

120° to give 0.050 g. of 2-cyano-1-phenylpropane, n_D^{25} 1.5087, $\alpha_D^{25} +5.32^\circ$ (l 1 dm., neat). Further elution of the column with pure ether yielded no additional material. Extraction of the aqueous layer (from the pentane extractions) with 200 ml. of ether and evaporation of the ether gave 0.050 g. of starting alcohol, m.p. 103–106°, $[\alpha]_D^{25} +17.6^\circ$ (c 4.9, CHCl_3).

Run 10.—Optically pure alcohol III, 0.203 g., was refluxed in a solution of 10 ml. of 0.10 *M* lithium methoxide in methanol for 159 hours. The cooled solution was diluted with 50 ml. of water and extracted with two 20-ml. portions of pentane. The pentane layer was washed with two 50-ml. portions of water, dried, evaporated, and the residue was distilled at 2 mm. to give 0.11 g. of 2-cyano-1-phenylpropane, n_D^{25} 1.5089, $[\alpha]_D^{25} -2.96^\circ$ (l 1 dm., neat).

Run 15.—Optically pure alcohol III, 0.203 g., was heated in 10 ml. of 0.10 *M* tetramethylammonium hydroxide at 65° for 105 minutes. The solution was acidified with glacial acetic acid, and most of the solvent evaporated at 100° and 20 mm. The residual oil was chromatographed on a 2 by 20 cm. column of neutral activated alumina with 5% ether-pentane as developer. The first 200 ml. of eluant was evaporated and the residue distilled at 2 mm. (pot temperature 120°) to give 0.11 g. of 2-cyano-1-phenylpropane, n_D^{25} 1.5089, $\alpha_D^{25} -2.30^\circ$.

Other Runs.—Runs 7 and 8 were carried out by the procedure for run 6; runs 9, 11, 12, 16 and 17 by the procedure for run 10; and runs 13 and 14 by the procedure for run 15. The indices of refraction of the product were in all cases between n_D^{25} 1.5087 to n_D^{25} 1.5093. Infrared spectra of the product of runs 8, 10, 16 and 17 were taken and found to be identical in detail with that of authentic material.

Stability of (+)-3-Cyano-2,3-dimethyl-4-phenyl-2-butanol (III) in Solvent in the Absence of Base.—Optically pure III (0.101 g.) was dissolved in 5 ml. of methanol, $\alpha_D^{25} +0.33^\circ$ (l 1 dm.). The solution was heated at 65° for 23 hours, after which the solution had $\alpha_D^{25} +0.34^\circ$ (l 1 dm.). The solvent was evaporated and the residue recrystallized from ether-pentane to give 0.097 g. of starting material,

m.p. 108–109°. A solution of 0.203 g. of optically pure III in 10 ml. of ethylene glycol showed no rotational change when held at 100° for 44 hours. The initial and final rotations were $\alpha_D^{25} +0.44^\circ$ (l 1 dm.).

Typical Rate Measurements for Cleavage of (+)-3-Cyano-2,3-dimethyl-4-phenyl-2-butanol (III): Run 14.—A solution of 0.203 g. of optically pure III in 10 ml. of a 0.10 *M* solution of lithium *n*-butoxide in *n*-butyl alcohol was placed in a 65° constant temperature bath; aliquots were taken at intervals, and their rotations measured in a 1-dm. tube. First-order rate constants were calculated and averaged.

Time, hr.	$[\alpha]_D^{25}$	k_1 , sec. ⁻¹ $\times 10^3$
0.0	+0.29°	..
2.0	+ .26	1.7
4.0	+ .19	2.8
7.5	+ .13	2.8
10.5	+ .08	
Av. 2.4		

The rate constants, which are recorded in Table II, are clearly very approximate.

Approximate Rates of Racemization of (–)-2-Cyano-1-phenylpropane Under Conditions of Its Formation.—Approximate rates of racemization were measured for (–)-2-cyano-1-phenylpropane (II), under the exact conditions of its formation in runs 6, 7, 9, 10, 12, 14, 15, 16 and 17, except that an 0.10 *M* solution of II was substituted for the 0.10 *M* solution of III used in the cleavage reaction. Aliquot techniques were employed, five to eight points were taken, and the reaction was carried through several half-lives. Probable errors for all values for the first-order rate constants (Table II) are less than 50%.¹²

(12) An extensive kinetic investigation of racemization rates of II with a variety of bases and solvents has been carried out, the results of which will be reported in a later study.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

Triarylcyclopropenium Ions. Synthesis and Stability in the Phenyl *p*-Anisyl Series¹

BY RONALD BRESLOW AND HAI WON CHANG

RECEIVED NOVEMBER 2, 1960

A novel synthesis is reported for triarylcyclopropenium ions, involving the reaction of an arylchlorocarbene with a diarylacetylene. Using this reaction, the triphenyl-, diphenyl-*p*-anisyl-, di-*p*-anisylphenyl- and tri-*p*-anisylcyclopropenium ions have been prepared, and their spectra and pK_R 's determined. The pK 's are correlated with the predictions of molecular orbital theory.

Although the synthesis of the triphenylcyclopropenium ion was described some time ago,^{2,3} the approach was not suited to the preparation of substantial amounts of materials, and more seriously the scheme, involving reaction of phenyldiazoacetone with diphenylacetylene, and subsequent conversion of the resulting triphenylcyclopropenyl cyanide to the cation with boron trifluoride, has proved unsuitable for extension to the anisyl series, and thus does not promise to be a general method. We accordingly have investigated an alternative approach, and have found that phenylchlorocarbene, generated from benzal chloride and potassium *t*-butoxide, reacts with diphenylacetylene to form triphenylcyclopropenyl chloride.⁴

(1) This work was supported by a grant from the National Science Foundation.

(2) R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957).

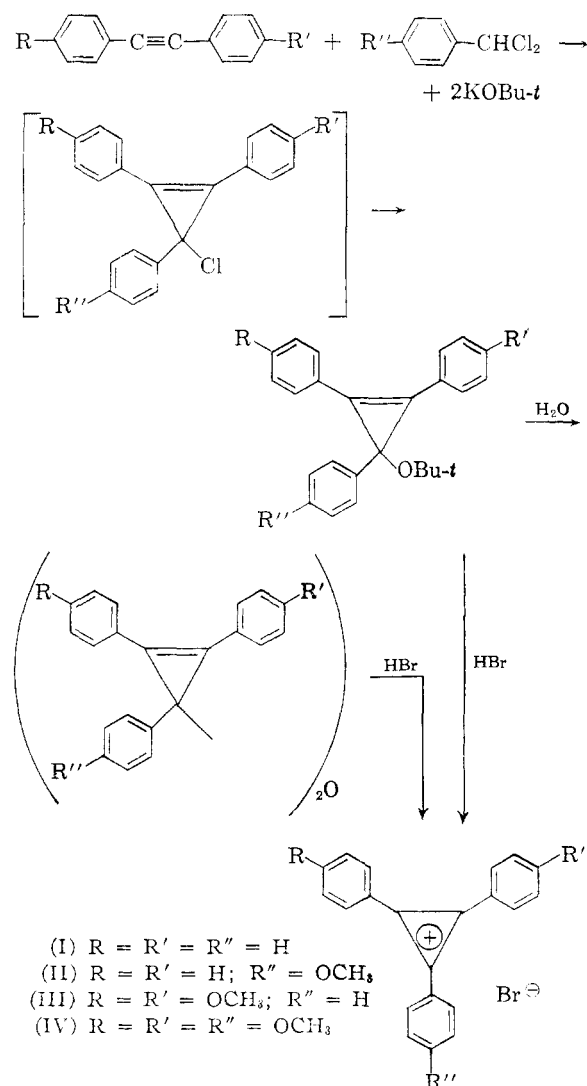
(3) R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958). Through a typographical error, $\Delta D.E_{ion}$ for triphenylcyclopropenyl cation was reported to be 4.38 instead of 2.38, the correct value.

Under the conditions of the experiment this is of course converted to triphenylcyclopropenyl *t*-butyl ether, and interestingly this is hydrolyzed to bis-triphenylcyclopropenyl ether during aqueous washing of the reaction product. Neither of these compounds need be isolated, however, for they are converted quantitatively to triphenylcyclopropenyl bromide (I)⁵ by treatment with hydrogen bromide, and since this salt is insoluble in non-polar solvents it can be isolated easily from the crude extracts. Accordingly, with the proper choice of reaction conditions large amounts of diphenylacetylene can be converted quantitatively to triphenylcyclopropenyl bromide in a few hours.

The reaction works also on *p*-anisylphenylacetylene and on di-*p*-anisylacetylene, or with *p*-anisal chloride instead of benzal chloride, and using the appropriate combinations it has been possible to

(4) This method was first reported at the Boston, Mass., Meeting of the American Chemical Society, April, 1960.

synthesize *p*-anisylphenylcyclopropenyl bromide (II), di-*p*-anisylphenylcyclopropenyl bromide (III) and tri-*p*-anisylcyclopropenyl bromide (IV). As is reported in the accompanying paper,⁵ monophenylacetylene is also a suitable component in the reaction, and it seems likely to be of wide generality although we have not explored its scope further.



Spectra.—The availability of this group of cations has allowed the further investigation of a puzzling earlier observation. It had been found³ that the ultraviolet spectrum of the triphenylcyclopropenyl cation is similar to that of covalent triphenylcyclopropenyl derivatives, such as the methyl ether, although the conjugated carbonium ion chromophore is not obviously similar to the distorted stilbene system in the covalent compounds. The spectra (Fig. 1A) have, of course, several differences, but the position of the major absorption band in the two is only a few μ apart. With the availability of the anisyl compounds it is now clear that this coincidence of covalent and cationic spectra is in fact only a chance coincidence, for the addition of methoxyl groups separates the

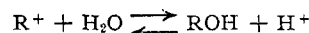
two until, in the trianisyl case (Fig. 1D), the major cation absorption occurs 25 μ higher than that of the related covalent compound. Accordingly, no special explanations seem warranted for the coincidence in the triphenyl cases.

The addition of methoxyl groups shifts the major absorption peak to progressively longer wave lengths, and as has been found in the triphenylcarbonium ion series⁶ the largest shift occurs with the first methoxyl, but the third methoxyl group in the cyclopropenyl series is still bathochromic, in contrast to the situation in the triphenylmethyl series. A comparison of the two sets of spectra is presented in Table I.

TABLE I
ULTRAVIOLET ABSORPTION MAXIMA IN THE TRIARYLCYCLOPROPENYL AND TRIARYLMETHYL CATION SERIES FOR PHENYL AND *p*-ANISYL SUBSTITUENTS

Substituent	Methyl ⁶ $\lambda_{\max}, m\mu (\log \epsilon)$	Cyclopropenyl $\lambda_{\max}, m\mu (\log \epsilon)$
Triphenyl	404(4.60), 431(4.60)	307(4.62)
Anisylphenyl	476(4.75)	341(4.74)
Dianisylphenyl	500(5.47)	352(4.84)
Trianisyl	483(5.02)	359(4.86)

pK_R^+ 's.—Because the related carbinols are not soluble in water the pK 's of these cations were determined in 23% aqueous ethanol. The stand-



ard procedure was adopted of examining the ultraviolet spectrum of solutions of the cations in various buffers at 26°, and plotting the extent of dissociation *vs.* pH , determined with a glass electrode and therefore subject to the small errors which accompany such determinations in mixed solvents. It was found that with this concentration of alcohol no turbidity was developed on neutralization of the salt, but the low intensity of the ultraviolet absorption of the neutralized cation suggested that as much as one-third of the carbinol from complete neutralization may have been invisibly out of solution. This amount of insolubility would not affect the pK 's, however, and we find that the same pK is observed for triphenylcyclopropenyl bromide when it is examined in a tenfold diluted solution using 10-cm. cells. This is also found for the anisyl derivatives, as expected, since preliminary studies showed that the anisyl derivatives are more soluble than is the triphenyl compound. The relative values of the pK 's observed are thus not in error because of any solubility problem. Furthermore, controls show that neither the nature of the buffers used nor the small variations in ionic strength which accompany the use of different buffer mixtures to achieve different pH 's have any effect on the pK 's. Partially neutralized solutions of these cations slowly decompose irreversibly, as evidenced by changes in their ultraviolet spectra, but the spectra were constant during the time required to perform all measurements.

In the monoanisyl and dianisyl cases a mixture of isomeric carbinols could be formed, and the spectra (Fig. 1) suggest that such a mixture is

(5) R. Breslow and J. Lockhart, *J. Am. Chem. Soc.*, **83**, 2375 (1961).

(6) N. Deno, *ibid.*, **77**, 3047 (1955).

present, with the predominant isomer being that with the maximum methoxylation of the stilbene system. In addition, the use of aqueous ethanol means that some of the mixed ether from reaction with ethanol must be formed as well as the carbinol from reaction with water, but a comparison of a series of carbonium ions, in the same medium, would be affected by this only if there were a special affinity for ethanol on the part of some of the ions. There is, of course, also an effect due to the altered solvating power of the medium, so the pK observed in mixed solvents will in general be different from that in water, but again one would expect in such a closely related series as ours that the differences between pK 's would be unaffected by the medium.⁷

In all cases a smooth classical titration curve was obtained whose inflection point was taken as the pK_R ; the results are presented in Table II. It is apparent that methoxyl groups stabilize the cations relative to the related carbinols, as expected, and thus raise the pK . However, the effect is relatively small, each methoxyl adding only 1.2 pK units. By contrast, Deno⁶ has found that the effect of methoxyls in the triphenylmethyl cation series is larger, the pK_R 's being -6.63 , -3.40 , -1.24 and $+0.82$ for triphenyl-, *p*-anisyl-, *p*-anisylphenyl- and tri-*p*-anisylcarbinols, respectively. This is so even though the benzene rings of the triphenylmethyl series cannot be coplanar, and the conjugating effect of the methoxyl groups is thus somewhat diminished. However, models show that the triphenylcyclopropenyl cation, and of course its *p*-methoxy derivatives, can be completely planar.⁸

TABLE II

pK 's IN 23% AQUEOUS ETHANOL SOLUTION	
Cyclopropenyl bromides	pK
Triphenyl (I)	2.80 ± 0.05
Diphenyl- <i>p</i> -anisyl (II)	$4.00 \pm .05$
Di- <i>p</i> -anisylphenyl (III)	$5.22 \pm .05$
Tri- <i>p</i> -anisyl (IV)	$6.42 \pm .05$

It is interesting that in both the triphenylmethyl and triphenylcyclopropenyl series there is no evidence for a special symmetry effect on stability. It has been stated that some special stability will be associated with a molecule in which all resonance forms are identical¹⁰ although it has been pointed out¹¹ that there does not appear to be either

(7) Cf. E. Grunwald and B. Berkowitz, *J. Am. Chem. Soc.*, **73** 4939 (1951); B. Gutbezahl and E. Grunwald, *ibid.*, **75**, 559 (1953).

(8) This planarity is indicated by Godfrey models, with which the entire molecule can be constructed, and by Courtald models, with which the central ring must be approximated. Although the Godfrey models permit construction of the triphenylmethyl cation with only 15° skewing of the phenyl groups, and thus probably underestimate the steric repulsions actually present, they also indicate no contact whatever between the ortho hydrogens of the triphenylcyclopropenyl cation. The Courtald models require a 40° twist of the phenyl groups for the construction of the triphenylmethyl cation (F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958), predicts a twist angle of 32° for the triphenylmethyl radical), but still allow planarity for our cations. Thus we conclude that the triphenylcyclopropenyl cation is planar, but if there is some small non-planarity not revealed by our models it must have a negligible effect on the calculated delocalization energies, since the extent of stabilization by the phenyl groups will vary as \cos^2 of the twist angle.⁹

(9) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952).

(10) Cf. L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 287.

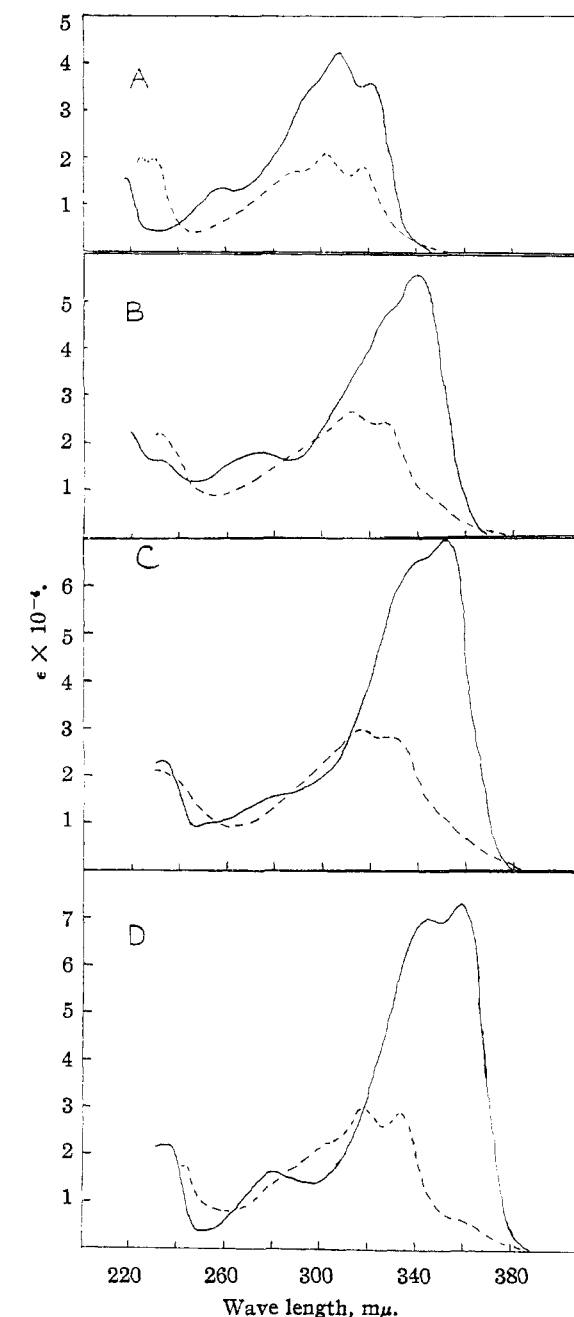


Fig. 1.—Ultraviolet absorption spectra of cyclopropenyl cations (—) and neutralized cations (-----) in 23% ethanol in water: A, triphenyl; B, anisyl-diphenyl; C, dianisylphenyl; D, trianisyl.

theoretical or experimental justification for this idea, but it is obvious that in the triphenylmethyl series the greatest increase in stability occurs when the symmetry is disturbed by the addition of the first methoxyl group, and the least when it is again restored by the addition of the third. Although the interpretation of this series is clouded by the non-planarity just discussed, it is apparent that in our probably planar series no special effect is associated with the loss of symmetry on the first

(11) G. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 358.

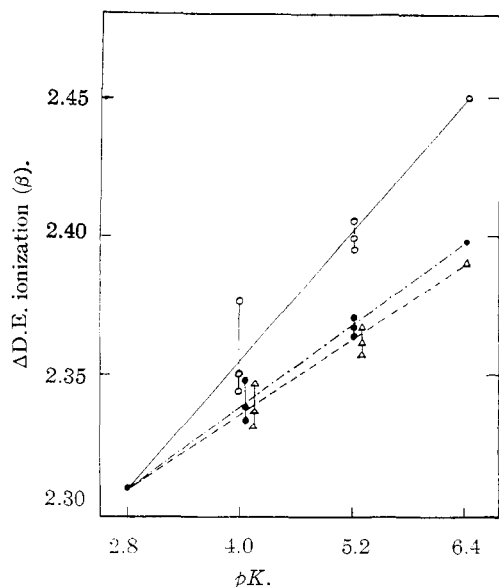


Fig. 2.— pK 's in 23% aqueous ethanol solution for triphenylcyclopropenium ion (2.80 ± 0.05), diphenyl-*p*-anisylcyclopropenium ion (4.00 ± 0.05), di-*p*-anisylphenylcyclopropenium ion (5.22 ± 0.05) and tri-*p*-anisylcyclopropenium ion (6.42 ± 0.05) vs. increase of D.E. on ionization. Three sets of parameters for oxygen were used: O, $\alpha_O = \alpha_C + \beta$; $\beta_{CO} = \sqrt{2}\beta_{CC}$; ●, $\alpha_O = \alpha_C + 2\beta$; $\beta_{CO} = \sqrt{2}\beta_{CC}$; Δ, $\alpha_O = \alpha_C + \beta$; $\beta_{CO} = \beta_{CC}$.

methoxylation or its restoration in the trianisyl cation.

Molecular Orbital Calculations.—Our series seems to represent an interesting situation for the testing of the quantitative accuracy of energy predictions by the molecular orbital method.¹² At first sight the results of the calculations seem to fit the experiment very poorly, for the pK_{R^+} of the triphenylcyclopropenyl cation is lower than that of the tropylium ion, although the simple molecular orbital method would predict the reverse.³ However there are obviously differences between the two compounds besides the amount of resonance energy gained when the related carbinol ionizes, which is the only factor considered in the m.o. calculations, and in particular there are major differences in ring-strain effects, in inductive effects, and in hindrance to solvation of the carbonium ions, all of which would modify the prediction based only on resonance energy and in the observed direction. Thus I strain will destabilize our carbonium ion because the trigonal cation is more strained than the tetragonal related covalent alcohol. Some estimate of an order of magnitude for this effect can be made using the naive approach that the force constants for bending at a trigonal carbon and at a tetragonal carbon are the same, an assumption which errs on the side of underestimating the strain effect, and that both can be

taken as 0.8×10^{-11} erg/radian,² a value which results in a small overestimate of the strain energy in cyclobutane.¹³ If it is further assumed that in both the cation and the covalent cyclopropene all the ring angles are 60° , it then turns out that the cation has 20 kcal. of extra strain energy compared to the covalent alcohol. In view of the approximations this must be considered only a rough order-of-magnitude calculation. The inductive effect of phenyl groups compared to hydrogen would also raise the pK of the cation, but an effect of one or two pK units seems the most one could expect. The phenyl groups, even though planar, may disturb the solvation of the charge, among other reasons because they themselves are of low dielectric constant and fill space which would otherwise be available for polar solvent molecules.

Even in the cyclopropenium ion series it would be surprising if the molecular orbital method could predict the difference in pK between the triphenyl and diphenyl cations, since here too inductive effects and solvation hindrance effects should play a role. Evidence for this inadequacy of the simple calculations is presented in the accompanying paper.⁵ However, in the presently discussed series inductive and solvation effects should be almost constant since it is expected that much of the positive charge will be localized in the three-membered ring, far removed from the methoxyl groups. Accordingly, the major effect of the methoxyl groups should be to change the resonance energy of the cation relative to the carbinol, and thus the relative pK 's should be directly calculable.

The simplest method, examined first, was the l.c.a.o. method with Hückel's approximations, including neglect of overlap.¹⁴ This type of calculation is the one most often applied to large organic molecules, and it can be handled conveniently with the help of simple elements of group theory, to assist in factoring secular determinants where possible, and manual or machine calculation. We diagonalize the secular determinants on an I.B.M. 650 computer using standard programs; the numerical method used gives eigenvalues accurate in the fourth decimal, and all values reported were checked carefully. The results are listed in Table III and presented graphically in Fig. 2, where the observed pK 's are plotted against the calculated increase in delocalization energy on ionization, in units of the resonance integral β . For the monoanisyl and dianisyl compounds there are two different covalent alcohols possible, and the ultraviolet spectra (Fig. 1) show that a mixture is actually formed. Consequently $\Delta D.E._{ion}$ was calculated for both forms and a vertical line drawn connecting the two values, with the bottom point representing the isomer with the greater number of methoxyl groups on the stilbene system, the top point representing the greater gain in resonance energy which results from ionization of the less stable carbinol which has a methoxyl on the

(12) Such correlations have been examined for other carbonium ion series by many authors: (a) A. Streitwieser, *J. Am. Chem. Soc.*, **74**, 5288 (1952), examined the correlation in a series of triarylmethyl cations; (b) V. Gold, *J. Chem. Soc.*, 3944 (1956), extended it to some diarylmethyl cations as well; (c) N. Deno, P. Groves and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1949), point out the poor correlation found when structurally dissimilar cations are compared; (d) D. Meuche, H. Strauss and E. Heilbronner, *Helv. Chim. Acta*, **41**, 87 (1958).

(13) For a discussion of this type of calculation, cf. F. H. Westheimer in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 523.

(14) Cf. R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry. Methods and Applications," Interscience Publishers, Inc., New York, N. Y., 1959, p. 46 ff. for a discussion of this approach and its limitations.

TABLE III
DELOCALIZATION ENERGIES OF SOME CYCLOPROPENYL
CATIONS AND CARBINOLS FROM THE SIMPLE HÜCKEL TREAT-
MENT

Compound	Oxygen parameters	D.E. (in β)
Triphenylcyclopropenyl cation	..	29.1872
Triphenylcyclopropenol	..	26.8778
Anisylidiphenylcyclopropenyl cation	1	31.6628
	2	33.8479
	3	32.1142
Δ^1 -1-Anisyl-2,3-diphenylcyclopropenol	1	29.3318
	2	31.5142
	3	29.7700
Δ^1 -3-Anisyl-1,2-diphenylcyclopropenol	1	29.3164
	2	31.4998
	3	29.7374
Dianisylphenylcyclopropenyl cation	1	34.1370
	2	38.5062
	3	35.0352
Δ^1 -1,2-Dianisyl-3-phenylcyclopropenol	1	31.7792
	2	36.1417
	3	32.6397
Δ^1 -1,3-Dianisyl-2-phenylcyclopropenol	1	31.7704
	2	36.1362
	3	32.6296
Trianisylcyclopropenyl cation	1	36.6082
	2	43.1616
	3	37.9484
Trianisylcyclopropenol	1	34.2178
	2	40.7637
	3	35.4993

isolated benzene ring instead of on the longer stilbene system. Taking β as -32 kcal./mole (*vide infra*) we have also calculated the expected composition of the mixture of isomers obtained, using the calculated difference in energy between them, and the middle point on each vertical line represents the expected resonance energy gain on ionization of such a mixture. It is apparent that very good straight line plots are obtained for each of the sets of parameters used.

Three sets of values are plotted on the graph, since even in the simplest calculations it is necessary to take account of the difference between carbon and oxygen. This is done by using a different coulomb integral for oxygen than for carbon, reflecting its greater electronegativity, and a different resonance integral for the carbon-oxygen double bond, reflecting a different bond strength from that of the carbon-carbon double bond. There has been wide disagreement in the literature on the best parameters for heteroatoms,¹⁵ but the

(15) For example, (a) R. D. Brown, *Quart. Rev.*, **6**, 63 (1952), suggests the values $\alpha_N = \alpha_C + \beta$, $\alpha_O = \alpha_C + 2\beta$, $\beta_{C-N} = \beta_{C-O}$, $\beta_{C-O} = 1.4\beta$; (b) L. Orgel, T. Cottrell, W. Dick and L. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951), suggest the use of different values for double-bonded and single-bonded heteroatoms: $\alpha_{=O} = \alpha_C + 2\beta$, $\alpha_{-O} = \alpha_C + 3.2\beta$, $\alpha_{=N} = \alpha_C + \beta$, $\alpha_{-N} = \alpha_C + 2\beta$, $\beta_{C=O} = 1.4\beta$, $\beta_{C-N} = 1.2\beta$; (c) but P.-O. Löwdin, *J. Chem. Phys.*, **19**, 1323 (1951), points out that a better fit to the experimental data is obtained with the value $\alpha_{-N} = \alpha_C + 0.6\beta$; (d) C. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p. 242, suggests the value of $\alpha_N = \alpha_C + 0.5\beta$; (e) this has been used by R. Barnes, *J. Am. Chem. Soc.*, **81**, 1935 (1959); (f) B. Pullman and A. Pullman, *Colloq. intern. centre natl. recherche sci. (Paris)*, **74**, 201 (1958), have suggested $\alpha_{=O} = \alpha_C + 1.2\beta$, $\alpha_{-O} = \alpha_C + 2\beta$, $\alpha_{=N} = \alpha_C + 0.4\beta$, $\beta_{C=O} = 2\beta$, $\beta_{C-O} = 0.9\beta$; (g) R. Daudel, *et al.*, ref. 14, p. 532, point out that these parameters

usual procedure is to consider that the coulomb integral for a heteroatom is $\alpha_C + n\beta$, where n is proportional to the electronegativity difference between carbon and the heteroatom. For the C=O bond the resonance integral usually is taken as 1.4β , although Pullman^{15f} has suggested the value of 2β for carbonyl groups, and of 0.9β for ether substituents. Increasing the value of n reflects decreasing electron donation by the heteroatom, such as oxygen, because of its electronegativity; decreasing the resonance integral for the carbon-oxygen bond reflects decreased electron donation by the oxygen because there is less to gain from the extra bonding. It is obvious that pairs of parameters can be chosen so that these factors will compensate, and that any observed degree of stabilization by a methoxyl group can be accommodated by many such pairs of parameters. Three sets have been examined in this work:

$$\alpha_O = \alpha_C + \beta, \beta_{CO} = \beta \quad (1)$$

$$\alpha_O = \alpha_C + 2\beta, \beta_{CO} = \sqrt{2}\beta \quad (2)$$

$$\alpha_O = \alpha_C + \beta, \beta_{CO} = \sqrt{2}\beta \quad (3)$$

The plot (Fig. 2) shows that in the first two cases compensation has occurred, the increased value of n being balanced by a larger resonance integral, and a slope of $0.024\beta/pK$ unit being found. In the third case the low estimate of the electronegativity effect plus the high estimate of the bond strength in the double bond gives a slope of $0.039\beta/pK_R$ unit.

In order to decide whether either of these slopes is correct it is necessary to have an estimate for the value of β , the resonance integral. This is often taken to be -18 kcal./mole, but the origin of this value makes it clear that it is not suitable for our consideration.¹⁶ The observed "resonance energy" of benzene is -36 kcal./mole, from heats of hydrogenation data; since the simple calculations predict 2β of resonance energy it is apparent that β can be taken as -18 kcal./mole, but this figure includes two terms, only one of which is relevant to our cases. The comparison is made between benzene and an idealized cyclohexatriene with no conjugation, but the two differ not only in their resonance energies but also in their geometry. The bond distances in an unconjugated cyclohexatriene would be different from those in benzene, so that in order to transform it into benzene it must first be compressed into the correct geometry and then "allowed" to become conjugated. The resonance energy must therefore compensate for the compression, and the observed resonance energy is the true resonance energy of benzene itself plus the compressional energy. The compressional energy has been estimated to be 27 kcal./mole,¹⁷ so the true or "vertical" resonance energy is -63 kcal./mole, and β should be taken as -32 kcal./mole when comparisons are made which do not involve a change in compressional energy as well as in de-

all need reconsideration since, for pyridine, the value $\alpha_N = \alpha_C + 0.2\beta$ in the Hückel calculations gives the best fit with experiment and with the results of the more precise self-consistent field calculations.

(16) For a more extensive discussion with literature references, cf. ref. 11, p. 129.

(17) C. Coulson and S. Altman, *Trans. Faraday Soc.*, **48**, 203 (1952).

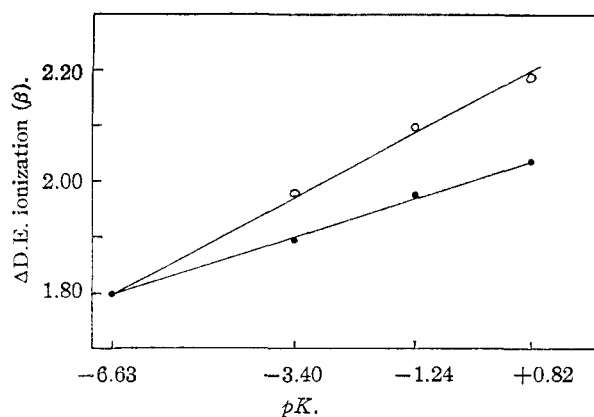


Fig. 3.— pK 's⁸ for triphenylmethyl, diphenyl-*p*-anisylmethyl, di-*p*-anisylphenylmethyl and tri-*p*-anisylmethyl cations vs. increase of D.E. on ionization; parameters for oxygen: O, $\alpha_o = \alpha_c + \beta$; $\beta_{co} = \sqrt{2}\beta_{cc}$; ●, $\alpha_o = \alpha_c + 2\beta$; $\beta_{co} = \sqrt{2}\beta_{cc}$.

localization energy.¹⁸ In our comparison series the changes in compression energy on ionization all cancel except for any compressional energy change involving the bond between the methoxyl group and the phenyl ring. It is likely that this bond is of slightly different length in the cation and in the related covalent compound, so there is a small compressional energy term, but the change must be very small compared to that involved in going from classical cyclohexatriene to benzene geometry. Accordingly the use of the benzene β , with such a large compression energy implied in it, is certainly unwarranted. Dewar has found that a value for β of -30 kcal./mole gives the best correlation in the calculation of a series of solvolysis rates,¹⁹ a process which is closely related to our ionizations, and in which the compressional energy changes would again be expected to be small. Streitwieser has examined the correlation between pK_R and $\Delta D.E.$ for a number of cations, and finds that the best correlation involves a value for β of -42 kcal./mole.²⁰ It is thus apparent that neglect of compressional energies in comparison of pK 's is warranted, and we have arbitrarily selected the "derived" value of -32 kcal./mole for β . Using this value it is seen that the predicted slope of our plot of pK_R vs. $\Delta D.E._{ion}$ is $0.43\beta/pK_R$ unit, corresponding closely to the last set of parameters chosen. The other parameters would require an even higher value for β . It is thus apparent that an adequate fit of theory to experiment can be achieved using the simple l.c.a.o. calculations, provided that parameters are chosen which imply considerably more electron release by a methoxyl than is ordinarily assumed in such calculations.

It is interesting that neither the regular increase of 1.2 pK units per methoxyl nor the regular increase in calculated $\Delta D.E._{ion}$ is a trivial result, depending on a predictable independent additive effect of the methoxyl groups, for both results are obtained only because a mixture of isomeric alcohols is obtained in the monoanisyl and dianisyl

cases. The pK observed is a weighted mean pK , and a good correspondence between calculation and experiment is obtained only when a weighted mean delocalization energy is calculated for the mixture of isomeric alcohols; the assumption that only the more stable isomer is present gives a considerably worse fit.

Our conclusion that, with β taken as -32 kcal./mole, the best results in the simple Hückel calculation on our series of cations are obtained with the parameters $\alpha_o = \alpha_c + \beta$; $\beta_{co} = \sqrt{2}\beta$ led us to examine these parameters with another series, the methoxylated triphenylmethyl cations measured by Deno⁶ and discussed earlier. Here too it might be hoped that the species are sufficiently similar that inductive and solvation effects will be constant, but it could at first sight be thought that the observed irregularity in the stabilizing effect of methoxyls is due to a special steric factor here. Thus the first methoxyl added 3.2 pK units, but the subsequent ones added only 2 units, and this might have been due to the non-planarity of the molecules; the monoanisyl cation might have distorted so as to put the anisyl ring into better conjugation with the central carbon at the expense of twisting the phenyls even further out of plane, but with succeeding methoxylation this process would not be as energetically desirable since now anisyl conjugation, not phenyl conjugation, would suffer from the distortion. Nonetheless we have performed the simple Hückel calculations on this series, using both our preferred parameters and the alternative set $\alpha_o = \alpha_c + 2\beta$, $\beta_{co} = \sqrt{2}\beta$ which gave poor agreement with experiment in the triphenylcyclopropenyl series because it emphasizes the electronegativity of oxygen more strongly, making it a poorer stabilizing substituent. The results of these calculations are listed in Table IV and are plotted in Fig. 3, where it can be seen that quite good agreement with experiment is found for either set as far as linearity of the relationship goes. The observed larger increase with the first methoxyl group is predicted by the calculations, and need not be ascribed to the non-planarity discussed above.

TABLE IV

DELOCALIZATION ENERGIES OF SOME TRIARYLMETHYL CATIONS AND CARBINOLS FROM THE SIMPLE HÜCKEL TREATMENT

Compound	Oxygen parameters	D.E. (in β)
Triphenylmethyl cation	..	25.8000
Triphenylcarbinol	..	24.0000
Anisyl-diphenylmethyl cation	2	30.5174
	3	28.8398
Anisyl-diphenylcarbinol	2	28.6220
	3	26.8596
Dianisylphenylmethyl cation	2	35.2166
	3	31.8170
Dianisylphenylcarbinol	2	33.2440
	3	29.7192
Trianisylmethyl cation	2	39.9042
	3	34.7680
Trianisylcarbinol	2	37.8660
	3	32.5788

(18) J. Lennard-Jones, *Proc. Roy. Soc. (London)*, **158A**, 280 (1937).

(19) M. Dewar and R. Sampson, *J. Chem. Soc.*, 2789 (1956).

(20) A. Streitwieser, private communication.

Here again it should be possible to decide which of these sets of parameters gives better agreement with the actual pK 's observed, for with our chosen value of β we expect a slope of $0.043\beta/pK_a$ unit. The slopes observed are 0.052 for our preferred parameters and 0.032 for the others. It might be decided from this that some intermediate set, implying an intermediate degree of electron release, is the correct one, but the non-planarity of the triphenylmethyl series should certainly be considered here. If the result is to decrease the effectiveness of the conjugation in the system then it would be expected that the calculations, which assume 100% conjugation, will overestimate the effectiveness of a methoxyl group in stabilizing a cation. If the non-planarity resulted in only 83% of the otherwise predicted conjugation effect then the calculation would fit experiment exactly, using our parameters, and the 10% overestimate which these parameters gave in the cyclopropenyl cation series would be observed if non-planarity in the triphenylmethyl series resulted in 75% of the expected conjugation effect. If the effectiveness of conjugation in such a system goes as \cos^2 of the angle, as Dewar has suggested,⁹ this would correspond to an angle of twist of 30° . It is thus apparent that our calculation gives an approximate prediction of the relative stabilities in the *p*-anisyl-phenyl triarylmethyl series, with the error in the expected direction if non-planarity is considered. Finally, it should be noted that our oxygen parameters are those predicted from the recent remarks of Daudel¹⁵ concerning the best parameters for nitrogen.

The Hückel approximations include a number of simplifications which could introduce serious errors, and in particular for our purposes the neglect of electron correlation has to be considered. This neglect is fundamental to the method, in which a set of orbitals is constructed with various energies and electrons are then fed in, it being assumed that the energies of the orbitals will not be affected by the number of electrons added. It would of course actually be expected that more will be gained by adding electrons to positively charged carbons than to neutral or negative ones, so that the energy of an orbital into which an electron is introduced will really depend on how many electrons have already been added, and on their distribution. For neutral molecules the neglect of this factor is apparently not serious, but for ions it is more important.²¹

One of the simplest improvements^{22,23} on the simple Hückel approximations for ions has been to adjust the coulomb integral of a given atom for the charge which it bears, thus recognizing the greater electronegativity of positively charged carbon over that of neutral carbon, for which the original values of the integrals are intended. This can be done, to the first approximation, by performing the Hückel calculation without any special adjustment of parameters, noting the charge distribution pre-

dicted by the calculation, and then recalculating with new parameters based on this charge distribution. This new delocalization energy is presumably thus an improved estimate, and obviously the process could be repeated with the new charge distribution, continuing the iterations until "self-consistency" has been achieved, *i.e.*, until the predicted charge distribution from a given iteration is the same as that obtained previously and used in setting the parameters for the iteration.

Streitwieser has used this approach²³ to calculate the ionization potential of a number of hydrocarbons, since he found that a poor correlation was observed with the use of the simple Hückel method. However, a fairly wide range of structures was considered, and the actual quantity of interest in this case is not the total delocalization energy of a molecule, but rather the energy of the orbital from which the electron is removed. He found good agreement in many cases when one iteration was performed, adjusting the coulomb integral for carbon to $\alpha_r = \alpha_0 + 1.4(1 - q_r)\beta$, the integral thus being decreased in energy (increased in β 's, which are negative) by an amount proportional to the positive charge at that carbon, since the calculated "charge" q is the π -electron density at carbon r , being 1 for a neutral carbon and 0 for a full carbonium ion. The proportionality constant 1.4 was found by Streitwieser to give the best fit with experiment, and we have used it in our calculations.

We have calculated the delocalization energies of the triphenylcyclopropenyl cation and of the related carbinol using both the first iteration and the self-consistent calculation, since in this case successive iterations converged. This required further calculation only for the cation, since the covalent alcohol contains two even alternant systems in which the charge is unity at all carbons. The calculated $\Delta D.E._{ion}$ is 3.46β for the first iteration and 3.49β for the converged value; the convergence was established by constancy in the energy to two decimals at five, six and seven iterations.

TABLE V
DELOCALIZATION ENERGIES OF SOME CYCLOPROPENYL CATIONS AND CARBINOLS FROM THE FIRST ITERATION OF THE ω TREATMENT

Compound	Oxygen parameters	D.E. (in β)
Triphenylcyclopropenyl cation	..	30.3407
Triphenylcyclopropenol	..	26.8778
Anisyldiphenylcyclopropenyl cation	2	35.2133
Δ^1 -1-Anisyl-2,3-diphenylcyclopropenol	2	31.6983
Δ^1 -3-Anisyl-1,2-diphenylcyclopropenol	2	31.6734
Dianisylphenylcyclopropenyl cation	2	40.0804
Δ^1 -1,2-Dianisyl-3-phenylcyclopropenol	2	36.5024
Δ^1 -1,3-Dianisyl-2-phenylcyclopropenol	2	36.4938
Trianisylcyclopropenyl cation	2	44.9396
Trianisylcyclopropenyl	2	41.2979

The trianisylcyclopropenium ion and its related carbinol were also examined in this calculation, but in this case the successive iterations did not converge for the carbonium ion.²⁴ However, the delocalization energies for successive iterations oscillated 0.02β above and below that for the first

(21) J. A. Pople, *J. Phys. Chem.*, **61**, 6 (1957).

(22) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(23) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960), and references therein.

(24) Cf. similar non-convergences for other compounds, observed by A. Streitwieser, Jr., *Tetrahedron*, **5**, 149 (1959).

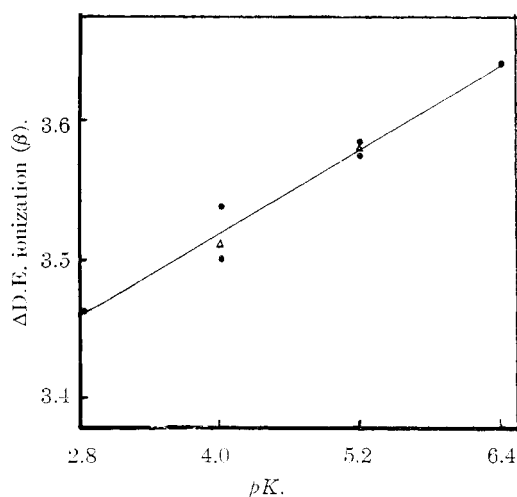


Fig. 4.— pK 's for triphenylcyclopropenium, diphenyl- p -anisylcyclopropenium, di- p -anisylphenylcyclopropenium ion and tri- p -anisylcyclopropenium ion vs. increase of D.E. on ionization obtained by first iteration of the ω method²³; parameters for oxygen: $\alpha_O = \alpha_C + 2\beta$; $\beta_{CO} = \sqrt{2}\beta_{CC}$; ●, calculated for the isomeric covalent compounds; ▲, calculated for the equilibrium mixture.

iteration, so an attempt was made to correlate the observed pK 's with the results of one iteration only for the four cyclopropenium derivatives. These results are presented in Table V and in Fig. 4, using only the parameters $\alpha_O = \alpha_C + 2\beta$, $\beta_{CO} = \sqrt{2}\beta_{CC}$. Again a straight line fit is obtained, and the slope ($0.049\beta/pK$) is close to that expected if β is taken as -32 kcal./mole. Here parameters involving less electron release have been used, and furthermore if Streitwieser's suggested value²³ for β of -2.11 e.v. were used even less electron release would be required. It is thus obvious that this calculation absorbs some of the greater stability of the anisyl compounds into an improved electrostatic energy term when the charge is more widely distributed. However, it is also obvious that, with the use of the proper parameters, the simple Hückel calculation is as satisfactory as the more difficult iterative procedure in accounting for the pK 's of our series of cations.

Acknowledgment.—We wish to thank Mr. I. Kelman Cohen for assistance with some of the synthetic work, and acknowledge helpful discussions with Professor Richard Bersohn.

Experimental

***sym*-Triphenylcyclopropenyl Bromide (I).**—The conditions for best yield in the reaction between benzal chloride, toluene and potassium *t*-butoxide were examined. In all cases the yield based on toluene was essentially quantitative, and the choice of high yield, based on the butoxide and benzal chloride, or of high conversion of toluene, which is easily recovered, dictates the proportions of reagents used. The following is the best procedure in which only a slight excess of carbene-forming reagents is employed, and in which consequently some toluene is recovered.

To a mixture of toluene (2.23 g., 0.0125 mole) and dry powdered potassium *t*-butoxide (3.5 g., 0.03 mole) in 50 ml. of dry benzene was added freshly distilled benzal chloride (2.42 g., 0.015 mole) with good stirring under nitrogen. The reaction mixture was refluxed for 3 hours, cooled, and water then was added to dissolve the inorganic salts. The layers were separated and the aqueous layer was extracted twice with ether, the ether extracts being pooled with the

benzene layer. After drying ($MgSO_4$) the combined organic layers were saturated with anhydrous HBr, when crude *sym*-triphenylcyclopropenyl bromide³ precipitated, m.p. 253–255° (2.6 g., 0.0075 mole). When the filtrate is evaporated and the residue percolated through alumina with hexane, toluene is recovered (0.8 g., 0.0045 mole) so the yield is 94%, the conversion 60%, based on toluene. The crude salt is suitable for most uses, although it was recrystallized from acetonitrile to constant m.p., 269–271° dec., for the pK measurements. Similar percentage yields are obtained when the reaction is run on a molar scale, using one-half the proportionate amount of solvent.

When the reaction was carried out in air rather than under dry nitrogen the conversion was only 50%. Slightly lower conversions were realized consistently when the reflux period was only 1 hour; when the reflux was omitted no product was obtained. No cation was obtained when sodium ethoxide was substituted for the potassium *t*-butoxide, and the use of a *t*-butyl alcohol solution of potassium, rather than the dry powdered base, gave only half the usual conversion; sodium hydride in *t*-butyl alcohol gave only one-third the usual conversion. In all cases the yield was extremely high, however, since quantitative recovery of the unreacted toluene was possible. The use of a twofold excess of the benzal chloride, with a corresponding increase in the base, gave better than 90% conversion, as well as yield, based on the toluene.

When the usual preparative procedure was interrupted before addition of water and the inorganic materials were removed by filtration, concentration of the solution and addition of hexane caused the crystallization of 1,2,3-triphenylcyclopropenyl *t*-butyl ether as white prisms, m.p. 143–144.5°.

Anal. Calcd. for $C_{26}H_{20}O$: C, 88.19; H, 7.10. Found: C, 87.59; H, 7.03.

The compound showed the infrared absorption at 5.5 μ characteristic of covalent cyclopropene derivatives, as well as the absorption at 7.2 and 7.3 μ for a *t*-butyl group²⁵ and was converted quantitatively to *sym*-triphenylcyclopropenyl bromide with gaseous HBr.

When solutions of this ether were shaken with water a new compound was formed, bis-1,2,3-triphenylcyclopropenyl ether, m.p. 175–177° dec.

Anal. Calcd. for $C_{42}H_{30}O$: C, 91.60; H, 5.49. Found: C, 91.77; H, 5.36.

In the infrared the compound showed the typical 5.5 μ band of covalent cyclopropenes and the expected weak C–H absorption for aromatic hydrogens; with gaseous HBr it was transformed quantitatively into triphenylcyclopropenyl bromide.

1-*p*-Anisyl-2,3-diphenylcyclopropenyl Bromide (II).—4-Methoxytoluene was prepared from 4-methoxystilbene dibromide by a modification of the procedure of Orekhoff and Tiffeneau,²⁶ using 24 hours of reflux with concentrated ethanolic KOH; m.p. 56–57° (reptd.²⁶ m.p. 89–90°). The infrared spectrum had major peaks at 4.5 and 8.0 μ .

Anal. Calcd. for $C_{18}H_{12}O$: C, 86.51; H, 5.80. Found: C, 86.64; H, 5.89.

Reaction of this acetylene with benzal chloride and potassium *t*-butoxide, by the procedure detailed above for toluene, yielded 1-*p*-anisyl-2,3-diphenyl bromide, m.p. 173–174° dec. after crystallization from methanol-ether. The conversion was approximately the same as that realized in the triphenylcyclopropenyl bromide synthesis under comparable conditions, and the same compound was obtained in similar yield from the reaction of toluene with *p*-anisal chloride and potassium *t*-butoxide. The compound was insoluble in benzene, ether and chloroform. It did not dissolve in water but was soluble in methanol or ethanol; its methanol solution gave an instantaneous precipitate of AgBr with $AgNO_3$ solution.

Anal. Calcd. for $C_{22}H_{16}OBr$: C, 70.03; H, 4.54. Found: C, 69.86; H, 4.71.

1,2-Di-*p*-anisyl-3-phenylcyclopropenyl Bromide (III).—Reaction of 4-methoxytoluene with *p*-anisal chloride or of 4,4'-dimethoxytoluene²⁷ with benzal chloride under the con-

(25) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., p. 23.

(26) A. Orekhoff and M. Tiffeneau, *Bull. soc. chim.*, **37**, 1416 (1925).

(27) W. Schlenk and E. Bergmann, *Liebigs Ann.*, **463**, 82 (1928).

ditions described above afforded 1,2-di-*p*-anisyl-3-phenylcyclopropenyl bromide in yield similar to that found for the triphenylcyclopropenyl cation synthesis. The compound had m.p. 178–179° dec. after crystallization from methanol-ether.

Anal. Calcd. for $C_{23}H_{19}O_2Br$: C, 67.81; H, 4.70. Found: C, 67.60; H, 4.99.

1,2,3-Tri-*p*-anisylcyclopropenyl bromide was prepared by the standard procedure from the reaction between 4,4'-dimethoxytolane and *p*-anisyl chloride with potassium *t*-butoxide. After crystallization from methanol-ether the compound had m.p. 210–212° dec.

Anal. Calcd. for $C_{24}H_{21}O_3Br$: C, 65.88; H, 4.84. Found: C, 66.01; H, 5.03.

Ultraviolet Spectra.—The spectra of these cations were determined in "23% aqueous ethanol" (*vide infra*) and are presented in Fig. 1, with the maxima also being listed in Table I. The spectra for the cations are those observed on the acid side of the *pK*'s, and they are unchanged on further addition of acid. The spectrum found for the sym-triphenylcyclopropenyl cation in this medium is essentially the same as that reported earlier in more standard solvents.

The spectra of the related covalent forms presented in Fig. 1 are simply the spectra observed on the basic side of the *pK* during the *pK* determination. Although the solutions were visually clear it is apparent from the observed intensities that there was some microscopic insolubility, and this is confirmed by our finding in the triphenylcyclopropenyl case that the covalent spectrum has the expected ϵ_{\max} of 30,000 at 302 m μ instead of 20,000 when one-tenth the concentration of cation is used in a 10-cm. cell. Accordingly, the covalent spectra in Fig. 1 are correct in shape but not in intensity, and additionally of course they are not necessarily the spectra of single chemical species, those from the dianisyl and monoanisyl cation in particular being, from their shape, apparently the spectra of mixtures.

***pK* Determinations.**—The solutions were prepared in a standard way. The cation (1 mg.) was dissolved in 5.27 ml. of 95% ethanol, which was then made up to 10 ml. with water. Buffer or acid solutions were prepared in 21.1 ml. of 95% ethanol diluted to 100 ml. with water, and 1 ml. of the "50%" ethanolic cation solution was diluted to 10 ml. with the "20%" ethanolic buffer solution, resulting in a medium which we call "23% aqueous ethanol." Preliminary studies indicated that this was the minimum amount of ethanol required to prevent turbidity when the triphenylcyclopropenyl cation was neutralized, although less alcohol was sufficient for the anisyl cations.

The standard procedure was adopted of examining the ultraviolet spectrum of each cation in nine solutions of buffer or acid spaced through a *pH* range of about two units on each side of the *pK*. The absorbancy at a wave length characteristic of the cation was plotted against *pH* and the mid-point of the resulting titration curve was taken as the *pK*. The wave lengths used were: triphenylcyclopropenyl, 321 m μ ; anisylcyclopropenyl, 341.5 m μ ; dianisylcyclopropenyl, 352.5 m μ ; trianisylcyclopropenyl, 359 m μ . The spectra were obtained on a Cary model 11 recording spectrophotometer; the *pH*'s were read on a Beckman model G *pH* meter calibrated with standard buffers before use. All spectra were taken within 4 minutes of mixing the solution of the cation with that of the buffer or acid. It was found that they were constant at least over 20 minutes, although after long periods they were irreversibly changed on the basic side of the *pK*'s, apparently by side reactions of the neutralized cations. The solutions as made up above were examined in 1-cm. silica cells, but because of the low absorbancy of the neutralized cations a determination also was performed with 10-cm. cells with one-tenth the above concentration of the triphenylcyclopropenyl cation, using the HCl and acetate buffer system without added salt (*vide infra*). In this system at normal concentration the *pK* of the triphenyl cation was found to be 2.77; at the tenfold dilution it was found to be 2.75, although the neutralized cation solution had ϵ_{\max} of 30,000 in the high dilution and only 20,000 in the standard conditions. The *pK* of the monoanisylcyclopropenyl cation also was redetermined at tenfold dilution, and it was found to be 3.87 compared to the 4.0 at normal concentration. Both of the values at higher dilution are within experimental error of the others, and both are below the previous values although any insolubility of the neutralized cations would have resulted in a change to higher apparent *pK*'s with dilution. Accordingly, the slight microscopic insolubility of the neutralized cations is not introducing any error in the *pK* determinations.

For *pH*'s below 3, HCl solutions were used. The region between 3 and 7 was covered with buffers made up from mixtures of 0.1 *M* citric acid and 0.2 *M* Na_2HPO_4 , 50 ml. of buffer being prepared according to the procedure of Gomori²⁸ and used, with the 21.1 ml. of ethanol, to prepare 100 ml. of solution by the addition of water. The *pH*'s greater than 7 were obtained with a similar 50 ml. of Gomori phosphate buffer, containing various proportions of 0.2 *M* NaH_2PO_4 and of 0.2 *M* Na_2HPO_4 solutions. To examine the role of the nature of the buffer the *pK* of the triphenyl cation was determined, using the citrate-phosphate system, to be 2.80; a second determination was performed using Gomori acetate buffer, consisting of mixtures of 0.2 *M* acetic acid and 0.2 *M* sodium acetate, and the *pK* was found to be 2.77. The solutions used vary somewhat in ionic strength, so a determination was performed in the acetate buffer system on the triphenyl cation with sufficient added KCl to give a constant ionic strength of 0.1. The *pK* was found to be 2.85. Since at low *pH*'s the acetate buffer has a rather low ionic strength, this represents a bigger ionic strength change than occurs in any of the normal determinations.

(28) G. Gomori in S. P. Colowick and N. O. Kaplan, "Methods in Enzymology," Vol. I, Academic Press, Inc., New York, N. Y., 1955, p. 138.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

The Diphenylcyclopropenyl Cation. Synthesis and Stability¹

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RECEIVED NOVEMBER 2, 1960

Diphenylcyclopropenyl bromide has been synthesized by a sequence whose essential reaction is that between phenylchlorocarbene and phenylacetylene. Its *pK_R* in water is 0.3, while that of the triphenylcyclopropenyl cation is +3.1. This difference is less than is predicted only from simple Hückel m.o. calculations; furthermore the *pK* of the diphenyl cation is more sensitive to the nature of the medium. These facts are discussed in terms of inductive and solvation effects which modify the m.o. predictions.

The relatively high stability of salts of the triphenylcyclopropenyl cation² might be due in large

(1) This work was supported by a grant from the Sloan Foundation, which is gratefully acknowledged. A preliminary report of the work has been made in ref. 6.

(2) R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957); R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958).

part to the phenyl substituents, by analogy with triphenylmethyl cation. Since the triphenylcyclopropenyl cation is probably planar, as judged from models, while the triphenylmethyl cation is not,³

(3) For an estimate of the effect of this non-planarity on the resonance energy, cf. F. J. Adrian, *J. Chem. Phys.*, **23**, 608 (1955).