

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<sub>22</sub>H<sub>19</sub>O<sub>2</sub>Br: 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<sub>24</sub>H<sub>21</sub>O<sub>3</sub>Br: 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  $\epsilon_{\max}$  of 30,000 at 302 m $\mu$  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: triphenylcyclo-

propenyl, 321 m $\mu$ ; anisyl-diphenylcyclopropenyl, 341.5 m $\mu$ ; dianisylphenylcyclopropenyl, 352.5 m $\mu$ ; trianisylcyclopropenyl, 359 m $\mu$ . 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  $\epsilon_{\max}$  of 30,000 in the high dilution and only 20,000 in the standard conditions. The *pK* of the monoanisyl-diphenyl 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<sub>2</sub>HPO<sub>4</sub>, 50 ml. of buffer being prepared according to the procedure of Gomori<sup>28</sup> 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<sub>2</sub>PO<sub>4</sub> and of 0.2 *M* Na<sub>2</sub>HPO<sub>4</sub> 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 Stability<sup>1</sup>

BY RONALD BRESLOW, JOYCE LOCKHART AND HAI WON CHANG

RECEIVED NOVEMBER 2, 1960

Diphenylcyclopropenyl bromide has been synthesized by a sequence whose essential reaction is that between phenylchlorocarbene and phenylacetylene. Its *pK<sub>R</sub>* 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 cation<sup>2</sup> 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,<sup>3</sup>

(3) For an estimate of the effect of this non-planarity on the resonance energy, cf. F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

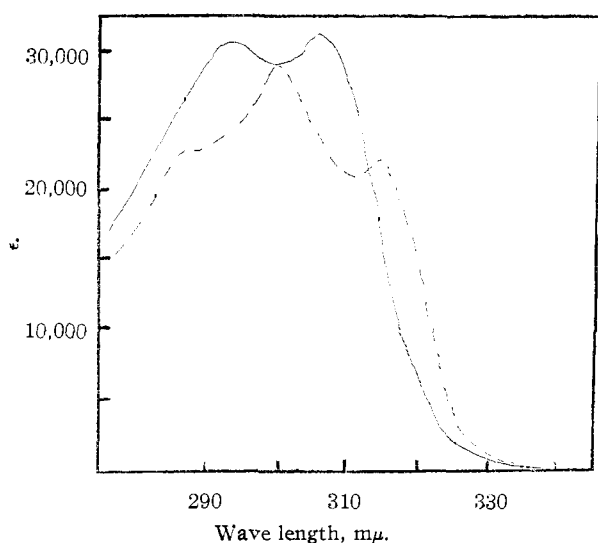


Fig. 1.—Ultraviolet spectra of diphenylcyclopropenyl cation derivatives in 4% acetic acid in water: —, the cation, observed in the presence of 10 volume % added sulfuric acid; ----, the neutralized cation, observed when either the cation or one of its covalent ether derivatives was utilized without added acid.

it might even be thought that the greater stability of the triphenylcyclopropenyl cation is due to its more effective planar conjugation alone, and that little significance attaches to the presence *per se* of a cyclopropenyl cation system, an "aromatic" system. That some factor other than simply more effective phenyl conjugation is involved is indicated by evidence on the relative instability of highly conjugated derivatives of the cyclopropenyl anion<sup>4</sup> and by the fact that the dimer of the triphenylcyclopropenyl radical shows no tendency to dissociate,<sup>5</sup> but it seemed desirable to study the properties of diphenylcyclopropenyl cation salts in order to elucidate the precise role of the phenyl groups. More recently the dipropylcyclopropenyl cation has been prepared,<sup>6</sup> and while the inductive effect of the propyl groups undoubtedly is important, the properties of this system demonstrate that phenyl substituents are not necessary for the preparation of stable cyclopropenyl cations.

Although the availability of diphenylcyclopropenecarboxylic acid<sup>7</sup> suggested it as a suitable starting material for preparation of diphenylcyclopropenyl cation salts, and Farnum has independently synthesized diphenylcyclopropenyl perchlorate from this acid,<sup>8</sup> the success of the phenylchlorocarbene approach to other arylcyclopropenyl cations<sup>9</sup> prompted us to examine it here. Phenylchlorocarbene, generated *in situ* from reaction of benzal chloride with potassium *t*-butoxide, was added to phenylacetylene and the product, after aqueous washing during extractions, was bis-diphenylcyclopropenyl ether (III). The presumed

(4) R. Breslow and M. Battiste, *Chemistry & Industry*, 1143 (1958).

(5) R. Breslow and P. Gal, *J. Am. Chem. Soc.*, **81**, 4747 (1959).

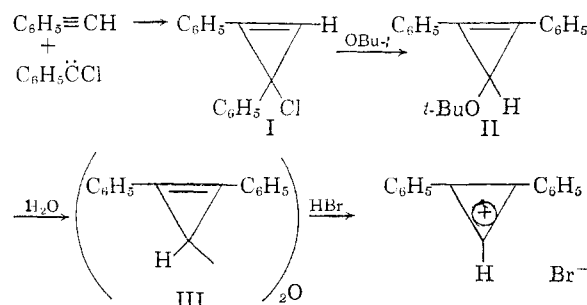
(6) R. Breslow and H. Höver, *ibid.*, **82**, 2644 (1960).

(7) R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(8) D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960).

(9) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).

sequence here is: reaction of the carbene with the acetylene forms diphenylcyclopropenyl chloride (I), which ionizes and reacts with *t*-butoxide to form the diphenylcyclopropenyl *t*-butyl ether (II); the mixed ether is then hydrolyzed to the symmetrical ether, as has been observed in the triphenylcyclopropenyl series.<sup>9</sup> In the present case it was found necessary to isolate the final ether product since the crude reaction mixture did not give satisfactorily pure cation directly, but when the isolated ether was treated with hydrogen bromide, diphenylcyclopropenyl bromide was formed in moderate over-all yield. The ready availability of the starting materials makes this an attractive preparative procedure.



Structure proof for the cation was obtained by hydrolysis to  $\alpha$ -phenylcinnamaldehyde and also by reaction of the cation with cyanide ion to form the covalent diphenylcyclopropenyl cyanide, which had been prepared independently from diazoacetonitrile and diphenylacetylene.

As was found for triphenylcyclopropenyl cation derivatives,<sup>2,9</sup> the diphenylcyclopropenyl bromide, in ethanol solution, has the typical absorption spectrum of covalent diphenylcyclopropenes, since of course it forms an ether under these circumstances; in acetonitrile solvent or in strong acid solution, however, the cation itself has two equal absorption maxima at 293 and 307 m $\mu$  (log  $\epsilon$  4.60). The spectra are presented in Fig. 1.

Utilizing the observed differences in spectra between cation and covalent derivative it was possible to determine the  $pK_R$  of the diphenylcyclopropenyl cation. In order to obtain a direct comparison with the previous work this was first done in "23% aqueous ethanol," prepared as described elsewhere.<sup>9</sup> In contrast to the situation in the triaryl series,<sup>9</sup> however, the  $pK$  of the diphenylcyclopropenyl cation lies outside the region accessible with a pH meter, so an acidity function approach was required.<sup>10</sup> Ionization ratios for the diphenyl cation and for the Hammett indicators *o*- and *p*-nitroaniline were measured spectrophotometrically, pH measurements being possible directly with a pH meter in the *p*-nitroaniline case and by stepwise comparison for the other two. The use of these two indicators permitted a direct correlation between pH readings of a meter in this solvent and an acidity function which was thus defined for the region inaccessible with the pH meter. The type of acidity function established by the use of these two amines is of course  $H_0$ , although no claim is here made for the generality of this func-

(10) M. Paul and F. Long, *Chem. Revs.*, **57**, 1 (1957).

tion for our solvent. Grunwald has discussed<sup>11</sup> the failure of acidity functions in aqueous ethanol, a failure reflected simply in a serious dependence of the apparent  $H_0$  in such systems on the precise indicator selected. More importantly, the type of function in which we are interested for our cation is  $J_0$  (also called  $H_R$ ),<sup>10</sup> since the ionization of a carbinol has a different dependence on the activity of water than does the protonation of an amine. However, we find that the ionization trends of the cation and of the two Hammett indicators are the same until the cation is half ionized, although after this point the difference between  $H_0$  and  $J_0$  causes a deviation in the expected direction. Accordingly, a reasonable estimate of the  $pK_{R^+}$  of the cation is possible from the first half of the ionization curve; it is found to be  $-0.67$ . As a check, the  $pK_{R^+}$  of triphenylcyclopropenyl bromide was redetermined in the same solvent and was found to be  $+2.80$ , as reported.<sup>9</sup>

Because the solvent 23% ethanol is not readily referred to water, the standard solvent for  $pK$ 's, we have examined other systems. The neutralized cations are insufficiently soluble in pure water even for the preparation of the dilute solutions used in spectrophotometric  $pK$  determinations, but we find that a  $pK$  of the diphenylcyclopropenyl cation can be determined in 4% acetic acid in water, and our examination of *o*-nitroaniline in this solvent and in water shows that  $H_0$  in the two is the same in the region of interest. Assuming that this is also true of  $J_0$ , and using Deno's reported<sup>12</sup> values of  $J_0$ , we find that the  $pK_{R^+}$  of diphenylcyclopropenium ion in water is  $+0.32$ . The triphenylcyclopropenyl cation is too stable for determination in such an acidic medium, but in 6% ethanol in water, using long-path cells to accommodate the low concentrations required for solubility, it was possible to measure a  $pK_a$  for the triphenylcyclopropenium ion,  $+3.12$ . A comparison of values obtained in these different ways is valid since Deno<sup>13</sup> has shown that the  $J_0$  and  $pH$  scales merge.

These  $pK$ 's are listed in Table I, together with values derived for aniline from extrapolation of Grunwald's data.<sup>11</sup> In spite of the small uncertainties introduced by unavoidable variations in the conditions of the various determinations it is quite apparent that there is no uniquely defined difference in  $pK$ 's between the triphenyl- and the diphenylcyclopropenyl cation, for in 23% aqueous ethanol this difference is 3.5  $pK$  units, while in water the triphenylcyclopropenium ion's  $pK$  is only 2.9 units higher. It is apparent that this difference is related to the solvating properties of the two different media, and at first sight it seems that it is the diphenyl cation which shows an abnormally high change in  $pK$  with the changed solvent, since the  $pK$ 's of the three anilines all change by about the same amount as does that of triphenylcyclopropenium ion. However, the effect of solvent on  $pK$ 's of anilinium ions and of carbo-

(11) B. Gutbezahl and F. Grunwald, *J. Am. Chem. Soc.*, **75**, 559 (1953).

(12) N. Deno, J. Jaruzelski and A. Schriesheim, *ibid.*, **77**, 3044 (1955).

(13) N. Deno, H. Berkheimer, W. Evans and H. Peterson, *ibid.*, **81**, 2344 (1959). From an extrapolation of Grunwald's results (ref. 11) this small amount of ethanol is predicted to have no effect.

TABLE I  
 $pK_a$  VALUES IN WATER AND IN 23% ETHANOL

Compound	$pK_a$	
	In water	In 23% ethanol
Triphenylcyclopropenyl cation	+3.18	+2.80
Diphenylcyclopropenyl cation	+0.32	-0.67
Aniline	+4.46	+4.15
<i>o</i> -Nitroaniline	-0.28	-0.66
<i>p</i> -Nitroaniline	+0.99	+0.62

nium ions is not expected to be the same,<sup>14</sup> so it can only be concluded that any attempt to correlate the effect of the third phenyl group on the  $pK$  of the cation with calculations, using molecular orbital theory, cannot be fully successful since no solvent dependence, of the kind noted, can be predicted from such calculations.

Nonetheless, it might be hoped that a rough order of magnitude for the effect would be predicted by the simple Hückel molecular orbital calculations, but this is not the case. The calculated  $\Delta D.E._{ion}$  for the triphenyl cation is  $2.309\beta$ , while for the diphenylcyclopropenium ion it is  $1.903\beta$ .<sup>15</sup> The difference between the two,  $0.4\beta$ , corresponds to 12.8 kcal./mole if  $\beta$  is taken as  $-32$  kcal./mole as was done in the previous paper.<sup>3</sup> Once again the justification for this is that it is expected that any compressional energy changes on ionization of these two compounds will be similar for both of them, so they will cancel in the comparison. Again this will not be strictly true since there will be some compressional energy associated with the repositioning of the extra phenyl group when the carbinol ionizes, but again it is expected that this change will be small compared with that involved in the cyclohexatriene to benzene change, so that it can be ignored. Although there is no general agreement on the correct value for  $\beta$  in cases where compressional energies do not play a major role in the comparison, it seems clear that some value more negative than  $-18$  kcal./mole must be used. With the value of  $-32$  kcal./mole the energy difference corresponds to a prediction that  $pK_{R^+}$  of the diphenylcyclopropenyl cation should be more than eight units below that of the triphenyl cation, while the observed difference is less than half that. To be sure, the calculations involved use the simple Hückel approximations, but we have also tested an improvement. Since we are dealing with carbonium ions here we have examined the  $\omega$  procedure<sup>9,17</sup> in which some account is taken of the effect of the charge; but using this method, with one iteration, the  $\Delta D.E._{ion}$  for the triphenylcyclopropenyl cation is  $3.462\beta$  while that for the diphenyl cation is  $2.997\beta$ . The difference is thus even larger, so the change is in the wrong direction; this is expected, since the  $\omega$  method, in which electrostatic repulsion is explicitly considered,

(14) Cf. R. W. Taft, *J. Am. Chem. Soc.*, **82**, 2965 (1960).

(15) Our total calculated delocalization energy for the diphenylcyclopropenyl cation,  $20.7813\beta$ , does not agree with that reported by S. Mannatt and J. D. Roberts.<sup>16</sup> Their value, reported without subtraction of the double bonds, would be  $20.70\beta$ , but we have carefully rechecked our value, even to the extent of writing the secular determinant with two different numbering schemes, and must ascribe their value to a typographical error.

(16) S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959).

(17) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

will for this reason alone predict greater stability for a larger ion in which the charge can be more spread out. It is possible that the difficulty may still lie in the simplicity of the assumptions underlying the calculations, such as the assumption of equal resonance integrals for all bonds; however, the replacement of a hydrogen atom by a phenyl group will change other factors in addition to resonance energy, and in particular the phenyl group is more electron withdrawing, so the inductive effect destabilizes the carbonium ion, and it is more bulky, so the solvation of the carbonium ion may be made more difficult. Consequently there is no reason at the present time to consider that simple molecular orbital calculations do not accurately predict the amount by which a phenyl group contributes resonance stabilization to a cyclopropenyl cation, as long as it is kept in mind that other factors besides resonance effects will determine the over-all stability of the cations, as of all molecules. In this case the two major additional effects expected, an inductive effect and an effect on the solvation energy of the ion, both modify the prediction, which is based solely on m.o. calculations, in the correct direction to accord with experiment.

It is interesting to try to extrapolate our results to the case of the unsubstituted cyclopropenyl cation. If the effects of the phenyl groups were strictly additive it would be predicted that the unsubstituted cation would have a  $pK_{R^+}$  in water of  $-5.3$ , higher than that of the triphenylmethyl cation. However, in any form the molecular orbital calculations do not predict an additive effect. The simple Hückel calculations predict that the diphenylcyclopropenyl cation, with a  $\Delta D.E._{ion}$  of  $1.90\beta$ , should be less stable than the unsubstituted cyclopropenyl cation, whose  $\Delta D.E._{ion}$  is  $2.0\beta$ . This is not because the phenyls do not increase the delocalization energy of the cation, but because their stabilizing effect on the covalent cyclopropenol is even greater. Thus the delocalization energy for the cyclopropenyl cation is only  $2.0\beta$  while that of the diphenylcyclopropenyl, after subtraction of the value for double bonds and benzene rings, is  $2.78\beta$ . However, cyclopropenol has no delocalization energy (over that of the double bond) while diphenylcyclopropenol has  $0.87\beta$  of delocalization energy, from the conjugation of the stilbene system. In the triphenylcyclopropenyl system the third phenyl group increases the  $\Delta D.E._{ion}$  considerably since it adds to the delocalization energy of the cation but not of the related carbinol. It is thus predicted by the simple Hückel calculations that the  $pK_{R^+}$  of the cyclopropenyl cation should be even greater than that of the diphenylcyclopropenyl cation, and consideration of the inductive and solvation effects discussed earlier strengthens this conclusion. Of course the electrostatic repulsion which is not considered in these calculations operates in the other direction, but even the  $\omega$  calculations in which this is considered predict a  $\Delta D.E._{ion}$  of  $2.96\beta$  for the cyclopropenyl cation compared with the  $2.99\beta$  and  $3.46\beta$  of the diphenyl and triphenyl derivatives, respectively. Thus it is reasonable to expect a  $pK_{R^+}$

of greater than zero for the simple cyclopropenyl cation, and this is supported by the recent finding<sup>18</sup> that the dipropylcyclopropenium ion has a  $pK$ , in water, greater than  $+2.7$ . Here, of course, the alkyl groups are contributing inductive stabilization of the charge, which must also be considered, so the  $pK$  of the unsubstituted cyclopropenium ion is still a matter for conjecture.

### Experimental

**Bis- $\Delta^1$ -1,2-diphenylcyclopropenyl Ether.**—Phenylacetylene (102 g., 1.0 mole) and benzal chloride (193 g., 1.2 moles) were dissolved in dry benzene (2 l.), and powdered dry potassium *t*-butoxide (278 g., 2.5 moles) was added slowly with stirring while the reaction mixture was kept at  $5^\circ$ . The mixture then was refluxed for 30 min. and cooled. Water was added, the aqueous layer was extracted twice with ether and the combined ether and benzene layers were dried and concentrated *in vacuo*. The residue, on crystallization from benzene-hexane, afforded bis-diphenylcyclopropenyl ether,<sup>19</sup> m.p.  $169$ – $172^\circ$  dec., (38.85 g., 0.097 mole). The compound was recrystallized for analysis; m.p.  $170$ – $172^\circ$  dec.

*Anal.* Calcd. for  $C_{30}H_{22}O$ : C, 90.42; H, 5.57. Found: C, 90.58; H, 6.11.

In the ultraviolet the compound had the expected spectrum, with a maximum (in acetonitrile) at  $302 m\mu$  (59,000) and at  $318 m\mu$  (44,000) and a shoulder at  $288 m\mu$  (46,000). In the infrared it showed the expected bands, including the typical weak absorption at  $5.5\mu$  for covalent cyclopropenes.

Chromatography of the compound on alumina converts it to  $\alpha$ -phenylcinnamaldehyde, identified by comparison with an authentic sample<sup>20</sup> (infrared, ultraviolet, mixed m.p.).

**Diphenylcyclopropenyl Bromide.**—The dimeric ether (0.7 g., 1.7 mmoles) was dissolved in dry benzene (30 ml.) and cooled in an ice-bath while dry HBr was bubbled in. After standing, the precipitated diphenylcyclopropenyl bromide was collected, washed with hexane, and vacuum dried; m.p.  $105$ – $106^\circ$  (0.37 g., 40% yield).

*Anal.* Calcd. for  $C_{18}H_{11}Br$ : C, 66.43; H, 4.09; Br, 29.46. Found: C, 66.21; H, 4.22; Br, 29.38.

The somewhat low yield of the bromide, while consistent, apparently is due to solubility problems with this particular salt, since quantitative yields of the fluoroborate salt have been obtained from this ether.<sup>21</sup>

With aqueous alkali the salt is reconverted to the dimeric ether. Accordingly, the ultraviolet spectrum in 4% acetic acid in water is the same as that of the dimeric ether, but on addition of 10% sulfuric acid the cation is observed, with maxima at  $293 m\mu$  (30,400) and  $306 m\mu$  (31,200). These spectra are presented in Fig. 1.

**$\Delta^1$ -1,2-Diphenylcyclopropenyl Cyanide.**—Diphenylcyclopropenyl bromide (0.11 g.) was dissolved in 30 ml. of dry acetonitrile, potassium cyanide (0.2 g.) was added, and the mixture was stirred at room temperature for 5 hours. The solution was filtered and evaporated and the residue chromatographed on alumina to afford  $\Delta^1$ -1,2-diphenylcyclopropenyl cyanide, m.p.  $115$ – $116^\circ$  (0.07 g., 80%), identical by infrared and mixed melting point comparison with an authentic sample.

The authentic sample had been prepared previously by reaction of diazoacetonitrile with diphenylacetylene, using the procedure outlined earlier<sup>7</sup> for the reaction of ethyl diazoacetate with the acetylene. In the ultraviolet (ethanol) the compound showed the expected absorption for a diphenylcyclopropene chromophore, with maxima at  $318(29,400)$ ,  $303(38,400)$ ,  $295(28,700)$ ,  $287(26,800)$ ,  $231(20,200)$  and  $223 m\mu$  (22,100).

*Anal.* Calcd. for  $C_{16}H_{11}N$ : C, 88.44; H, 5.10; N, 6.45; mol. wt., 217. Found: C, 88.88; H, 5.05; N, 6.34; mol. wt. (Rast, camphor), 237.

(18) R. Breslow and H. Höver, ref. 6, and subsequent unpublished work.

(19) D. Farnum and M. Burr, ref. 8, have also prepared this compound, and report m.p.  $163$ – $165^\circ$  dec. and ultraviolet spectra for the ether and the cation in agreement with ours.

(20) H. Burton, *J. Chem. Soc.*, 748 (1932).

(21) Unpublished work of H. W. Chang.

From the reaction of the cation with cyanide a 5% yield of  $\alpha$ -phenylcinnamaldehyde also was recovered, but no other product could be detected.

$pK_{R^+}$  Determinations.—Standard spectrophotometric methods were used for the  $pK$  determinations, both for the Hammett indicators used to establish acidity functions in

our media and for the cyclopropenyl cation derivatives. The spectra of solutions of the cation did not change appreciably in the time periods of less than an hour used in the measurements, and isosbestic points at 300 and 313  $m\mu$  were observed (*cf.* Fig. 1), which indicated that there was no problem with insolubility.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL RESEARCH SECTION, LEDERLE LABORATORIES DIVISION, AMERICAN CYANAMID CO., PEARL RIVER, N. Y.]

### Unsaturated Cyclopropanes. III.<sup>1</sup> Synthesis and Properties of Alkylidenecyclopropanes and Spiropentanes

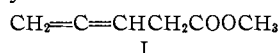
By EDWIN F. ULLMAN AND WILLIAM J. FANSHAWE

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A method is described for the conversion of allenes to alkylidenecyclopropanes and thence to spiropentanes with methylene iodide-zinc-copper couple. Some reactions of these compounds are discussed.

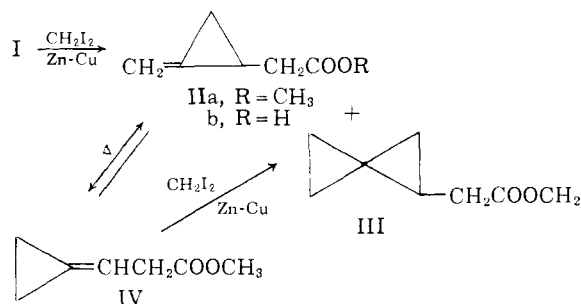
The recent discovery of a simple general method for the synthesis of cyclopropanes from olefins with methylene iodide-zinc-copper couple<sup>2</sup> presents the possibility that heretofore difficult obtainable unsaturated cyclopropanes may now be prepared from suitable multiply-unsaturated precursors. Indeed, the synthesis of sterculic acid from stearolic acid<sup>3</sup> has already demonstrated the practicability of the method as applied to the synthesis of cyclopropanes. We now wish to report the successful use of this reagent for the synthesis of alkylidenecyclopropanes and spiropentanes.

Aside from the classical preparation of spiropentane from pentaerythryl tetrabromide<sup>4</sup> and the formation of chlorospiropentane by photochlorination of the hydrocarbon,<sup>5</sup> the only other synthesis of this system appears to be the recently reported reaction of 7,7-dibromonorcarane with an alkyl lithium and an olefin.<sup>6,6a</sup> The use of an allene in the Simmons-Smith cyclopropane synthesis appeared to afford a simple route to this system. Methyl 3,4-pentadienoate<sup>7</sup> (I) was chosen for initial study.

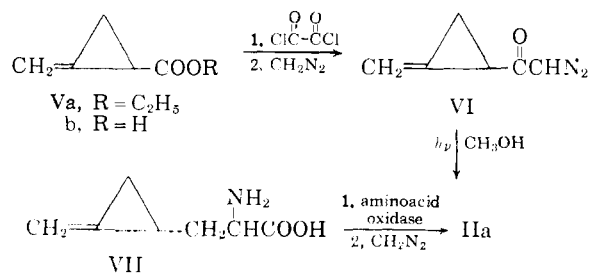


When Compound I was treated with an eight-fold excess of methylene iodide and zinc-copper couple, two products were isolated by vapor-phase chromatography in roughly equal amounts along with a little of the unreacted allene. The

faster moving component was found to have intense terminal methylene absorption in the infrared at 11.15  $\mu$  which, together with its nuclear magnetic resonance spectrum (see Experimental) and combustion analysis, provided strong support for its formulation as IIa. The second chromatographic peak was a saturated compound with spectral characteristics not inconsistent with the spiropentane III. By increasing the reagent to allene ratio to 10:1 the ratio of III to IIa increased to about 4.5:1. Unexpectedly, no methyl  $\beta$ -cyclopropylidenepropionate (IV) could be detected in the reaction mixture even though it was subsequently found that IIa, III and IV were readily separable by vapor-phase chromatography.



Chemical evidence for structure IIa was provided by an independent synthesis from ethyl methylenecyclopropanecarboxylate (Va)<sup>8</sup> which, after hydrolysis to the corresponding acid Vb, was subjected to the Arndt-Eistert sequence.



(1) For papers I and II of this series see (a) E. F. Ullman, *J. Am. Chem. Soc.*, **81**, 5386 (1959); (b) **82**, 505 (1960).

(2) H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); **81**, 4256 (1959).

(3) N. T. Castellucci and C. E. Griffin, *ibid.*, **82**, 4107 (1960).

(4) (a) Gustavson, *J. prakt. Chem.*, [2] **54**, 97 (1896). For additional references see (b) D. E. Applequist, G. F. Fanta and B. W. Henrikson, *J. Org. Chem.*, **23**, 1715 (1958).

(5) D. E. Applequist, G. F. Fanta and B. W. Henrikson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

(6) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(6a) NOTE ADDED IN PROOF.—Recently a second communication on the formation of spiropentanes from cyclopropyl carbenes has appeared; W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960). In addition, D. E. Applequist and G. F. Fanta, *ibid.*, **82**, 6393 (1960), have recently reported some transformations of chlorospiropentane leading to spiropentane derivatives.

(7) *Cf.* E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).

(8) (a) J. A. Carbon, W. B. Martin and L. R. Swett, *J. Am. Chem. Soc.*, **80**, 1002 (1958); (b) U. S. Patent 2,956,077. We wish to thank Dr. Carbon for providing us with details of the preparation of ethyl 2-bromo-2-methylcyclopropanecarboxylate.