7)

I

II

Hexamethylbenzene was dissolved in 97% D_2SO_4–D_2O at 25°. The infrared absorption spectra of the hexamethylbenzene reisolated after 12 hr. exhibited absorption at 4.60 μ indicating the presence of C–D and that H–D exchange had occurred to a small extent on the methyl groups. Recrystallization of the partially deuterated hexamethylbenzene did not change the ratio (20/1) of the optical densities of the C–H (3.45 μ) to the C–D (4.60 μ) bands, and it appears that the C–D absorption was not due to an impurity. The expected splitting or broadening of the C–H band in the n.m.r. spectra was not observed.[13] However, there are several explanations for this result, and it seems clear that a slow H–D exchange took place. This exchange could have occurred *via* compounds of the type represented by structure II.

Partition of Arylolefins between Cyclohexane and Sulfuric Acid.—The partition of three arylolefins (1,1-diphenylethylene, triphenylethylene and 1-(1′-naphthyl)-1-phenylethylene) between cyclohexane and sulfuric acid was reported for several different acid concentrations.[14] These data can now receive a simple interpretation in terms of eq. 4. The concentration of olefin in cyclohexane (c'_{ol}) will bear a constant ratio to the concentration of olefin in the acid solution (c_{ol}) for the narrow range of acid concentrations reported in ref. 14. Equation 4 can thus be regrouped to eq. 8 where $K = c_{ol}/c'_{ol}$. All of the data in ref. 14 fit eq. 8.[8] In eq. 8, the concentration of protonated olefin (R^+) in the acid layer is c_{R^+}. Since in the data reported, c_{R^+} was always much larger than c_{ol}, c_{R^+} equals the stoichiometric concentration of olefin in the acid layer and c'_{ol}/c_{R^+} is the apparent stoichiometric distribution ratio.

$$\log (c'_{ol}/c_{R^+}) = H_R - \log a_{H_2O} - \log K - pK'_{R^+} \quad (8)$$

Absorption Spectra of Arylalkyl Cations.—The LCAO MO theory (neglecting electron repulsion and overlap integrals)[15] predicts that mono-, di- and triphenylmethyl cations should have the same λ_{max}. This can be regarded as in good agreement with experiment since the experimental λ_{max} are

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[10] M. Kilpatrick and H. Hyman, THIS JOURNAL, **80**, 80 (1959).

[11] C. Reid, *ibid.*, **76**, 3264 (1954).

[12] Reports that hexamethylbenzene is stable in concentrated sulfuric acid (L. I. Smith, "Organic Reactions," John Wiley and Sons, New York, 1942, vol. 1, p. 376) appear to be due to failure to dissolve the hexamethylbenzene.

[13] The n.m.r. spectra were kindly run by Mr. Ralph Mumma and Mr. John W. Carten.

[14] V. Gold and F. L. Tye, *J. Chem. Soc.*, 2181 (1952).

[15] The authors are indebted to Dr. Lionel Goodman for discussions concerning these calculations.

404 and 434 mμ for the triphenylmethyl cation, 442 mμ for the diphenylmethyl cation, and 400–420 mμ for several monophenylmethyl cations.

The above calculations have taken into account that the rings are rotated about 45°[16] out of coplanarity.[17] Actually the rotation of the phenyl rings has little effect on the LCAO calculated $\lambda_{\max}$ since the zero energy and the A_2 MO's are invariant to steric inhibition of resonance due to non-planarity of the rings. Alternately, this can be seen by noting that the mono-, di- and triphenylmethyl cations have the same calculated $\lambda_{\max}$ so that complete steric inhibition of resonance between phenyl rings would leave the calculated $\lambda_{\max}$ unchanged.

The effect of substituents on $\lambda_{\max}$ of arylmethyl cations will be very much like their effect on the spectra of benzene. This is because the conversion of the triarylmethane or methanol to the triarylmethyl cation, and similarly for diaryls and monoaryls, introduces a zero energy orbital between the highest filled orbital and the lowest unfilled orbital. This cuts the energy difference in half so that arylmethyl cations will absorb at about twice the wave length of the similarly substituted benzene derivatives. The abundant data in past papers in this series are in complete accord with this relation.

The oscillator strengths were also calculated for mono-, di- and triphenylmethyl cations using the approximation that the oscillator strength is proportional to the square of the difference in dipole moment between the first excited state and the ground state.[18] These calculations predict that the oscillator strengths of mono-, di- and triphenylmethyl cations will be in the ratio 0.25/0.94/1.60. The experimental oscillator strengths for the di- and triphenylmethyl cations, obtained by integrating *εν* between 350 and 500 mμ, were 1.1 and 1.6.

More important is the prediction that oscillator strengths are little affected by rotation of the phenyl rings since the vectors contributing over 96% of the dipole moment are invariant to rotation of the phenyl rings.

This calculation indicates that absorption spectra cannot be used to measure steric inhibition of resonance in arylmethyl cations. This would completely invalidate our original argument[19] as to why charge delocalization in the triphenylmethyl cation was limited to two of the three phenyl rings. Whether or not the triarylmethyl cations have a threefold axis of symmetry remains an open question. A careful examination of the effects of successive substitution did not yield a conclusive answer.[20]

ΔD.E. (difference in delocalization energy between R$^+$ and ROH) can be readily obtained from the orbital energy levels of R$^+$ and ROH. However, these ΔD.E. are in error for reasons beyond those inherent in the LCAO MO method. The assumption of a coplanar ion when the rings are actually rotated close to 45° must be important since rotation to 90° would decrease ΔD.E. to that of a monophenylmethyl cation. Also the calcd. ΔD.E. assumes that compressional energies (energy needed to equalize the C—C and C═C bond distances by compression and expansion) cancel. This could be a significant error because the unequal charge distribution in the ions will lead to unequal carbon–carbon distances in the ring and thus smaller compressional energy terms than in the unconjugated phenyl rings.

Although a parallel has been claimed between such calcd. ΔD.E. and exptl. pK_{R^+} values,[21,22] further calculations indicate that the parallel is not general. The most obvious discrepancy is between the diphenylmethyl cation (ΔD.E. = 1.55 β) and the benzcycloheptatrienyl cation[23] (ΔD.E. = 1.40 β). Although the former ion has the greater ΔD.E., it is actually much less stable, $pK_R{}^+ = -13.3$, compared to $pK_{R^+} = +1.6$ for the benzcycloheptatrienyl cation.[24] Also the fluorenyl cation[25] (ΔD.E. = 3.38 β) is less stable than the diphenylmethyl cation although its ΔD.E. is larger.

The arguments supporting the contention that triphenylmethyl cations are more stable than diphenylmethyl cations because of steric repulsion energies[7] seem to us unaffected by the present LCAO calculations although this view has been contested.[22]

A final interesting relation is that LCAO calculations indicate that the cycloheptatrienyl cation[26] (D.E. = 10.10 β) should be more stable than the isomeric benzyl cation (D.E. = 8.72 β). This is in agreement with electron impact experiments which have been interpreted as showing that the benzyl cation spontaneously rearranged to the cycloheptatrienyl cation.[27] Rearrangements of this type do not as yet appear to have been observed in solution.

Experimental

Equilibria Determinations.—The procedure used was to add 0.0604 ml. of an acetic acid solution of the diarylolefin or diarylalkanol (either specie led to the same equilibrium) to 10 ml. of the appropriate sulfuric acid solution. The small amount of acetic acid introduced did not affect the position of equilibrium. The data in reduced form are summarized in Table I. The greatest source of error was precipitation of the free olefin at high values of $c_{\text{ol}}/c_{\text{R}^+}$. In the

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[16] The value 45° was computed from normal bond distances and angles, the van der Waals radii for hydrogen and the condition that the van der Waals radii of the ortho-hydrogens meet but do not overlap.

[17] A. Brickstock and J. A. Pople (*Trans. Faraday Soc.*, **50**, 901 (1954)) and H. C. Longuet-Higgins and J. A. Pople (*Proc. Phys. Soc. (London)*, **68*A***, 591 (1955)) have made LCAO MO calculations on these same ions which included electron repulsion. However, the effect of non-planarity was not discussed.

[18] J. N. Murrell and J. A. Pople, *Proc. Roy. Soc. (London)*, **69**, 245 (1956).

[19] M. S. Newman and N. Deno, This Journal, **73**, 3644 (1951).

[20] N. N. Lichtin and M. J. Vignale, *ibid.*, **79**, 579 (1957).

[21] A. Streitwieser, Jr., *ibid.*, **74**, 5288 (1952).

[22] V. Gold, *J. Chem. Soc.*, 3944 (1956).

[23] The orbital energy levels were 2.25, 1.81, 1.41, 1.10, 0.56, 0.23, −0.80, −1.16, −1.41, −1.67, −2.28.

[24] H. H. Rennhard, E. Heilbronner and E. Eschenmoser, *Chemistry & Industry*, 415 (1955); G. Berti, *J. Org. Chem.*, **22**, 230 (1957).

[25] The orbital energy levels were 2.47, 2.29, 1.41, 1.32, 1.30, 1, 1, 0.18, −0.71, −0.81, −1.41, −1.88, −2.13.

[26] The orbital energy levels were ±0.45, ±1.25, ±1.80, +2. A more detailed calculation of this ion and a comparison of calcd. and exptl. spectra have been reported by J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23**, 2347 (1955).

[27] S. Meyerson and P. N. Rylander, *ibid.*, **27**, 901, 1116 (1957.)

10^{-6} molar concentrations that were used, it is not possible to see the precipitation visibly so that the best indication was failure to follow Beer's law.

In several cases the sulfuric acid solutions of the diarylalkyl cations were not completely stable. Readings were made during the first 100 sec. and the data extrapolated to obtain an estimate of the optical density at zero time.

With several diarylalkyl cations, only visual observations were made, generally because of extreme instability. These visual estimates of the equilibria appear in Table II.

Recovery Experts.—Samples of the diarylolefins were shaken for 3 min. with 10 times their weight of 97% sulfuric acid and then poured into water. The yields of products recovered were 1,1-diphenylethylene (35%) and its dimer (50%), 1,1-diphenyl-2-methylpropene (75%), 1,1-diphenylpropene (80%), 1,1-bis-(4'-methoxyphenyl)-ethylene (100%), 1,1-bis-(4'-methylphenyl)-ethylene (100%) and 1,1-bis-(4'-chlorophenyl)-ethylene (90%). All precautions were taken to prevent any dehydration of alcohol to olefin during the recovery procedure, and in the last four cases, the olefins were crystalline and were directly filtered off and recrystallized. With several of the olefins, recovery experiments were also conducted at the acid concentration at which the olefin is half-converted to cation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Stereochemistry of the Base-catalyzed Addition of p-Toluenethiol to Sodium and Ethyl Phenylpropiolate[1,2]

BY WILLIAM E. TRUCE AND DAVID L. GOLDHAMER

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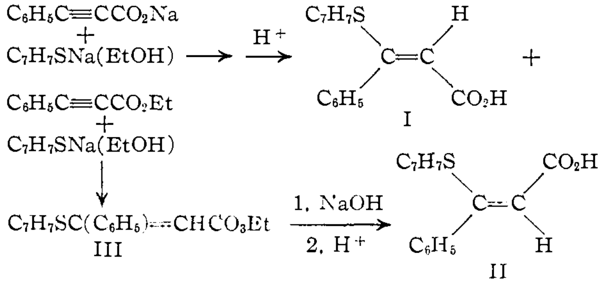
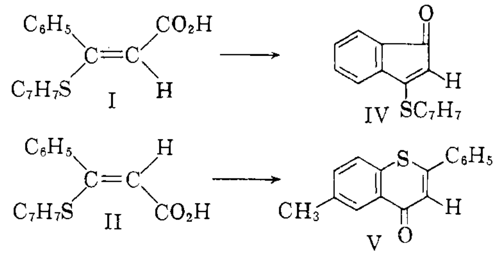
p-Toluenethiol was added to ethyl phenylpropiolate to give, after saponification, *trans*-β-p-tolylmercaptocinnamic acid, in accord with the Rule of *trans*-Nucleophilic Addition. However, a violation of this rule is observed when p-toluenethiol is added to sodium phenylpropiolate to give *cis*-β-p-tolylmercaptocinnamic acid.[3] Dipole moment measurements are used in support of these tentative configurational assignments.

Ruhemann added sodium p-toluenethiolate, in toluene, to ethyl phenylpropiolate to form ethyl β-p-tolylmercaptocinnamate, which was converted to "*trans*"-β-p-tolylmercaptocinnamic acid, m.p. 167° dec.,[4] upon saponification with alcoholic base and subsequent acidification. When the latter acid was treated with phosphorus pentachloride and aluminum chloride, 6-methylthioflavone was formed.

In order to establish the configuration of Ruhemann's addition product, it was decided to synthesize both *cis*- and *trans*-β-p-tolylmercaptocinnamic acids, compounds I and II, respectively. Accordingly, p-toluenethiol in the presence of a small amount of sodium p-toluenethiolate was refluxed in an aqueous ethanolic solution with sodium phenylpropiolate to give a 65% yield of a mixture of two acids, m.p. 189° dec. (I) and 175° dec. (II), after a series of fractional crystallizations. Isomer I made up 92% of the total product, the remainder being II. Characterization of the isomeric acids was based on analyses, neutral equivalents, mixture melting points[5] infrared spectra and the ability to isomerize I and cyclize it, as well as II, by Friedel–Crafts conditions, to the same 6-methylthioflavone (V), m.p. 150°.



An attempt was made to establish the geometrical configurations of the isomeric acids I and II by relating them to two different possible cyclic compounds IV and V, or at least to the single cyclic compound V which would be preferentially formed from isomer II, as outlined.



However, treatment of both of the isomeric arylmercaptocinnamic acids I and II with phosphorus pentachloride followed by aluminum chloride as well as treatment with anhydrous liquid hydrogen fluoride resulted in the formation of one and the same product from each acid.

$$\text{I or II} \xrightarrow{PCl_5} ; \xrightarrow{AlCl_3} \text{V} \xleftarrow{HF} \text{I or II}$$

These apparent isomerizations, preceding cyclization, are also noted in Ruhemann's cyclization of a mixture of I and II, leading to compound V exclusively.[4,5]

Perhaps this isomerization occurs in the following manner, at the stage shown below.

Presumably a greater contribution from resonance forms b and d (involving C–C single bonds

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[1] This constitutes Paper XII in the series, "Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides"; for preceding paper see THIS JOURNAL, **81**, 4931 (1959).

[2] Abstracted from the Ph.D. Thesis of David L. Goldhamer, Purdue University, 1959.

[3] An exception to the Rule of *trans*-Nucleophilic Addition was noted in the base-catalyzed addition of p-toluenethiol to sodium propiolate to give *trans*-β-p-tolylmercaptoacrylic acid; W. E. Truce and R. F. Heine, THIS JOURNAL, **79**, 5311 (1957).

[4] Upon heating, β-arylmercaptocinnamic acids liberate carbon dioxide and are converted to arylmercaptostyrenes; S. Ruhemann, *Ber.*, **46**, 3388 (1913).

[5] Ruhemann reports a product with a melting point of 167° resulting from the addition of sodium p-toluenethiolate to ethyl phenylpropiolate. This melting point corresponds closely to that of the mixture melting point of acids I and II, m.p. 165–166°; see ref. 4.