TABLE IV

RELATIVE REACTIVITIES OF THE METHYLBENZENES

Reagent	kr/kp	Rel. kr/kp^a	Basicity[13]	Bromination[14]	Iodination[15]	Mercuration[16]
Toluene	0.00884	0.84	0.01	0.33	0.14	0.61
p-Xylene	.01055	1	1	1	1	1
o-Xylene	.083	7.9	3	2.3	1.3	2.0
m-Xylene	.134	12.8	18	7.1	23	4.2
Mesitylene	.0073	.70	1400	625	1800	26
Durene	....	...	60	65	23	3.5
Pentamethylbenzene	0.0104	.99	4300	2580	740	24
Hexamethylbenzene	....	...	445000	.....	.....	...

[a] Relative to an assigned value of unity for *p*-xylene.

son, the relative basicities as found by McCaulay and Lien,[13] the relative reactivities in bromination[14] and iodination[15] as determined by Andrews and Keefer and in mercuration as determined by Brown and McGary,[16] are also given. It is assumed that the reaction of the carbonium ion–anion pair is one of high reactivity, comparable with *t*-butylation.[17] It can be seen that, in iodination and in mercuration, mesitylene and pentamethylbenzene are in the reverse order of their basicities; both of these reactions have high steric requirements. The steric requirement for mercuration is especially large and only here do the reactivities of the more highly methylated benzenes compare even reasonably well with their reactivities toward the polymeric carbonium ion–anion pair of the present systems. This fact and the facts that the reactivities of mesitylene and pentamethylbenzene are so much smaller than their relative base strengths would appear to indicate that durene does not seem to be subject to appreciable electrophilic substitution in this system, leads to the conclusion that this polymeric carbonium ion–anion pair has a very large steric requirement, indeed.

[13] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

[14] R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 5623 (1956).

[15] L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 4549 (1956).

[16] H. C. Brown and C. W. McGary, *ibid.*, **77**, 2310 (1955).

[17] H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

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An Unusual Rearrangement in the Cyclopropene Series[1]

BY RONALD BRESLOW AND MERLE BATTISTE[2]

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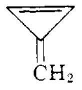
It has been found that Δ^1-1,2-diphenylcyclopropenyldiphenylcarbinol (III) rearranges, under a variety of dehydrating conditions, to 1,2,3-triphenylazulene and 1,2,4-triphenylnaphthalene. A possible mechanism for this unusual rearrangement is discussed.

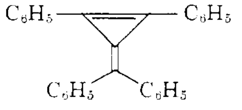
Among the compounds of theoretical interest in the cyclopropene series are the derivatives of methylenecyclopropene (I), which is related to the fulvenes. Compounds of this type are predicted to have appreciable resonance stabilization,[3] and their properties would accordingly be of great interest.



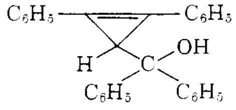
I

Although several schemes come to mind for the synthesis of such a derivative as, for instance, tetraphenylmethylenecyclopropene (II), it seemed to us that one obvious possibility was the dehydration of the carbinol III which should be readily available from the reaction of phenylmagnesium bromide with the previously described diphenylcyclopropenecarboxylic ester.[4] Unfortunately, although this type of intermediate is of course the usual one in syntheses of fulvenes[5] it has not proved useful in approaches to heptafulvenes, which are more closely related to methylenecyclopropenes; in the cyclopropenes as well as in the cycloheptatrienes, the cation, not the anion as in cyclopentadiene compounds, is the stable ion, and the dehydration requires removal of a non-acidic hydrogen in the three- and seven-membered ring cases, to form a product whose eventual polarization should be the reverse of that of the transition state for dehydration; this is again in contrast to the situation in the (successful) syntheses in the five-membered ring series. Accordingly, some difficulty was anticipated.

More seriously, the carbinol III was expected to form a carbonium ion with extraordinary ease.



II



III

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[1] These results were first reported at the Boston Meeting of the American Chemical Society, April, 1959. This work was in part supported by a grant from the National Science Foundation, which is gratefully acknowledged.

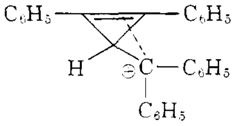
[2] American Cyanamid predoctoral fellow, 1958–1959.

[3] G. Berthier and B. Pullman, *Bull. soc. chim. France*, **16D**, 457 (1949).

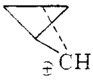
[4] R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

[5] E. D. Bergmann, in "Progress in Organic Chemistry," Vol. III, Academic Press, Inc., New York, N. Y., 1955, p. 81. *Cf.* also W. Doering, Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., 1959.

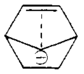
This carbonium ion IV is stabilized by the two attached phenyl groups, of course, and additionally it is related to both the cyclopropyl carbinyl cation[6] V and the 7-norbornenyl cation[7] VI, both of which are known to be strongly stabilized. Thus like both of these species the carbonium ion IV should be stabilized by non-classical interaction with a nearby electron pair, in this case the π-electrons of ring double bond (this interaction is indicated by dotted lines in the drawings). Models reveal, in fact, that the geometry of IV is extremely similar to that of VI as regards the position of the cationic carbon relative to the double bond. The possibility of carbonium ion rearrangements was present, therefore; this possibility apparently was realized.



IV



V



VI

The carbinol III readily was prepared. It shows, in the ultraviolet spectrum, the usual pair of bands 15 mμ apart above 300 mμ, and the second pair below 230 mμ, which are characteristic of Δ^1-1,2-diphenylcyclopropenes, but in this case the long wave length bands are 15 mμ higher than usual for such systems. This is apparently due to interaction of the stilbene chromophore with the diphenylcarbinol substituent. When the carbinol was treated with acetic anhydride and sodium acetate, dehydration occurred and two hydrocarbons, $C_{28}H_{20}$, could be isolated: a major product, which was white, and a minor component whose blue color facilitated isolation. The major product reacted neither with bromine nor with permanganate, and its ultraviolet spectrum showed a maximum in the benzenoid region at 246 mμ, which seemed unlikely for a compound such as II. It thus seemed to be a product of rearrangement.

Ignoring the possibility that the blue compound was actually II, the most likely alternative structure, considering the color, was a substituted azulene of some sort. Considerations of possible rearrangement mechanisms convinced us that one possibility was 1,2,3-triphenylazulene (VII). This compound has been obtained by Kharasch[8] from a very interesting rearrangement reaction, involving the action of dinitrobenzenesulfenyl chloride and aluminum chloride on diphenylacetylene, and he has demonstrated its structure unambiguously. Comparison of our compound with an authentic sample of VII,[9] by the use of mixed melting point, ultraviolet and visible spectra, established their identity. Thus the minor component of our reaction was indeed triphenylazulene (VII). The major component, m.p. 160–162°, seemed most likely to be a naphthalene derivative, and our considerations of mechanism suggested specifically that it should be 1,2,4-triphenylnaphthalene (VIII), a known compound (reptd.[10] m.p. 158–159°).

The alternate possibility, 1,2,3-triphenylnaphthalene, m.p. 151°, is easily prepared,[11] and is proved to be different from our compound by mixed melting point test and by subtle but real differences in the infrared and ultraviolet spectra. These spectra were so similar, however, that it was felt that identification of the 1,2,4-triphenylnaphthalene could be effected without a direct comparison, and accordingly the reduction of the compound, reported by Blum[10] for the authentic naphthalene compound, was carried out by us on our own sample.

Blum reports that when VIII is treated with sodium in boiling amyl alcohol two isomeric tetrahydro compounds are formed, which may be separated by fractional crystallization. The major product, which is isolated first, crystallizes in prisms, m.p. 125–129°. From the mother liquors the second isomer may be obtained as needles, m.p. 186–187°. We followed the described procedure with our compound and obtained, as major product, prisms, m.p. 125–128°, and from the mother liquors we obtained needles, m.p. 184–188°. The observed solubility properties of our compounds also matched those reported, so we conclude that the white material from our dehydration is identical with Blum's 1,2,4-triphenylnaphthalene. The previously reported structure proof for the naphthalene seems to us unambiguous.

Kharasch reported[8] that a white compound, m.p. 154–155°, accompanied his triphenylazulene, and although in our case the azulene was the minor product and in his case the major one it seemed possible that his white compound was also VIII. The two have now been compared[12] and they are not identical. Thus, although very similar mechanisms could have been written for both the reactions, apparently the only coincidence in product is the azulene.

The most likely mechanism for the formation of our products seems to involve the carbonium ion IV. If this rearranges to the cyclobutenyl cation IX, by analogy with similar ring expansions of cyclopropylcarbinyl cations to cyclobutyl cations, the resulting allylic cation may attack a neighboring phenyl group to form two different spirocyclic systems, X and XI. The compounds formed are cyclopropylcarbinyl cations, and may undergo the well known rearrangements of such systems. Thus if X rearranges to the isomeric cyclopropylcarbinyl cation XII, and this then loses a proton as shown, the result is VII. With XI, the corresponding rearrangement leads to XIII, in which loss of a proton to afford an azulene is not possible, but in which an alternative form of proton loss leads, as shown, to VIII. A similar reaction with XII would have led to 1,2,3-triphenylnaphthalene, which was not observed, but an amount of this colorless compound which was comparable to that of the blue azulene might well have gone unnoticed.

Variants of this scheme can be suggested, as in all such speculative "mechanisms," but at least it

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(6) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, THIS JOURNAL, **81**, 4390 (1959).

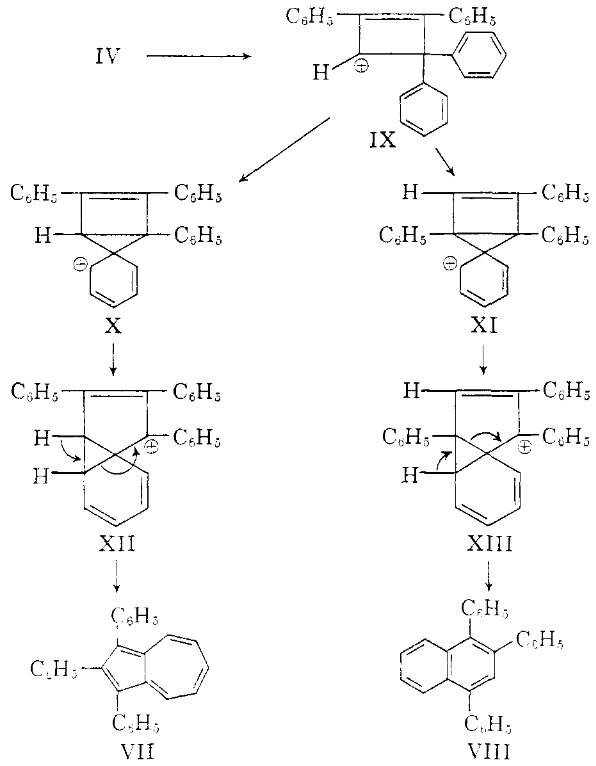
(7) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

(8) S. J. Assony and N. Kharasch, *ibid.*, **80**, 5978 (1958).

(9) The authentic sample was kindly supplied by Professor George Büchi, who has obtained the azulene from still another rearrangement reaction.

(10) O. Blum, *Ber.*, **62**, 881 (1929).

(11) L. I. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1184 (1941).



demonstrates that only a few steps, quite closely analogous to reactions already known, need be drawn to account for the formation of our products, unusual though the reaction appears at first sight.

Several attempts were made to avoid the formation of the postulated carbonium ion by altering the dehydration conditions and reagents. Although the yields of the two products varied with the conditions, they were formed in all cases, even with the use of phenyl isocyanate which might have been expected to remove the hydroxyl and the proton almost simultaneously. Consequently alternative approaches to tetraphenylmethylenecyclopropene have been taken up, and will form the substance of subsequent publications.

Experimental

Diphenyl-(Δ^1-1,2-diphenylcyclopropenyl)-carbinol (III).—Reaction of Δ^1-1,2-diphenyl-3-carbomethoxycyclopropene[4] with an excess of phenylmagnesium bromide in ether solution for 30 min. yielded, after the usual isolation procedures, 60–70% of III, m.p. 172–175°. Recrystallization from benzene gave white crystals, m.p. 173.5–174.5°. The infrared spectrum had the expected absorption bands for the assigned structure, and the ultraviolet spectrum had absorption maxima at 335 (17,000), 319 (27,500), 227 (28,500) and 220 mμ (30,000).

Anal. Calcd. for $C_{28}H_{22}O$: C, 89.80; H, 5.92. Found: C, 89.91, 90.11; H, 5.94, 6.05.

Dehydration of III.—When 150 mg. of the above carbinol was refluxed for 18 hours with 5 ml. of acetic anhydride and 100 mg. of sodium acetate there was isolated, after chromatography on alumina, 67 mg. (47%) of a white flaky material which was crystallized from methanol, m.p. 160–162°. A more polar material also was isolated from the chromatogram; 2 mg. (1.4%) of a blue material, m.p. 215–218°. The white compound was sublimed for analysis. The compound did not react with Br_2 in CCl_4 or with $KMnO_4$ in acetone. In the ultraviolet it absorbed at 246 (49,000) and 303 mμ (13,000).

Anal. Calcd. for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.47, 94.30; H, 5.70, 5.95.

Reaction of 200 mg. of III with 1.5 ml. of acetyl chloride at room temperature led to vigorous evolution of HCl and the formation of a deep blue color. Isolation by chromatography of the products yielded 133 mg. (70%) of the white material, m.p. 162–163°, and 6 mg. (3.2%) of a blue substance from hexane–benzene, m.p. 216–217°, which was recrystallized for analysis.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.60; H, 5.69.

This material was identified as 1,2,3-triphenylazulene (VII), reptd. m.p. 215.5–216°, by comparison of the ultraviolet and visible spectra and by a mixed melting point test with an authentic sample.[9]

When the dehydration was carried out with 1 ml. of acetyl chloride in 5 ml. of acetic anhydride at room temperature there was obtained 87% of the white compound and 1% of the azulene. The same results were obtained with iodine in boiling xylene. Phenyl isocyanate at 90° yielded these two and also two other unidentified substances which showed carbonyl absorption in the infrared, and were therefore not further investigated. The carbinol did not react with $POCl_3$ in pyridine at room temperature, with TsCl in pyridine, or with acetic anhydride and sodium hydride in ether. Pyridine with acetyl chloride or with thionyl chloride afforded polymeric material.

Identification of the M.p. 162° Compound.—1,2,3-Triphenylnaphthalene was prepared from diphenylacetylene and lithium as described by Smith and Hoehn[11] in 70% yield, m.p. 154–155° (reptd. m.p. 151°). In the ultraviolet the compound showed a maximum at 246 mμ (52,000) but not at 303 mμ. There were differences in the infrared spectra of this compound and of the 162° material in the fingerprint region, and the two gave a 25° mixed melting point depression.

Following the procedure described by Blum[10] for the reduction of 1,2,4-triphenylnaphthalene, 130 mg. of our 162° material was treated with 0.2 g. of sodium metal in boiling amyl alcohol (3 ml.). After workup, crystallization from ethyl acetate–methanol yielded 68 mg. (52%) of white prisms, m.p. 125–128° (reptd. prisms m.p. 125–129°). From the mother liquors it was possible to obtain, after recrystallization from *n*-propyl alcohol, 6 mg. (4.5%) of white needles, m.p. 184–188° (reptd. needles, m.p. 186–187° from propyl alcohol).[12]

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(12) This comparison, which was kindly arranged by Professor Kharasch, was performed by Dr. C. M. Buess. Balaban, *Tetrahedron Letters*, **5**, 14 (1959), has recently suggested that Kharasch's compound is actually tetraphenylcyclobutadiene, but there seems to be no evidence yet available to support this unusual suggestion.