

at 3.15 and 2.58. From the ratio of the N-methyl protons the ratio of XIV to XV at  $-20^\circ$  was 9:1. Rapid heating to  $+70^\circ$  caused coalescence<sup>14</sup> of the N-methyl peaks in each compound, leading to two broad peaks at  $\delta$  3.50 and 2.66. Heating for 2 hr. caused a decrease in the  $\delta$  3.50 band in favor of the 2.66 band. At room temperature, the equilibrium ratio of  $\delta$  3.50 to 2.66 was about 3:1, in agreement with the ratio of rate constants from the ultraviolet equilibrations above.

*Treatment of the Mixture of XIV and XV with Base.* A solution of 104 mg. of the mixture of XIV and XV in 7 ml. of acetonitrile with 3 ml. of triethylamine and 5 ml. of furan was allowed to stand at room temperature in the dark for 5 days, at which time  $\lambda_{\max}$  shifted from 378 to 358 m $\mu$ . Aqueous work-up afforded 75 mg. of brown tar; addition of silver nitrate to the acidified aqueous solution afforded *ca.* 30 mg. of crude AgBr (theoretical 20 mg.). Chromatography of the brown tar on silica gel afforded 10 mg. of XIII, m.p. 133–135° dec., as the only defined product. A similar reaction for 20 hr. afforded 30 mg. of XIII, m.p. 130–133° dec., and 28 mg. of a mixture of XIII and XIV (and XV), identified by infrared spectra, m.p. 128–129°.

*1-Dimethylamino-2-nitro-3-phenylcyclobuten-4-one (XVII).* A warm solution of 1.560 g. (4.54 mmoles) of the iodo compound X in 35 ml. of acetonitrile was poured into 6.00 g. (35.5 mmoles) of silver nitrate and 1.43 g. (18.1 mmoles) of pyridine in 10 ml. of acetonitrile; a yellow precipitate formed immediately. After 45 min. of stirring at room temperature in the dark, the silver iodide was collected, washed, and dried, yielding 1.006 g. (94%). The filtrate was poured into ice water and the resulting precipitate was recrystallized from methanol, affording 1.111 g. (88%) of *1-dimethylamino-2-nitro-3-phenylcyclobutenyl 4-nitrate* (XVIII), m.p. 106–108° dec.

*Anal.* Calcd. for  $C_{12}H_{13}N_3O_5$ : C, 51.61; H, 4.69; N, 15.05. Found: C, 51.68; H, 4.90; N, 14.59.

The infrared spectrum showed peaks at 6.0, 6.9, 7.2, 7.7, etc.  $\mu$ , while the ultraviolet spectrum had  $\lambda_{\max}$  372 (log  $\epsilon$  4.26). The n.m.r. spectrum showed a sharp five-proton peak at  $\delta$  7.58, two one-proton apparent singlets at 5.43 and 4.28, and two broad<sup>14</sup> (half-width: 10 c.p.s.) three-proton bands at 3.67 and 3.12.

A solution of 1.000 g. (3.58 mmoles) of the above nitrate in 25 ml. of acetonitrile with 2.424 g. (22.6 mmoles) of 2,6-lutidine was heated at reflux for 2 hr. The mixture was poured into 100 ml. of water containing 1.36 g. (22.6 mmoles) of acetic acid, and the product was collected in the usual way with methylene chloride. Chromatography on silica gel afforded the ketone XVII in the first benzene eluate, 162 mg. (19.5%), m.p. 85–86° from petroleum ether. It was recrystallized from benzene–petroleum, m.p. 86.5–87.5°.

*Anal.* Calcd. for  $C_{12}H_{12}N_2O_3$ : C, 62.20; H, 5.21; N, 12.06. Found: C, 62.22; H, 5.39; N, 11.80.

In the infrared (KBr) the compound showed strong bands at 5.67 and 6.00  $\mu$ . The ultraviolet spectrum had  $\lambda_{\max}$  403 m $\mu$  (log  $\epsilon$  4.04). In the n.m.r. ( $CCl_4$ ) there was a five-proton sharp band at  $\delta$  7.19, a one-proton singlet at 4.78, and a broad six-proton band<sup>14</sup> at 3.35. In  $CH_2Cl_2$  the latter was split into two broad peaks<sup>14</sup> at  $\delta$  3.44 and 3.27, while in pyridine the two  $NCH_3$  peaks<sup>14</sup> were separated by 16 c.p.s.

When a few drops of  $D_2O$  were added to the pyridine n.m.r. solution (external TMS standard) the CH band at  $\delta$  4.4 and the two  $NCH_3$  groups at  $\delta$  2.65 and 2.40 decreased over 1–2 hr. at the same rate, apparently in favor of singlets at  $\delta$  5.05 and 2.25 (in an area ratio of 1:3.7), respectively. The n.m.r. spectrum of XVII in  $CS_2$  was unchanged by 3 days of shaking with  $D_2O$ .

## Isomerization of Biscyclopropenyls to Benzenes<sup>1,2</sup>

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*Reduction of triphenylcyclopropenyl cation (I) with zinc affords a dimer, bistrisphenylcyclopropenyl (II). The dimer does not dissociate to trisphenylcyclopropenyl radical, but on heating, irradiation, or treatment with potassium amide it rearranges to hexaphenylbenzene. Reduction of ethyldiphenylcyclopropenyl cation (V) yields a dimer (VI) which rearranges on heating to a mixture of 1,2-diethyltetraphenylbenzene (VII) and 1,4-diethyltetraphenylbenzene (VIII). Reduction of diphen-*

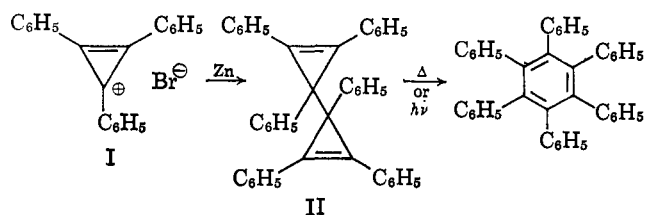
*ylcyclopropenyl cation (III) affords directly 1,2,4,5-tetraphenylbenzene (IV); the desired dimer IX was prepared by an alternate route. As part of the structure proof, IX was converted to a cyclopropenyl cation XI. On heating at 135° IX is converted to 1,2,4,5-tetraphenylbenzene (IV) and 1,2,3,4-tetraphenylbenzene (XII) in a ratio of 10:1. At 300°, the rearrangement gives a IV/XII ratio of 3.5. Photochemical rearrangement of IX reverses the ratio: XII/IV = 2.2; potassium amide rearranges IX to XII. Mechanisms to explain these results involve, for the thermal and photochemical reactions, progression through Ladenburg and Dewar benzene structures.*

(1) Work on dimer II has been reported in a preliminary communication: R. Breslow and P. Gal, *J. Am. Chem. Soc.*, **81**, 4747 (1959). The work on dimer IX and its rearrangement, as evidence for path 3, was reported at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, and by R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(2) Support of this work by the National Science Foundation and the Petroleum Research Fund is gratefully acknowledged.

With the finding of aromatic stability in cyclopropenyl cations, it became of interest to examine the three

$\pi$ -electron cyclopropenyl radicals. Accordingly, triphenylcyclopropenyl cation (I) was reduced by metals in an attempt to produce the corresponding radical; as we have already reported,<sup>1</sup> this reduction affords not the free radical, but its undissociated dimer (II). On heating or irradiation, II rearranges to hexaphenylbenzene rather than dissociate. Subsequently, special electrochemical techniques were used to obtain rapid reversible reduction of triphenylcyclopropenyl cation to the radical<sup>3</sup>; in this way it was demonstrated that the radical has considerably less resonance stabilization than the cation.<sup>3,4</sup> However, the rearrangement of II to a benzene is of interest in its own right. In this paper, we report the results of our studies of this rearrangement.



The structure of dimer II is established by its typical diphenylcyclopropene absorptions in the infrared ( $5.5 \mu$ ) and ultraviolet ( $306 m\mu$ ) and by its cleavage with  $\text{Br}_2$  to 1.56 moles of isolated triphenylcyclopropenyl bromide. This is the expected result of ionic attack on a double bond of dimer II; it does not represent dissociation of II to radicals, since II is unaffected by  $\text{I}_2$  or  $\text{O}_2$ . The thermal rearrangement of II to hexaphenylbenzene is similarly unaffected by the presence of  $\text{I}_2$  or  $\text{O}_2$ .

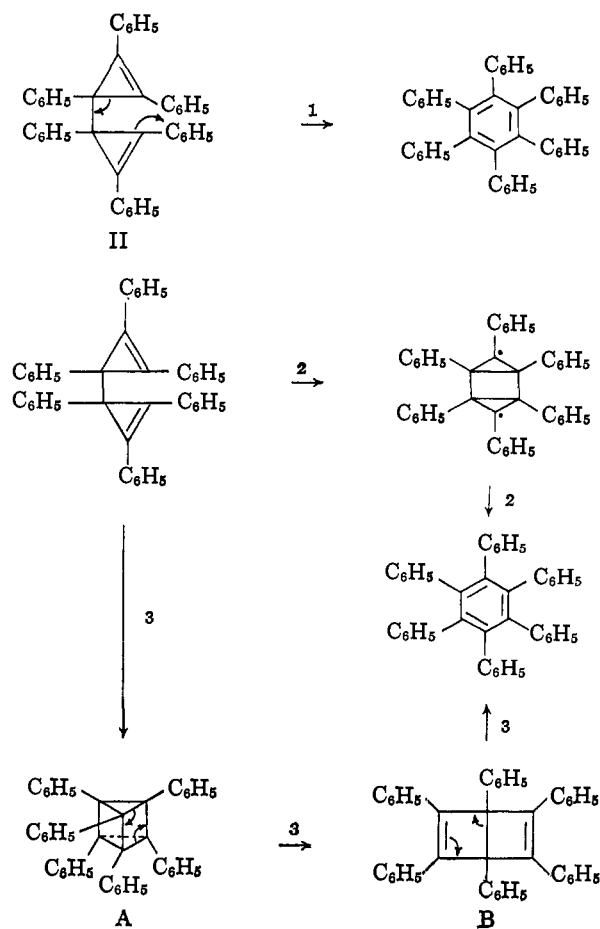
When II is heated at its melting point ( $255^\circ$ ), it rapidly resolidifies by rearrangement to hexaphenylbenzene; the same rearrangement occurs on 3 days of refluxing of II in xylene. Furthermore, irradiation of a solution of II affords hexaphenylbenzene. *A priori*, a number of mechanisms seem possible for the rearrangement. In one set (paths 1 and 2) a more or less direct change is postulated. A third mechanism (path 3) involves formation of a derivative of Ladenburg benzene, hexaphenylprismane (A), its rearrangement to a Dewar benzene (B), and its final opening to the Kekulé form.<sup>5</sup> As we have already pointed out,<sup>1</sup> path 3 is supported not only by its intrinsic historical nature but also by the data to be discussed below.

A major difference between paths 1 and 2 and path 3 is that the first two mechanisms predict retention of the bond between the two rings of II in the final benzene; in path 3, the symmetry of A means that this bond may be broken. Accordingly, it was of interest to produce an analog of II which was labeled so that this point could be examined.

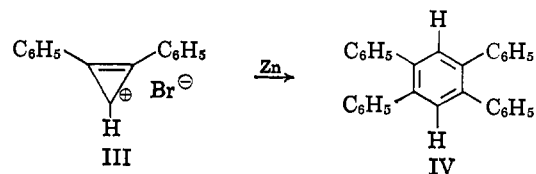
(3) R. Breslow, W. Bahary, and W. Reinmuth, *J. Am. Chem. Soc.*, **83**, 1763 (1961).

(4) For a similar conclusion based on relative hydrogen abstraction rates by methyl radical from triphenylcyclopropene and triphenylmethane, see P. Gal, Ph.D. Thesis, Columbia University, 1962.

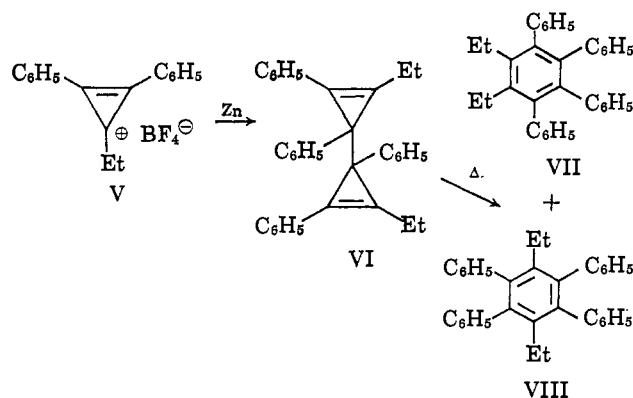
(5) Since this work was first reported,<sup>1</sup> several examples of Dewar benzenes have been reported, the first by E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962). Furthermore, a prismane derivative has been reported by H. G. Viehe, *et al.*, *Angew. Chem.*, **76**, 922 (1964). Finally, several rearrangements of substituted benzenes, *e.g.*, that reported by A. Burgstahler and P. L. Chien, *J. Am. Chem. Soc.*, **86**, 2940 (1964), may proceed by photochemical reversal of path 3. Some of the history of this field has been reviewed by D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 121 (1965).



Reduction of diphenylcyclopropenyl cation (III) with zinc (or other metals) affords, not a simple dimer, but instead 1,2,4,5-tetraphenylbenzene (IV). No major amount of any other isomer could be detected. Reduction of diphenylethylcyclopropenyl cation (V)



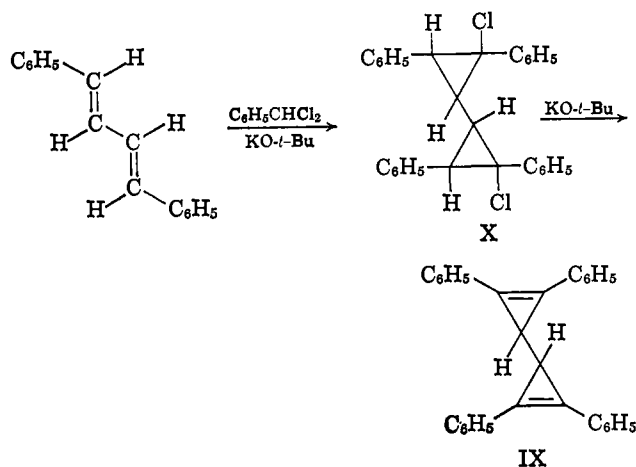
yields a dimer (VI) whose ultraviolet, n.m.r., and infrared spectra indicate that it is coupled, as shown, on the phenyl-bearing carbon.<sup>6</sup> Thermal rearrangement



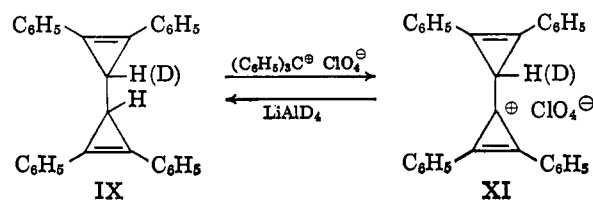
(6) Both VI and F could have two stereoisomers. Assuming that the thermal rearrangements are topologically specific (*e.g.*, as indicated in path 3) then only one isomer of VI or of F could afford the *ortho* and

of VI affords a mixture of 1,2-diethyl-3,4,5,6-tetraphenylbenzene (VII) and 1,4-diethyl-2,3,5,6-tetraphenylbenzene (VIII).

Neither of these experiments is a test of the mechanisms, but the observation that reduction of V produces the dimer VI suggested that reduction of the diphenyl cation (III) may not have proceeded through the desired dimer IX, but instead through a dimer analogous to VI. This was confirmed by a direct synthesis of IX, which proved to be quite stable. Addition of phenylchlorocarbene to diphenylbutadiene affords X, and this with potassium *t*-butoxide yields the desired



dimer IX. The structure of IX follows from spectra, including the cyclopropene band at  $5.5 \mu$  and the distorted stilbene absorption at  $326 \text{ m}\mu$ . For further structure proof, IX was treated with triphenylmethyl perchlorate and converted into a cyclopropenyl cation XI. Reduction with lithium aluminum deuteride afforded monodeuterio IX, and this with triphenylmethyl perchlorate yielded XI with about 50% of one deuterium atom (by n.m.r. analysis). This sequence proves the chemical symmetry of the compound.

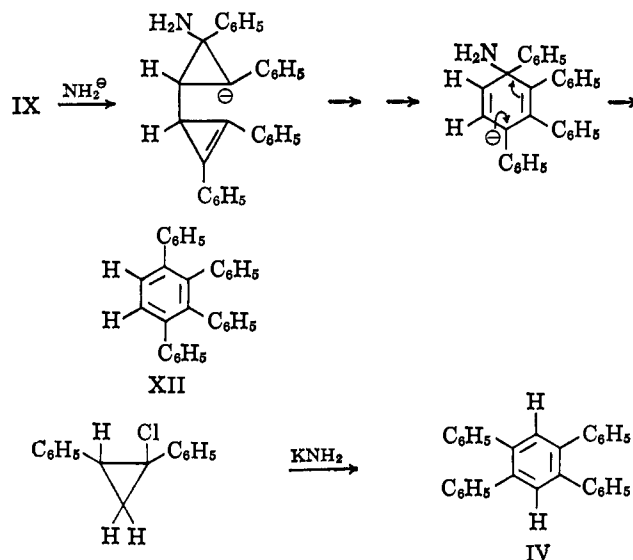


In the course of studies on the conversion of X to IX, it was observed that excessively vigorous base treatment produces 1,2,3,4-tetraphenylbenzene (XII) instead, and subsequently it was shown that IX is converted to XII by potassium amide, and the original dimer II to hexaphenylbenzene. Interestingly, even chlorodiphenylcyclopropane (XIII) is converted to 1,2,4,5-tetraphenylbenzene under these conditions; this latter process is presumably related to that described earlier<sup>7</sup> for conversion of triphenylcyclopropene to hexaphenylbenzene.

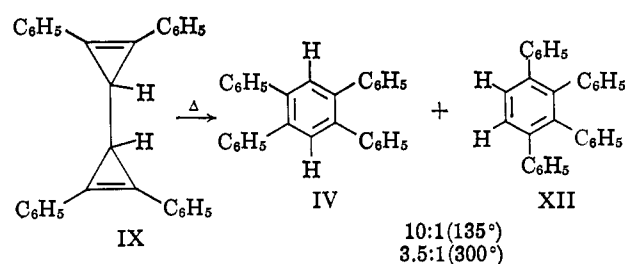
In the critical experiments, dimer IX was rearranged thermally. Four separate runs at  $135^\circ$  produced both 1,2,4,5-tetraphenylbenzene (IV) and 1,2,3,4-tetraphenylbenzene (XII), in an average ratio of about 10:1.

*para*, and not *meta* products. It is striking that this is the only isomer of VI actually isolated, and in the case of F apparently the only one formed, since in neither sequence was a *meta* isomer detected.

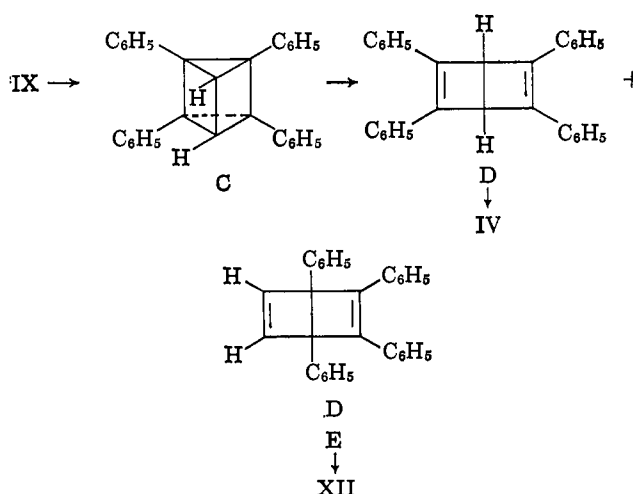
(7) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).



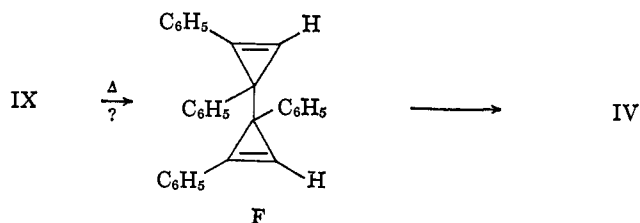
Rearrangement at  $300^\circ$  produced the same mixture, but in a ratio of 3.5:1. These results certainly exclude paths 1 and 2 in their simplest forms, and are almost



uniquely consistent with path 3, involving the prismane. Thus the prism (C) derived from IX may open to two different Dewar benzenes, D and E, leading, respectively, to IV and XII. The path through E is statistically favored, but opening to D should be better energetically: two stilbene systems are formed, and more steric interaction is relieved. Accordingly, the preponderance of IV is explained. The only other

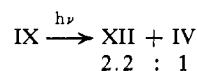


serious possibility which could explain these findings is the hypothesis that IX undergoes a Cope rearrangement to the isomer F, and that this isomer by path 1 or 2 gives IV. Studies of the thermal rearrangement of IX, by quantitative ultraviolet determination during the reaction, give no indication of the buildup of any



intermediates, since good isosbestic points are observed.<sup>4</sup> However, F is undoubtedly very reactive, for this must be the intermediate in the conversion of diphenylcyclopropenyl cation directly to IV by zinc reduction.<sup>6</sup> The chief arguments against this alternative mechanism are the improbability of a rapid endothermic<sup>8</sup> Cope rearrangement of IX to F under these conditions, and the absence of a good reason for F, by paths 1 or 2, to rearrange preferentially to IV. Both steric and electronic considerations<sup>9</sup> indicate that F should preferentially rearrange to XII. The observed high preference for the formation of IV, both in the room temperature reduction of the diphenyl cation (III) and (with decreasing selectivity at higher temperatures) in the thermal rearrangements of IX, are best consistent with the idea that both dimers, IX and F, close to the prism C and thus follow path 3.

The photochemical rearrangement of IX proceeds much more slowly than does that of the hexaphenyl dimer II. Both this fact and the slower thermal isomerization of IX relative to II must reflect conformational differences: in IX the two cyclopropene rings lie, on the average, far apart, while the extra phenyls in II make the *endo* conformation relatively better. Side reactions also intervene in the slow photolysis of IX, so that the yields of tetraphenylbenzenes are less than 10% at best. However, both IV and XII were produced, but in reversed proportion—XII predominates over IV by a ratio of  $2.2 \pm 0.3$ . At the very least,



this change in ratio indicates that the mechanism is not precisely the same. It may well be that several paths are operating simultaneously, *e.g.*, some rearrangement through the prism to produce IV, some rearrangement by another path to produce XII.<sup>10</sup> However, it is striking that the ratio of XII to IV, about 2:1, is almost exactly that expected for strictly statistical opening of the prism C. In the thermal processes this is dominated, according to our interpretation, by the activation energy difference between the paths leading to D and E, but if the photochemical process produces a thermally excited prism then statistical opening might well be observed.

Thus the data so far available are consistent with a prism intermediate for the thermal rearrangement, and possibly a "hot prism" in the photochemical processes. An attempt was made to observe an intermediate by photolyzing the hexaphenyl dimer (II)

(8) In F, compared with IX, two stable stilbene systems are replaced by styrenes, and hindrance around the central bond is increased.

(9) In the direct path 1, formation of IV from F involves reaction of the more hindered carbons, while in the indirect path 2 it involves as well formation of the less stabilized intermediate.

(10) For instance, there may be enough energy to permit attack in an *exo* conformation, leading to a chair-like transition state which must produce XII, while *endo* closure through a boat-like transition state could lead to the prism and thus on to a mixture of IV and XII.

at  $-58^\circ$  and directly observing the ultraviolet spectrum of the solution. The dimer disappeared in favor of a new substance whose ultraviolet spectrum is quantitatively identical with that of hexaphenylbenzene. Thus, whatever intermediates there are in the photochemical process rearrange to the final product even under these low-temperature conditions.

## Experimental Section

**Bistriphenylcyclopropenyl (II).** A suspension of 3.0 g. of triphenylcyclopropenyl bromide (I)<sup>11</sup> in 400 ml. of dry benzene was heated at reflux for 3 hr. with a large excess of zinc powder. The solids were removed by filtration and the solution was concentrated *in vacuo* to ca. 50 ml. **Bistriphenylcyclopropenyl (II)** crystallized as a white powder, which was collected and washed with ether, yielding 1.30 g. The compound had a melting point of  $255\text{--}256^\circ$  (placed on a hot stage at  $250^\circ$ ), but it rapidly resolidified to melt at  $420^\circ$ .

*Anal.* Calcd. for  $\text{C}_{42}\text{H}_{30}$ : C, 94.38; H, 5.62. Found: C, 94.40; H, 5.57.

The infrared spectrum showed a cyclopropene band<sup>11</sup> at  $5.5 \mu$ , and the ultraviolet spectrum showed the expected<sup>11</sup>  $\lambda_{\text{max}}$   $306 \text{ m}\mu$  ( $\epsilon$  32,000). The n.m.r. spectrum showed only aromatic hydrogens. The compound could be recrystallized from xylene.

A solution of 0.2 g. of II in 50 ml. of xylene was treated with an excess of  $\text{Br}_2$ . The precipitated **tristriphenylcyclopropenyl bromide (I)**<sup>11</sup> (0.2 g., 78% of 2 moles) was collected and identified by melting point, infrared, and ultraviolet spectra.

**Hexaphenylbenzene.** The material above from melting of II was identified as hexaphenylbenzene by comparison with an authentic sample<sup>12</sup> (melting point and infrared spectrum). Refluxing a solution of 0.2 g. of II in 100 ml. of xylene for 3 days afforded 0.18 g. (90%) of hexaphenylbenzene; under the same conditions in the presence of iodine or with a stream of air hexaphenylbenzene was again the exclusive product. Irradiation of 0.2 g. of II in 100 ml. of xylene with a Hanovia 140-w., general-purpose ultraviolet lamp for 10 hr. afforded 0.16 g. (80%) of hexaphenylbenzene. Irradiation of a solution of II in cyclopentane at  $-58^\circ$  for 1 hr. (450-w. medium-pressure mercury arc, Corex filter) in a jacketed ultraviolet cell, immediately followed by spectroscopy at this temperature, afforded a solution whose ultraviolet spectrum was identical with that of hexaphenylbenzene.

To a solution of potassium amide, from 0.2 g. of potassium in 100 ml. of dry liquid ammonia, was added 150 mg. of II in 100 ml. of dry dimethoxyethane. The mixture was allowed to warm to room temperature overnight, affording 130 mg. (87%) of hexaphenylbenzene. An identical control in which potassium was omitted yielded recovered starting material.

**Dimerization of Diphenylcyclopropenyl Cation.** A suspension of 1.016 g. of diphenylcyclopropenyl bromide (III)<sup>13</sup> and 2 g. of zinc powder in 150 ml. of dry benzene was stirred under  $\text{N}_2$  for 10 hr. The solution was filtered and concentrated. Chromatography of the residue on alumina afforded 0.238 g. (33%) of

(11) R. Breslow and H. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

(12) W. Dilthey and G. Hurtig, *Chem. Ber.*, **67**, 2004 (1934).

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

1,2,4,5-tetraphenylbenzene (IV), m.p. 265–266°, identified by comparison (mixture melting point, infrared, thin layer chromatogram) with an authentic sample.<sup>14</sup> In other runs the yield varied from 17 to 42%, but it was not raised when the reaction was continued for 5 days. Thin plate chromatography (silica, CCl<sub>4</sub>) easily resolved authentic 1,2,3,4- (XII)<sup>15</sup> and 1,2,4,5-tetraphenylbenzenes; no 1,2,3,4-isomer could be detected in the reaction mixture by thin plate or vapor phase chromatography (5% could have been detected). Reduction of diphenylcyclopropenyl perchlorate with lithium amalgam in acetonitrile afforded 31% of 1,2,4,5-tetraphenylbenzene.

**Dimerization of Diphenylethylcyclopropenyl Cation.** A mixture of 7.7 g. of diphenyl-3-ethylcyclopropenyl fluoroborate (V)<sup>16</sup> and 5 g. of zinc powder in 200 ml. of acetonitrile was stirred at room temperature for 2 days. The solution was filtered and concentrated and the residue was chromatographed on alumina, affording 0.17 g. (3%) of 3,3-bis( $\Delta^1$ -1-ethyl-2,3-diphenylcyclopropenyl) (VI), m.p. 182–182.5°.

*Anal.* Calcd. for C<sub>34</sub>H<sub>30</sub>: C, 93.11; H, 6.89. Found: C, 93.54; H, 6.81.

In the ultraviolet the compound<sup>17</sup> had  $\lambda_{\max}$  271 m $\mu$  ( $\epsilon$  16,900) and in the infrared a cyclopropene peak at 5.5  $\mu$ . The n.m.r. spectrum had a triplet at  $\delta$  1.33, a quartet at 2.8 ( $J = 7$  c.p.s.), and phenyl hydrogens at 7.03; the areas were in the ratio 3:2:10. When the reduction was run for 10 days, the yield was still only 3%.

This dimer VI (0.091 g.) was heated in a sealed tube under N<sub>2</sub> at 300–315° for 5 min. The product was chromatographed on alumina with CCl<sub>4</sub>, affording 0.056 g. (61%) of a mixture of 1,2-diethyl-3,4,5,6-tetraphenylbenzene (VII)<sup>18</sup> and 1,4-diethyl-2,3,5,6-tetraphenylbenzene (VIII), m.p. 230–260°. The infrared spectrum was a composite of the spectra of VII and VIII. Thin-plate chromatography (silica, CCl<sub>4</sub>) resolved the two compounds, VIII running ahead of VII. The thin layer bands were isolated by micro-extraction and pure VII and VIII were identified by mixture melting point and ultraviolet spectral comparisons; they were present in a ratio VII to VIII of about 2:1.

**1,4-Diethyl-2,3,5,6-tetraphenylbenzene (VIII).** Tolan (5 g.) and 2,5-diethyl-3,4-diphenylcyclopenten-4-olone<sup>19</sup> (8.6 g.) were heated under N<sub>2</sub> at 275° for 1 hr. Crystallization from benzene-ligroin afforded VIII (5.3 g., 43% yield), m.p. 310–315°. The analytical sample was chromatographed on alumina and recrystallized, m.p. 321–322°.

*Anal.* Calcd. for C<sub>34</sub>H<sub>30</sub>: C, 93.10; H, 6.90. Found: C, 93.16; H, 7.10.

**1,2-Diphenyl-1-chlorocyclopropane (XIII).** To 6.5 g. of freshly distilled styrene and 20 g. of potassium *t*-butoxide in 80 ml. of cyclohexane at reflux under N<sub>2</sub>

was added 12 g. of benzal chloride in 25 ml. of cyclohexane over 2 hr. Distillation and alumina chromatography afforded 2.6 g. of 1,2-diphenyl-1-chlorocyclopropane (XIII), m.p. 80–81°. The compound had no ultraviolet absorption above 300 m $\mu$ .

*Anal.* Calcd. for C<sub>15</sub>H<sub>13</sub>Cl: C, 78.77; H, 5.69; Cl, 15.53; mol. wt., 228.5. Found: C, 78.63; H, 5.96; Cl, 14.96; mol. wt. (osmometer), 226.

Reaction of XIII (0.3 g.) in 50 ml. of dimethoxyethane with potassium amide (from 0.6 g. of potassium in 60 ml. of ammonia) overnight afforded 1,2,4,5-tetraphenylbenzene (IV) in 36% yield, identified by infrared and melting point comparison with an authentic sample.<sup>14</sup> No other isomer could be detected.

**3,3-Bis(1,2-diphenyl-1-chlorocyclopropyl) (X).** To a boiling solution of 20 g. of 1,4-diphenyl-1,3-butadiene and 80 g. of benzal chloride in 400 ml. of dry cyclohexane, 100 g. of powdered potassium *t*-butoxide was added at a rate which maintained gentle reflux. After 8 hr. of additional reflux, the mixture was poured into water and the product was collected with benzene and ether. The solution was taken to dryness and the residual product X was washed with ether and recrystallized from benzene-ligroin, 9.2 g. (20%), m.p. 207–208°.

*Anal.* Calcd. for C<sub>30</sub>H<sub>24</sub>Cl<sub>2</sub>: C, 79.12; H, 5.31; Cl, 15.57. Found: C, 78.84; H, 5.30; Cl, 15.43.

In some experiments a small amount of another isomer was obtained as well, m.p. 235–237°.

*Anal.* Found: C, 79.25; H, 5.51; Cl, 14.54.

Both compounds had only weak absorption near 265 m $\mu$  and strong end absorption. Both gave the same product (IX) with potassium *t*-butoxide.

**3,3-Bis( $\Delta^1$ -1,2-diphenylcyclopropenyl) (IX).** A solution of 4.5 g. of X and 11 g. of potassium *t*-butoxide in 300 ml. of dry *t*-butyl alcohol was refluxed for 48 hr. under N<sub>2</sub>. Work-up and chromatography afforded 2.9 g. (76%) of the dimer IX, m.p. 165–166°.

*Anal.* Calcd. for C<sub>30</sub>H<sub>22</sub>: C, 94.24; H, 5.76; mol. wt., 382. Found: C, 94.25; H, 5.92; mol. wt. (Rast, camphor), 319.

The infrared spectrum of IX has the characteristic 5.5- $\mu$  cyclopropene band, and the ultraviolet spectrum has  $\lambda_{\max}$  326 m $\mu$  ( $\epsilon$  30,000). The n.m.r. spectrum has a sharp peak at  $\delta$  2.42, of area 1, and a multiplet centered at  $\delta$  7.3, of area 10.

**Hydride Abstraction from IX.** The dimer IX (1.264 g.) in 20 ml. of warm benzene was treated with 1.2 g. of triphenylmethyl perchlorate in 30 ml. of acetonitrile. After a few minutes, 3 ml. of ethyl acetate was added, then dry ether to induce cloudiness. When crystallization started, more ether was added and 1.59 g. (100%) of 1,2-diphenyl-3( $\Delta^1$ -1,2-diphenylcyclopropenyl)cyclopropenyl perchlorate (XI) was isolated, m.p. 112° (explodes).<sup>20</sup>

*Anal.* Calcd. for C<sub>30</sub>H<sub>21</sub>ClO<sub>4</sub>: C, 74.91; H, 4.41. Found: C, 74.41; H, 4.55.

The infrared spectrum showed a strong cyclopropenyl cation band at 7.1 and perchlorate absorption at 9.1  $\mu$ . The ultraviolet spectrum (9 ml. of 95% ethanol, 1 ml. of 12 *N* HCl) had  $\lambda_{\max}$  303 m $\mu$  ( $\epsilon$  20,200), 295

(20) Treatment of XI with triethylamine apparently results in removal of the aliphatic proton, as judged from n.m.r. and ultraviolet studies, but attempts to isolate a monomeric product from this reaction have so far proved abortive.

(14) W. Diltthey and G. Hurtig, *Chem. Ber.*, **67**, 2005 (1934).

(15) V. S. Abramov, *Bull. Acad. Sci. URSS Classe sci. chim.*, **330** (1945).

(16) Prepared analogously to the 3-propyl compound (R. Breslow, H. Höver, and H. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962)) and fully characterized.

(17) The ultraviolet spectrum indicates a styrene, not stilbene, system and the n.m.r. spectrum shows that both ethyls are equivalent and, from the chemical shift of methyl vs. methylene, on unsaturated carbon.

(18) W. Hübel and C. Hoogzand, *Chem. Ber.*, **93**, 103 (1950).

(19) F. R. Japper and A. N. Meldrum, *J. Chem. Soc.*, **79**, 1041 (1901).

(25,000), 288 (21,800), and 278 (20,800). The n.m.r. spectrum (dry  $\text{CH}_3\text{CN}$ ) had a peak at  $\delta$  4.28 (area 1) and a multiplet near 7.9 (area 20); in  $\text{CF}_3\text{CO}_2\text{H}$ , with 5% benzene, the phenyl multiplets were centered 0.5 p.p.m. below benzene, and the single proton 3.16 p.p.m. above benzene.

The perchlorate XI (1.59 g.) was stirred with 0.55 g. of  $\text{LiAlD}_4$  in 30 ml. of anhydrous ether overnight. Aqueous work-up and chromatography yielded IX-d, identical in melting point and infrared spectrum with IX. In the n.m.r., the singlet at  $\delta$  2.38 was only  $1/20$  the area of the phenyl protons. Treatment of this compound with triphenylmethyl perchlorate, as above, afforded partially deuterated XI whose n.m.r. spectrum (in  $\text{CH}_3\text{CN}$ ) had the peak at  $\delta$  4.28 with an area roughly  $1/40$  that of the phenyl protons.

**Reaction of IX with Potassium Amide.** A solution of 0.15 g. of IX in 60 ml. of dimethoxyethane was added to potassium amide (from 0.8 g. of potassium) in 60 ml. of liquid ammonia. After standing overnight, aqueous work-up and chromatography afforded 1,2,3,4-tetraphenylbenzene (XII, 0.030 g., 20%) as the only crystalline product. No other isomer could be detected.

**Thermal Rearrangement of IX.** Four separate samples of the dimer IX (150–440 mg.) in 60 ml. of purified ethoxyethanol (b.p. 133–135°) were heated under reflux ( $\text{N}_2$ ) for 7 days. In one run the reaction was followed by periodic sampling and quantitative ultraviolet determination; good isosbestic points at 275 and 355  $\text{m}\mu$  were observed, the final spectrum being that of a mixture of tetraphenylbenzenes. The solvent was removed *in vacuo* and the total product was taken

up in  $\text{CCl}_4$  and analyzed by vapor phase chromatography (5-ft. 5% SE-30 on 60–80 mesh Firebrick with  $\text{N}_2$  carrier, column at 300°). 1,2,4,5-Tetraphenylbenzene (IV) and 1,2,3,4-tetraphenylbenzene (XII) were identified by identical retention times (14.5 min. for IV and 9 min. for XII) with those of authentic samples. Quantitative analysis by comparing peak areas with those from authentic mixtures gave ratios of IV/XII in the four separate runs of (average of at least three measurements on each):  $11 \pm 1$ ,  $13 \pm 1.5$ ,  $4.2 \pm 0.4$ , and  $8.4 \pm 0.8$ . In a preliminary run, IV and XII were separated and identified by melting point and spectral criteria. In four separate runs, rearrangement of IX by injection directly into the 300° v.p.c. column gave a ratio IV/XII of  $3.5 \pm 0.5$ .

**Photochemical Rearrangement of IX.** A stirred solution of 3.78 g. of IX in 500 ml. of anhydrous ether was irradiated for 41 hr. under  $\text{N}_2$  (Hanovia 450-w. medium-pressure lamp in an immersion well with a Pyrex filter). The ether was evaporated and the crude product was analyzed by vapor phase chromatography, as above. The ratio of the two tetraphenylbenzenes, XII/IV, was  $2.2 \pm 0.3$ . Alumina chromatography of the crude product afforded only 0.300 g. of the mixture of IV and XII, whose infrared spectrum was a composite of those of the authentic compounds. Analysis of this purified fraction by vapor phase chromatography gave a ratio XII/IV of  $2.8 \pm 0.3$ . The mixture was also identified by thin layer chromatography (silica gel,  $\text{CCl}_4$ ,  $\text{H}_2\text{SO}_4$  spray; IV  $R_f$  0.51, blue spot; XII  $R_f$  0.46, pink-purple spot). A control irradiation of IV under the same conditions gave quantitative recovery of the starting material.

## Small-Ring Compounds. XLIV. Interconversion of Cyclopropylcarbinyl and Allylcarbinyl Grignard Reagents<sup>1</sup>

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Contribution No. 3255 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Received July 6, 1965

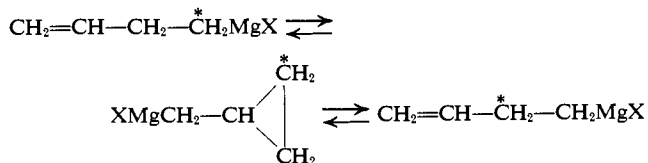
The previously postulated rapid conversion of the cyclopropylcarbinyl Grignard reagent to the allylcarbinyl Grignard reagent has been confirmed by partial trapping of cyclopropylcarbinylmagnesium chloride prepared in refluxing diethyl ether in the presence of benzoic acid as methylcyclopropane and formation of cyclopropylcarbinylmagnesium bromide at  $-24^\circ$  from the corresponding bromide and magnesium in dimethyl ether. The rearrangement of cyclopropylcarbinylmagnesium bromide to allylcarbinylmagnesium bromide appears to be a first-order reaction and has a half-life of 121 min. at  $-24^\circ$ .

### Introduction

In recent years, there has been considerable interest in interconversions of cyclopropylcarbinyl, allylcarbinyl, and cyclobutyl compounds in reactions involving

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a potential anionic center. It has been shown that Grignard reagents prepared in the ordinary way from both cyclopropylcarbinyl and allylcarbinyl halides possess the allylcarbinyl structure to the extent of more than 99%.<sup>2,3</sup> The allylcarbinylmagnesium halides, however, were found to undergo an extraordinary rearrangement in which the  $\alpha$ - and  $\beta$ -carbons exchange positions. This reaction was presumed to occur



(2) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(3) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).