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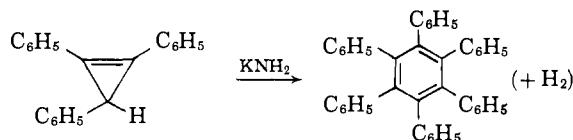
The Dimerization of Triphenylcyclopropene¹

BY RONALD BRESLOW AND PAUL DOWD

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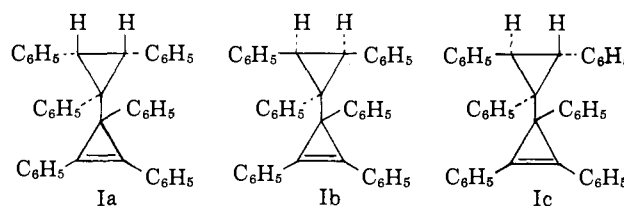
Triphenylcyclopropene is converted to hexaphenylbenzene on treatment with potassium amide in liquid ammonia, but with sodium amide or lithium amide a simple dimer can be intercepted, triphenylcyclopropyl-triphenylcyclopropene (Ia). This dimer is also formed when triphenylcyclopropene is heated in refluxing xylene. Treatment of the dimer with potassium amide converts it to hexaphenylbenzene, while pyrolysis of the dimer at 280° affords triphenylazulene and *trans*-stilbene. These unusual reactions have been studied by a variety of techniques, and mechanisms are proposed for all of them. It is shown that triphenylcyclopropene is not converted to the triphenylcyclopropenyl anion by strong base, and from kinetic evidence a lower limit is placed on the pK_a of triphenylcyclopropene.

A variety of studies have demonstrated the unusual stability of the cyclopropenyl cation system,² and other work has shown that the expected magic number effect is present in a diminished stability of the cyclopropenyl radical.³ Although kinetic evidence is also available that the cyclopropenyl anion is strongly destabilized,⁴ we felt it desirable to obtain additional data on this four- π -electron cyclic conjugated system. Accordingly we set out to examine base-catalyzed proton-exchange reactions of triphenylcyclopropene in the hope of comparing its acidity with that of triphenylmethane; the triphenylcyclopropenyl cation⁵ and radical³ have been compared with the analogous triphenylmethyl species. However, when triphenylcyclopropene was treated with potassium amide in liquid ammonia it was converted almost quantitatively to hexaphenylbenzene. In this paper we wish to describe experiments designed to assist in understanding this remarkable change.



A. Dimerizations.—The reaction using potassium amide was too rapid for convenient study, but it was found that with sodium amide or lithium amide the conversion occurred more slowly and an intermediate compound, m.p. 179.5–180.5°, could be isolated. This was converted to hexaphenylbenzene on more prolonged treatment, or rapidly with potassium amide; it had the composition of a simple dimer of triphenylcyclopropene, in which the two hydrogen atoms lost in the over-all change were still present. Preliminary considerations of possible mechanisms suggested that this dimer might be *trans*-1,2-dihydrohexaphenylbenzene,⁶ m.p. 179–180°, but comparison with the authentic sample showed that the two were not the same; the fact that the aliphatic protons of our compound were found at 6.78 τ in the n.m.r. compared with the 6.0 τ for authentic dihydrohexaphenylbenzene suggested that our material was not the unknown *cis* isomer, or either of the 1,4-dihydrohexaphenylbenzenes. Another alternative, benzylpentaphenylcyclopentadiene, was

easily disposed of by synthesis. It then seemed that the only likely possibility was triphenylcyclopropyl-triphenylcyclopropene (I). This conclusion was supported by the ultraviolet spectrum of the dimer, which was typical of a diphenylcyclopropene chromophore. Thus it had $\lambda\lambda_{\max}$ 330 $m\mu$ (ϵ 20,000), 318 $m\mu$ (ϵ 23,800), and 225 $m\mu$ (ϵ 64,000); for comparison, the ultraviolet spectrum of triphenylcyclopropene has $\lambda\lambda_{\max}$ 334 $m\mu$ (ϵ 22,800), 318 $m\mu$ (ϵ 28,000), and 218 $m\mu$ (ϵ 27,800). The stronger absorption for our dimer at low wave length is presumably due to the extra phenyl groups.



Although it seemed that our compound was probably a *cis* isomer (Ia or Ib) because the aliphatic protons are an unsplit singlet in the n.m.r., the *trans* compound Ic could be prepared easily and it served as a comparison substance for our material. When *trans*-chloro-1,2,3-triphenylcyclopropane⁷ was converted to its Grignard reagent, and the solution was mixed with triphenylcyclopropenyl bromide, *trans*-1,2,3-triphenylcyclopropyl-1,2,3-triphenylcyclopropene (Ic) was obtained in fair yield accompanied by a considerable amount of *trans*-triphenylcyclopropane.⁸ This dimer, m.p. 155–157°, was almost identical with our unknown material in its ultraviolet and infrared spectra, and in the n.m.r. it showed the aliphatic protons as an AB quartet centered at 6.84 τ . The large coupling constant ($J_{AB} = 7.5$ c.p.s., $\delta_{A-B} = 0.16$ p.p.m.) reveals that the protons are vicinal, so no unusual rearrangement has occurred in this reaction. The *trans* dimer Ic was converted to hexaphenylbenzene by potassium amide under the same conditions as were used for our unknown, and like the latter it could be pyrolyzed to 1,2,3-triphenylazulene⁹ (*vide infra*). Accordingly, it seemed clear that our triphenylcyclopropene dimer was one of the *cis* isomers, and this was confirmed by synthesis. Catalytic hydrogenation of triphenylcyclopropene afforded *cis*-triphenylcyclopropane, and when this was metalated with *sec*-butyllithium, and triphenylcyclopropenyl cation was added to the solution, a small yield was obtained of a dimer identical in all respects with our unknown material. Assuming steric preference for addition

(1) Taken in part from the doctoral thesis of Paul Dowd. Support by the Eastman Kodak Co. (Fellowship to P. D.), the Sloan Foundation, and the Petroleum Research Fund is gratefully acknowledged. The formation of hexaphenylbenzene on treatment of triphenylcyclopropene with potassium amide was first noted by Mr. Merle Battiste, Ph.D. thesis, Columbia University.

(2) R. Breslow, H. Hover, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962), and references therein.

(3) R. Breslow, W. Bahary, and W. Reinmuth, *ibid.*, **83**, 1763 (1961).

(4) R. Breslow and M. Battiste, *Chem. Ind. (London)*, 1143 (1958).

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

(6) W. Dilthey, U. S. Patent 2,097,854 (1937); *Chem. Abstr.*, **32**, 3674 (1938).

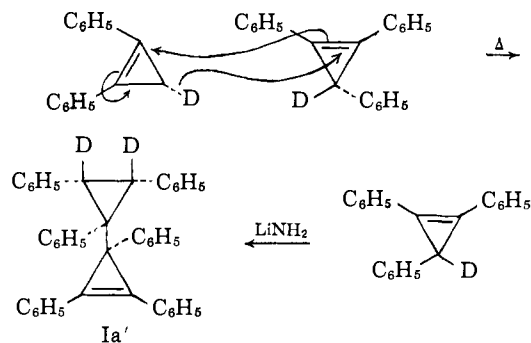
(7) P. Gal, Ph.D. Thesis, Columbia University. This compound was prepared from the addition of phenylchlorocarbene to *trans*-stilbene, and it has been fully characterized.

(8) F. S. Bridson-Jones, G. D. Buckley, L. H. Gross, and A. P. Driver, *J. Chem. Soc.*, 2999 (1951).

(9) N. Kharasch and N. J. Assony, *J. Am. Chem. Soc.*, **80**, 5978 (1958).

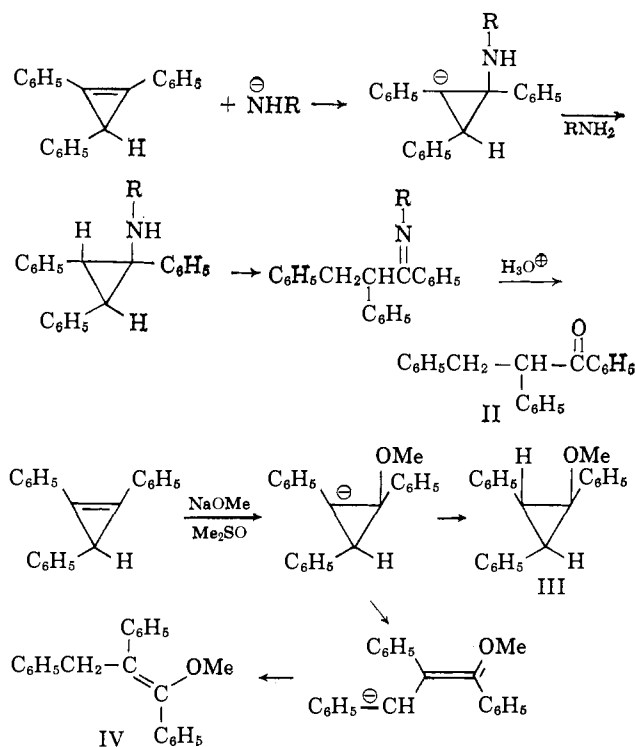
to the unhindered side in this reaction and in the two dimerization reactions (*vide infra*) we assign this compound the structure Ia.

Interestingly, it was found that this same dimer is formed when triphenylcyclopropene is simply heated in solution in organic solvents. In a typical reaction, triphenylcyclopropene was 20% converted to this dimer after 39 hr. of refluxing in toluene solution; the remainder of the material was unchanged cyclopropene. When Δ^2 -1,2,3-triphenylcyclopropane-1-*d* was used both deuterium atoms were found in the dimer. Although a radical chain could be written for this reaction, involving addition of triphenylcyclopropenyl radical to triphenylcyclopropene, steric arguments indicate that the product should be the *trans* dimer Ic from such a process.¹⁰ A radical chain was also excluded by the finding that the rate of conversion of triphenylcyclopropene to dimer was the same in the presence of 2 mole % of di-*t*-butyl peroxide.¹¹ Accordingly, it seems clear that our thermal dimerization is simply a four-center process of the type which has been observed previously with dienophiles and monoolefins.¹² On the basis of this mechanism the stereochemistry of the dimer should be Ia, assuming preferential approach of both cyclopropenes from the less hindered side.

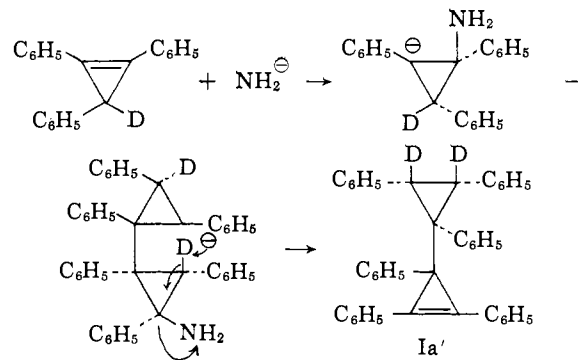


The mechanism of the base-catalyzed dimerization is more unusual. Treatment of deuteriotriphenylcyclopropene with lithium amide in ammonia affords the dimer Ia' with deuterium atoms in both aliphatic positions. It is thus apparent that triphenylcyclopropenyl anion is not an intermediate in this reaction. The over-all process could have been written as addition of this anion to a cyclopropene double bond followed by protonation, but it is clear that such a mechanism should have produced the *trans* dimer in any case if all steps were to go by the least hindered path. Accordingly, the base must be performing a function other than to remove this proton. The only likely alternative is addition to the cyclopropene double bond, and with most bases such addition is readily demonstrated. Thus, treatment of triphenylcyclopropene with sodium *p*-toluidide in *p*-toluidine or with lithium propylamide in propylamine affords, on hydrolysis, benzyldeoxybenzoin (II) by a process which clearly seems to require addition of the base.

Reaction of triphenylcyclopropene with sodium methoxide in dimethyl sulfoxide also illustrates this mode of attack, the products III and IV being derived from an addition reaction. In this last case a small amount of hexaphenylbenzene is also formed. It seems that lith-



ium amide should attack in a fashion analogous to lithium propylamide, adding to the double bond. Then the dimerization reaction mechanism can be written as shown.



Here it is suggested that the intermediate cyclopropenyl anion is not protonated in the liquid ammonia system, but that it adds to another cyclopropene species. The resulting anion must abstract a proton internally with elimination of amide ion in order to account for the stereochemistry and the deuterium retention. It seems likely that the difference between the ammonia system and the others reflects a solubility problem as much as anything; while the other reactions are completely homogeneous, the reaction in liquid ammonia appears to involve two phases. If the triphenylcyclopropene is not in solution in the ammonia, but is present as a separate phase with some dimethoxyethane, protonation of the intermediate anion is less likely while addition to a second cyclopropene is more likely. This mechanism is in a sense an anionic polymerization in which an internal proton-transfer terminates the chain at the dimer.

Since the amide ion does not appear in the product, it might be wondered whether some other species in the system is the actual catalyst. However, when the sodium amide solution is quenched with a small excess of methanol before addition of the triphenylcyclopropene the starting material is recovered unchanged. Furthermore, lithium amide prepared by addition of

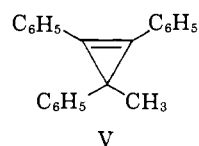
(10) Furthermore, the deuterium results would require a reactivity of the triphenylcyclopropene hydrogen atom in radical abstraction much greater than has been found by P. Gal, Ph.D. thesis, Columbia University.

(11) C. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 337 (1950), report 10% at 110° in *t*-butylbenzene is 76 hr.

(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 188, and references therein. See also J. C. Sauer and G. N. Sausen, *J. Org. Chem.*, **27**, 2730 (1962), for further examples of this reaction.

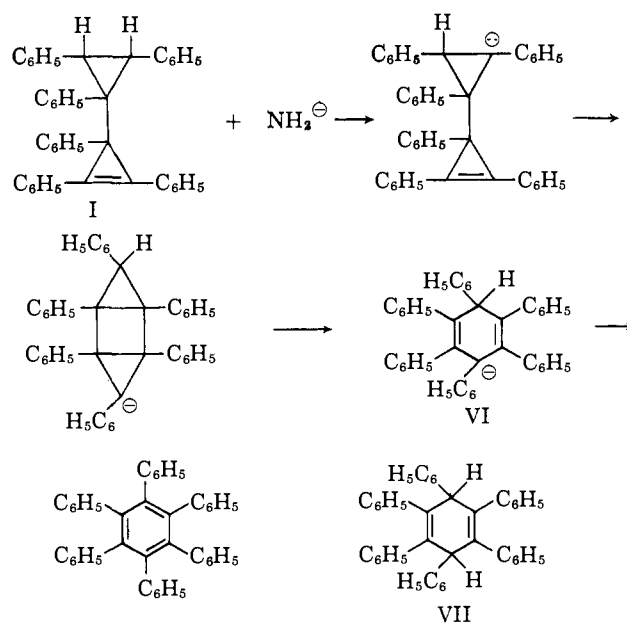
butyllithium to ammonia also catalyzes conversion of triphenylcyclopropene to the dimer Ia; under the conditions used some starting material is recovered as well. Accordingly, it seems that amide ion is the catalytic species.

Some features of this scheme are rather unsatisfying, and in particular the internal abstraction of carbon-bound rather than nitrogen-bound proton is surprising, but the mechanism seems to be required by the observations. It would of course be expected that amide ion, or the other anions, should add from the less hindered side of the triphenylcyclopropene. An indication of the sensitivity of such additions to steric hindrance is found in the observation that methyltriphenylcyclopropene (V) is recovered unchanged after prolonged treatment with either potassium amide or sodium *p*-toluidide.

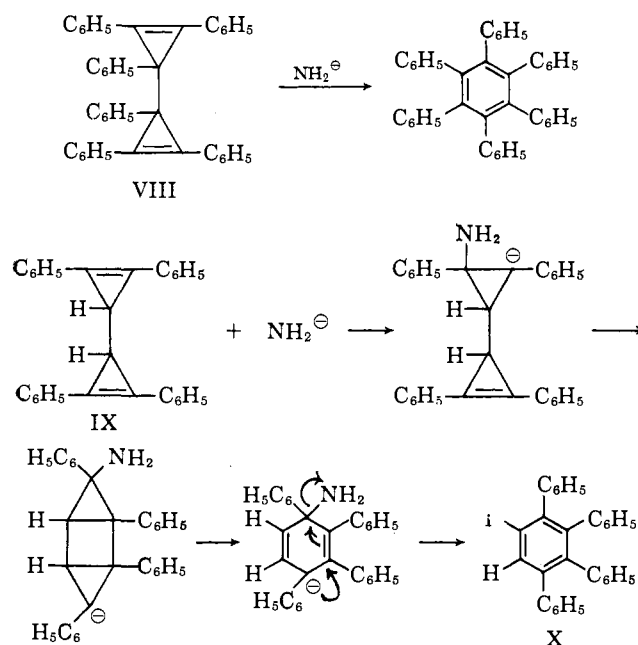


B. Rearrangement of the Dimer.—When either the *cis* dimer Ia or the synthetic *trans* isomer Ic is treated with potassium amide it is quantitatively converted to hexaphenylbenzene. This change can be rationalized in terms of the mechanism illustrated below, in which the strong base removes a proton and the resulting anion attacks the cyclopropene double bond to afford, after rearrangement, the anion VI of dihydrohexaphenylbenzene. Under the usual conditions this anion is converted to hexaphenylbenzene by hydride loss, but in one case it may have been intercepted. Treatment of triphenylcyclopropene with a suspension of sodium amide in dimethoxyethane afforded a mixture of hexaphenylbenzene, diphenylethane, and a compound with m.p. 224–226° which is identified as one of the 1,4-dihydrohexaphenylbenzenes (VII). Although the isolated yields were low, thin plate chromatography showed that these substances were the only major components of the mixture. The identification of VII rests on the analytical data, on the n.m.r. spectrum which shows two aliphatic protons, shifted down to 5.33 τ by the adjacent unsaturation, in addition to the thirty phenyl protons, and on the finding that this material affords hexaphenylbenzene in high yield on treatment with bromine. If this structure assignment is correct, the compound is formed by protonation of anion VI in the expected position.¹³ An alternative mechanism for rearrangement of I can be written in which amide ion adds to the cyclopropene double bond and internal displacement at saturated carbon occurs, but such a mechanism does not account for the formation of 1,4-dihydrohexaphenylbenzene. The diphenylethane formed in this sodium amide reaction probably results from Haller–Bauer cleavage¹⁴ of a benzyldeoxybenzoin equivalent, suggesting that here some ring-opening does occur.

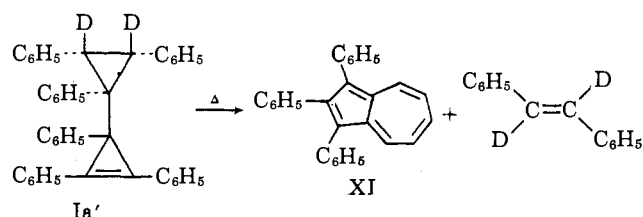
A very similar mechanism can be written for the rearrangement of bis-cyclopropenyls to benzenes by amide ion. Thus bis-triphenylcyclopropenyl (VIII) is rearranged to hexaphenylbenzene by potassium amide,¹⁵ and the corresponding dimer of diphenylcyclopropenyl, IX, affords 1,2,3,4-tetraphenylbenzene (X) under these conditions.¹⁵ These reactions are simply rationalized in terms of the mechanism illustrated; it is striking that such processes furnish analogs not only for the re-



arrangement of dimer I to hexaphenylbenzene but also for the mechanism which was postulated earlier to explain the amide-catalyzed formation of the dimer.



When either the *cis* dimer Ia or its *trans* isomer Ic is heated in the melt at 280° for a short time, a fragmentation reaction occurs. Triphenylazulene (XI) and *trans*-stilbene are formed in equal amounts; in the pyrolysis of the dideuterio dimer Ia' the two vinyl hydrogens of the stilbene are deuterium atoms, suggesting that the stilbene is formed by fragmentation of the cyclopropane ring.



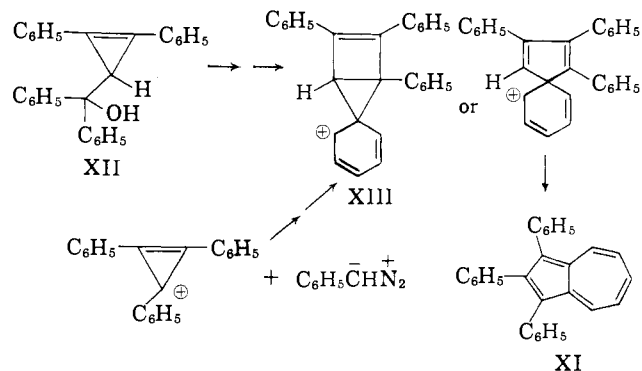
Although a detailed mechanism cannot be formulated for this change in the absence of further evidence, the reaction bears a strong resemblance to a number of

(13) A. J. Birch, *J. Chem. Soc.*, 1551 (1950).

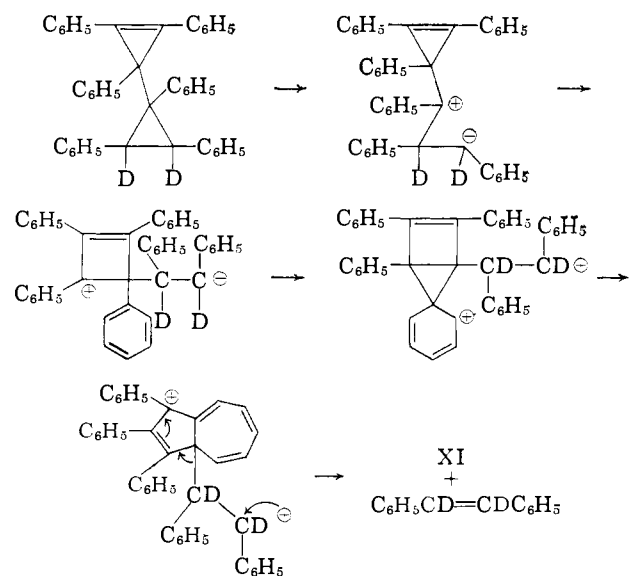
(14) K. E. Hamlin and A. W. Weston, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 1.

(15) P. Gal, ref. 7.

other processes in which triphenylazulene is formed. Thus the carbinol XII yields triphenylazulene with acid catalysts,¹⁶ and triphenylcyclopropenyl cation reacts with phenyldiazomethane to form this azulene as well¹⁷; both changes can be rationalized in terms of the common intermediate XIII, and a detailed scheme for the rearrangement of XII has been published.¹⁶ Similar paths can be formulated for the formation of this azulene from tetraphenylcyclobutadiene-like species, as in the work of Freedman¹⁸ or the photodimerization of diphenylacetylene¹⁹; a related mechanism can be proposed in the chemically-catalyzed dimerization of diphenylacetylene to this azulene.⁶ In these latter cases the required intermediates are closely related to XIII.



The thermal rearrangement of I to the azulene can be rationalized in terms of a similar scheme, in which the required cyclobutenyl intermediate is formed by fission of the cyclopropane ring followed by ring-expansion of the cyclopropenylcarbinyl species which results.²⁰ This process has been outlined using the simplest hypotheses, that a zwitterion undergoes the rearrangement and that the stilbene is formed in the last step. This is thus only a formal mechanistic scheme, for which a number of variants can be written which are indistinguishable on the basis of the experimental evidence so far available; some are indeed more attractive than this one.



C. The Acidity of Triphenylcyclopropene.—Although it is clear that the triphenylcyclopropenyl anion is not an intermediate in the base-catalyzed dimeriza-

tion which was discussed, we have been able to obtain some indication of its stability by a kinetic study. When tritiotriphenylmethane was refluxed with potassium *t*-butoxide in *t*-butyl alcohol for 8 hr. it lost 80% of its activity, while under the same conditions tritio-triphenylcyclopropene was unchanged after 242 hr. (*cf.* Experimental). Even if it were assumed that a loss of less than 10% of tritium would not have been detected, which seems an over-pessimistic estimate, this indicates that the pseudo-first-order rate constant for proton abstraction from triphenylcyclopropene is at most one-five-hundredths that for abstraction from triphenylmethane. Since the triphenylcyclopropene proton is less hindered than that in triphenylmethane, as judged from models, the equilibrium constants should differ by even more than the rate constants; in any case it seems that the equilibrium acidity of triphenylcyclopropene is less than that of triphenylmethane, for which a pK_a of 33 has been assigned.²¹

It has been reported²² that a pK_a of 28 is predicted for triphenylcyclopropene from simple molecular orbital theory, but the treatment ignores the extra strain energy introduced on ionization. This apparently plays a major role in the related triphenylcyclopropenyl cation.⁵ This factor can be treated empirically if it is noted that simple m.o. theory predicts that a triphenylcyclopropene derivative should be 1.008 β less stabilized as the anion than as the cation, while cation and anion have the same resonance energy in the triphenylmethyl series. On this basis the observation that triphenylcyclopropenyl cation has a pK_a approximately 10 units higher than that of triphenylmethyl cation⁵ can be translated into a prediction of the relative pK 's of triphenylcyclopropene and triphenylmethane in anion formation. If β is taken as -32 kcal./mole⁵ the pK_a of triphenylcyclopropene is predicted to be 13 units higher than that of triphenylmethane, and even if the unsuitable value of -18 kcal./mole is selected for β the pK for our compound is predicted to be higher. Accordingly, our observations are consistent with the predictions of simple theory.

Experimental²³

1,2,3-Triphenylcyclopropene.—Triphenylcyclopropene was prepared by adding solid *sym*-triphenylcyclopropenyl bromide to an excess of lithium aluminum hydride in ether. After being stirred at room temperature for 24 hr., the reaction was quenched with water and extracted with ether. Evaporation of the ether gave a yellow solid which was purified by chromatography on Merck acid-washed alumina (elution with *n*-hexane) followed by recrystallization from ethanol. The final product, m.p. 112–113°, was obtained in 60–70% yield. This compound has three distinct maxima in the ultraviolet at 334 $m\mu$ (ϵ 22,800), 318 $m\mu$, (ϵ 28,800), and 218 $m\mu$ (ϵ 27,800). The n.m.r. spectrum shows a 15-proton aromatic multiplet at 2.9 τ and a 1-proton singlet at 6.8 τ . There is a fairly strong band in the infrared at 5.5 μ , which is characteristic of a cyclopropene double bond carrying two phenyl groups.²⁴

Anal. Calcd. for C₂₁H₁₆: C, 93.99; H, 6.01. Found: C, 93.97; H, 6.12.

Reaction of 1,2,3-Triphenylcyclopropene with Lithium Amide.

—A solution of 0.60 g. (0.0021 mole) of triphenylcyclopropene in 10 ml. of dimethoxyethane was added to a white suspension of 3.3 g. (0.144 mole) of lithium amide in 40 ml. of liquid ammonia. The reaction mixture was stirred for 3 hr. and then quenched with water. After extraction with ether, the ether layer was dried and evaporated, giving 0.643 g. of material which was chromatographed on 45 g. of Merck acid-washed alumina. Elution with 20% benzene in hexane gave 0.457 g. (76%) of Δ^1 -3 β -(1' β ,2' β ,3' β -triphenylcyclopropyl)-1,2,3-triphenylcyclopropene, the *cis* dimer Ia. Recrystallization from benzene-hexane gave 0.342 g. of white crystalline material, m.p. 179.5–180.5°. An n.m.r. spectrum (CDCl₃) of this compound shows a 30-

(16) R. Breslow and M. Battiste, *J. Am. Chem. Soc.*, **82**, 3626 (1960).

(17) R. Breslow and M. Mitchell, unpublished work.

(18) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).

(19) G. Büchi, C. W. Perry, and E. W. Robb, *ibid.*, **27**, 4106 (1962).

(20) *Cf.* R. Breslow, J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962).

(21) W. K. McEwen, *ibid.*, **58**, 1122 (1936).

(22) A. Streitwieser, Jr., *Tetrahedron Letters*, No. 6, 23 (1960).

(23) Melting points are uncorrected.

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

proton aromatic multiplet at 2.7 τ and a 2-proton aliphatic singlet at 6.78 τ . The ultraviolet spectrum (95% ethanol) shows maxima at 330 $m\mu$ (ϵ 20,000), 318 $m\mu$ (ϵ 23,800), and 225 $m\mu$, (ϵ 64,000). The infrared spectrum (KBr) is unexceptional, but it does show a band (stronger than its neighboring aromatic overtones) at 5.5 μ .

Anal. Calcd. for $C_{24}H_{32}$: C, 93.99; H, 6.01; mol. wt., 536. Found: C, 94.08; H, 6.18; mol. wt., 561 (Rast, camphor).

Reaction of the *cis* Dimer Ia with Potassium Amide in Liquid Ammonia.—A solution of 0.355 g. (0.00062 mole) of *cis* dimer Ia in 11 ml. of dimethoxyethane was added all at once to 2.54 g. (0.046 mole) of potassium amide in 20 ml. of liquid ammonia. The reaction immediately became a dark blue. After stirring for 15 min. the reaction was quenched with water and extracted with ether. Hexaphenylbenzene²⁵ (0.306 g., 86%) was collected by filtration.

1,2-Dihydrohexaphenylbenzene.²⁷—*trans*-1,2-Dihydrohexaphenylbenzene was prepared by heating a melt of *trans*-stilbene and tetraphenylcyclopentadienone to 300° in an open tube. The product, m.p. 179–180° (reported²⁷ m.p. 179–180°), was obtained as a white solid which shows a band in the ultraviolet (95% ethanol) at 315 $m\mu$ (ϵ 10,500). The n.m.r. spectrum (CDCl₃) shows a single unsplit peak at 6.0 τ in addition to aromatic protons at 2.7 τ . The melting point of this compound was depressed by 27° on admixture with the *cis* dimer Ia, m.m.p. 152–164°.

Benzyl Pentaphenylcyclopentadiene.—Pentaphenylcyclopentadienyllithium was prepared from 1.02 g. (0.0023 mole) of pentaphenylcyclopentadiene, m.p. 252–255°, and 5 ml. of *n*-butyllithium (Lithium Corp. of America, 18% by wt., packed in *n*-heptane), using 8 ml. of dimethoxyethane as solvent. The reaction took place with evolution of 90 ml. (0.004 mole) of gas and the production of a dark violet mixture. To this was added 11.03 g. (0.082 mole) of benzyl chloride. The color disappeared and a water-soluble, white precipitate came out. The reaction mixture was extracted with ether and the ether layer dried and evaporated, giving an oil. When the oil was triturated with *n*-pentane, 5-benzyl-1,2,3,4,5-pentaphenylcyclopentadiene crystallized as a white solid. Two recrystallizations from *n*-hexane gave 0.222 g. (18%) of shiny white needles, m.p. 183.5–185°.

This compound has two broad maxima in the ultraviolet (cyclohexane) at 337 $m\mu$ (ϵ 9250) and 245 $m\mu$ (ϵ 30,000). The n.m.r. spectrum (CS₂) shows a 2-proton singlet at 6.45 τ and a 30-proton, aromatic multiplet at 3.2 τ .

Anal. Calcd. for $C_{45}H_{52}$: C, 93.99; H, 6.01; mol. wt., 536. Found: C, 93.92; H, 5.83; mol. wt., 540 (osm., 2-butanone).

Pyrolysis of the *cis* Dimer Ia to 1,2,3-Triphenylazulene (XI) and *trans*-Stilbene.—When 0.277 g. (0.00052 mole) of the *cis* dimer Ia was heated for 10 min. at 280° in an open tube, the melt became an intense dark blue. When cool, the resulting blue glass was dissolved in cyclohexane and chromatographed on 20 g. of Merck acid-washed alumina. Elution with *n*-hexane gave 0.019 g. (18%) of *trans*-stilbene, m.p. and m.m.p. 120–122°.

Further elution with *n*-hexane gave, in the fifth and sixth 40-ml. fractions, 0.032 g. (18%) of the blue triphenylazulene, m.p. 212–214° (reported²⁸ m.p. 213–215°), which was further identified by direct comparison with an authentic sample on a thin layer chromatoplate (silica gel G, eluted with 50% benzene in hexane, *R_f* 0.7). The ultraviolet spectrum of this compound is in good agreement with that reported by Kharasch and Assony²⁸ showing maxima at 315 $m\mu$, (ϵ 61,000), 250 $m\mu$ (ϵ 36,000), and 225 $m\mu$ (ϵ 36,000).

Pyrolysis of Dideuterio-*cis* Dimer Ia to Dideuterio-*trans*-stilbene.—When 0.140 g. (0.00026 mole) of *cis*-dideuterio dimer was heated at 275° for 40 min. in a sublimation tube, 0.061 g. of green, oily solid was collected on the cold finger. This material was dissolved in a few ml. of hot cyclohexane and chromatographed on 3 g. of Merck acid-washed alumina. The first 40-ml. fraction yielded 0.017 g. (33%) of *trans*-stilbene which after two recrystallizations from 95% ethanol had a m.p. of 120–124°. An n.m.r. spectrum (CS₂) of this material showed the absence of any vinyl hydrogens which in *trans*-stilbene are ordinarily found at 3.2 τ as a prominent, sharp, single peak. Accordingly, this is at least 95% *d*₂.

Synthesis of Δ^1 -3 β -(1' β ,2' β ,3' β -Triphenylcyclopropyl)-1,2,3-triphenylcyclopropane, the *trans* Dimer Ic.—A solution of 1.195 g. (0.039 mole) of 1-chloro-1,2,3-triphenylcyclopropane²⁹ in 10 ml.

of tetrahydrofuran was run into a 500-ml. Grignard flask containing 1.462 g. (0.061 g.-atom) of granulated magnesium. To initiate the reaction, 0.5 ml. of 1,2-dibromoethane was added, followed by more chlorocyclopropane solution and 1.277 g. (0.053 g.-atom) more magnesium turnings. When the vigorous reaction had subsided, the solution was filtered through a sintered glass filter into a lower flask containing 1.108 g. (0.0032 mole) of *sym*-triphenylcyclopropenyl bromide and then stirred at room temperature for 12 hr. At the end of this time the resulting heavy precipitate was filtered off and washed with ether. The filtrate was extracted with water, and the ether layer was dried and evaporated, giving 1.637 g. of red oil which was chromatographed on 100 g. of Merck acid-washed alumina. Elution with 10% benzene in hexane yielded 0.608 g. (56%) of the known *trans*-1,2,3-triphenylcyclopropane, m.p. 52–55° (reported³⁰ m.p. 63°). Four recrystallizations from *n*-pentane and two from ethanol gave white needles, m.p. 66–68°. This compound shows only weak absorption in the ultraviolet (95% ethanol) above 225 $m\mu$. The n.m.r. spectrum (CCl₄) shows a 3-proton singlet at 7.37 τ and a 15-proton aromatic multiplet centered at 3.1 τ . The infrared spectrum of this compound is similar to that reported.³⁰

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71; mol. wt., 270. Found: C, 93.00, 92.98; H, 6.93, 6.93; mol. wt., 302 (Rast, camphor).

Further elution with 20% benzene in *n*-hexane gave 0.300 g. (15%) of Δ^1 -3 β -(1' β ,2' α ,3' β -triphenylcyclopropyl)-1,2,3-triphenylcyclopropane, m.p. 152–155°. Recrystallization from hexane–benzene gave white crystals, m.p. 155–157°. The compound had maxima in the ultraviolet (95% ethanol) at 316 $m\mu$ (ϵ 17,800) and 225 $m\mu$ (ϵ 44,600). The n.m.r. spectrum (CS₂) shows a 30-proton, aromatic multiplet at 3.0 τ and a 2-proton AB quartet at 6.84 τ ($J_{AB} = 7.5$ c.p.s., $\delta_{A-B} = 0.16$ p.p.m.). Treatment of 0.050 g. (0.00093 mole) of *trans* dimer Ic with potassium amide in liquid ammonia gives 0.035 g. (70%) of hexaphenylbenzene.²⁵

Anal. Calcd. for $C_{42}H_{52}$: C, 93.99; H, 6.01; mol. wt., 536. Found: C, 94.19, 94.31; H, 6.38, 6.24; mol. wt., 347 (osm., benzene).

A small amount of the *trans* dimer Ic was heated for about 10 min. in a melting point capillary. The material melted from 155–158°; at 240° it started to turn green, and at 270° it had become a dark blue. When the sample had cooled, it was crushed in a small test tube and the blue triphenylazulene XI was dissolved in a few drops of benzene. This material was applied to a chromatoplate and showed the same retention time (direct comparison) as authentic triphenylazulene (silica gel G, elution with 50% benzene in hexane, *R_f* 0.7).

***cis*-1,2,3-Triphenylcyclopropane.**—A solution of 5.481 g. (0.020 mole) of 1,2,3-triphenylcyclopropane in 75 ml. of ethyl acetate was hydrogenated using 0.550 g. of Lindlar catalyst (calcd. hydrogen uptake 562 ml., obsd. 524 ml.). When the reaction was complete, the catalyst was filtered away and the solvent evaporated to give 5.358 g. (97%) of *cis*-1,2,3-triphenylcyclopropane. The compound was recrystallized from 95% ethanol, giving shiny, white platelets, m.p. 88–89°. The n.m.r. spectrum (CCl₄) showed a 3-proton singlet at 7.25 τ and a 15-proton aromatic singlet at 3.25 τ . The ultraviolet spectrum (95% ethanol) shows only weak absorption above 225 $m\mu$.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.43; H, 6.80.

Synthesis of Δ^1 -3 β -(1' β ,2' β ,3' β -Triphenylcyclopropyl)-1,2,3-triphenylcyclopropane (Ia).—Isobutyllithium (3 ml., 0.011 mole), 22.7% by wt. in Toluol, Lithium Corp. of America, was added to 2.141 g. (0.0079 mole) of *cis*-1,2,3-triphenylcyclopropane. Although this mixture was stirred for 3 hr. at room temperature, there was no gas evolved nor was there any other visible sign of reaction. The mixture was then cooled in ice and 5 ml. of ether was added. The reaction slowly turned red and after 30 min. 90 ml. (0.004 mole) of gas evolved. To this red solution was added 3.713 g. (0.0011 mole) of *sym*-triphenylcyclopropane bromide. The color disappeared immediately and more gas was evolved. The reaction mixture was extracted with ether; the ether layer was dried and evaporated to give 4.722 g. of orange oil, which was chromatographed on 100 g. of Merck acid-washed alumina. The first twelve fractions taken with *n*-hexane yielded an oil. Elution with 20% benzene in hexane yielded an oily solid. One of these solid fractions was taken and recrystallized from *n*-hexane to give a white solid, m.p. 200° and up. From the mother liquor more crystalline material appeared, m.p. 160–190°; recrystallization from hexane–benzene gave a m.p. of 169–190°. This material was triturated with hot *n*-hexane, the *n*-hexane was decanted from the solid material and concentrated, to give material, m.p. 172–177°. Two further recrystallizations from hexane–benzene gave material, m.p. 175–179°.

fully characterized spectroscopically and analytically, as well as by conversion to triphenylcyclopropane with base.

(30) F. S. Bridson-Jones, G. D. Buckley, L. H. Cross, and A. P. Driver, *J. Chem. Soc.*, 2999 (1951).

(25) Hexaphenylbenzene was characterized throughout this work as a white insoluble solid, m.p. near 400° with sublimation and without decomposition, whose highly characteristic infrared spectrum was identical with that of an authentic sample.²⁶ The m.p. is very sensitive to impurities, but purified samples had m.p. 416–418° (lit.²⁶ 425°).

(26) W. Dilthey and G. Hürtig, *Chem. Ber.*, **67**, 2004 (1934).

(27) W. Dilthey, U. S. Patent 2,097,854 (1937); *Chem. Abstr.*, **32**, 3674 (1938).

(28) N. Kharasch and N. J. Assony, *J. Am. Chem. Soc.*, **80**, 5978 (1958).

(29) P. Gal, Ph.D. Thesis, Columbia University. This compound was prepared by the addition of phenylchlorocarbene to *trans*-stilbene, and was

Admixture of this compound with the *cis* dimer, m.p. 179–180°, showed no mixture melting point depression, m.m.p. 177–181°. The identity of this material with the *cis* dimer was further confirmed by comparison of their infrared (KBr) and ultraviolet spectra (95% ethanol). In this synthesis the final isolated yield was only 1% of theory.

The Thermal Dimerization of 1,2,3-Triphenylcyclopropene.—A solution of 0.526 g. (0.0018 mole) of triphenylcyclopropene was refluxed in 25 ml. of toluene (oil bath at 156°) for 39 hr. The reaction was worked up by evaporation of the solvent and chromatography of the resulting oil on 30 g. of Merck acid-washed alumina. Elution with *n*-hexane gave 0.449 g. (86%) of the starting triphenylcyclopropene, m.p. 111–113°. Further elution with 20% benzene in hexane gave, after one recrystallization from hexane–benzene, 0.101 g. (19%) of the *cis* dimer Ia, m.p. and m.m.p. 178.5–181°.

This product was also obtained from reactions run in xylene, 95% ethanol, or *t*-butyl alcohol.

The Thermal Dimerization of Triphenylcyclopropene-*d*.—A solution of 0.143 g. (0.00053 mole) of deuteriotriphenylcyclopropene³¹ in 10 ml. of xylene was heated at 145° for 127 hr. At the end of this time the solvent was removed under a stream of nitrogen and the resulting solid was chromatographed on 30 g. of Merck acid-washed alumina. Elution with *n*-hexane gave a few mg. of starting material, m.p. 102–110°, after one recrystallization from 95% EtOH. Further elution with 20% benzene in hexane gave 0.142 g. of dideuterio *cis* dimer Ia', m.p. (after one recrystallization from *n*-hexane) 160–175°. Further recrystallization from hexane–cyclohexane gave material, m.p. 178–179.5°. An n.m.r. spectrum (CS₂) of this final product showed only aromatic protons at 2.7 τ , whereas the *cis* diprotio dimer Ia has, in addition to these aromatic protons, a prominent, sharp peak at 6.78 τ .

Treatment of 1-Deuterio-1,2,3-triphenylcyclopropene with Lithium Amide in Liquid Ammonia.—A solution of 0.370 g. (0.0014 mole) of deuteriotriphenylcyclopropene³¹ in 10 ml. of dimethoxyethane was added to 3.34 g. (0.143 mole) of lithium amide in 40 ml. of liquid ammonia. A deep blue color developed around the upper edges of the reaction mixture. After 35 min. the reaction was quenched with water and extracted with ether. The ether was dried and evaporated giving, after two recrystallizations from hexane–benzene, 0.177 g. (48%) of the *cis* dimer, m.p., m.m.p. 178.5–180°. The n.m.r. spectrum (CS₂) shows aromatic protons at 2.7 τ , but no signal between 3.0 τ and tetramethylsilane, whereas Ia shows a prominent, single, sharp line at 6.78 τ . Under the conditions used 0.1 proton could easily have been detected.

Methyltriphenylcyclopropene.—Treatment of 5.0 g. (0.0145 mole) of *sym*-triphenylcyclopropenyl bromide with 0.029 mole of methylmagnesium iodide gave, after chromatography on 50 g. of Merck acid-washed alumina and elution with *n*-hexane, 3.62 g. (89%) of methyltriphenylcyclopropene, m.p. 93–98°. After four recrystallizations from 95% ethanol, the compound had m.p. 95.5–97.5°. The compound shows a strong diphenylcyclopropene ultraviolet spectrum with maxima at 328 $m\mu$ (ϵ 25,000), 312 $m\mu$ (ϵ 30,000), and 227 $m\mu$ (ϵ 31,000). In the n.m.r. (CS₂) it has a 15-proton multiplet at 3.0 τ and a 3-proton singlet at 8.14 τ .

Anal. Calcd. for C₂₂H₁₈: C, 93.57; H, 6.43. Found: C, 93.86; H, 6.38.

A solution of 1.023 g. (0.0036 mole) of methyltriphenylcyclopropene in 19 ml. of dimethoxyethane was added to 2.4 g. (0.0435 mole) of potassium amide in liquid ammonia. The reaction mixture was stirred for 30 min., quenched with water, and extracted with ether. The ether layer was dried and evaporated, giving a slightly yellow solid, m.p. 92–97°. Chromatography on Merck acid-washed alumina yielded 0.985 g. (96%) of starting methylcyclopropene, m.p. 94–96°; undepressed on admixture with authentic material, m.m.p. 95–98°.

A solution of 1.834 g. (0.017 mole) of *p*-toluidine in 25 ml. of dimethoxyethane was added to 0.500 g. (0.0113 mole) of sodium hydride in mineral oil (54.5% by weight) and stirred at room temperature for 14 hr. A solution of 0.560 g. (0.0023 mole) of methyltriphenylcyclopropene in 25 ml. of dimethoxyethane was added and the resulting solution stirred at room temperature for 78 hr. At the end of this time, the reaction was quenched with water and extracted with ether. The ether layer was washed several times with 10% hydrochloric acid solution and once with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to give 0.871 g. of oily, red solid. Chromatography on 30 g. of Merck acid-washed alumina and elution with *n*-hexane gave 0.650 g. of material which was recrystallized from 95% ethanol, giving oily crystals, m.p. 86–96°. Two recrystallizations from *n*-pentane, one from 95% ethanol, and another from *n*-pentane gave 0.260 g. (41%) of white platelets,

(31) Generously furnished by Dr. Peter Gal. This material was prepared by reduction of triphenylcyclopropenyl bromide with lithium aluminum deuteride, and its identity fully established by P. Gal. Ph.D. thesis, Columbia University.

m.p. 95–97°, undepressed on admixture with starting methyltriphenylcyclopropene, m.m.p. 94–97°.

Reaction of 1,2,3-Triphenylcyclopropene with Sodium *p*-Toluidine.—A solution of 1.2 g. (0.011 mole) of *p*-toluidine in 25 ml. of dry, distilled dimethoxyethane was added to 0.5 g. (0.012 mole) of sodium hydride in mineral oil (54% by weight) and the mixture stirred at room temperature for 20 hr., giving a deep, blue-black solution. A solution of 0.50 g. (0.0019 mole) of triphenylcyclopropene and 0.16 g. (0.0056 mole) of *p*-toluidine in 25 ml. of dimethoxyethane was added, and the total reaction mixture stirred for 12 hr. at room temperature. The reaction was quenched with water and extracted with ether. The ether layer was dried over anhydrous sodium sulfate and then evaporated to give 0.625 g. of red oil which was chromatographed on 18 g. of Merck acid-washed alumina. Elution with 50% benzene in hexane yielded 0.28 g. (51.5%) of benzyldeoxybenzoin, n.p. 121–123° (reported³² m.p. 120°) after one recrystallization from 95% ethanol. An authentic sample of benzyldeoxybenzoin, m.p. 117–120°, was prepared by coupling the sodium salt of desoxybenzoin with benzyl chloride according to Meyer and Oelkers.³² The infrared spectra (KBr) of the two samples were identical, and the melting point was undepressed on admixture, m.m.p. 117–120°.

Reaction of Lithium *n*-Propylamide with Triphenylcyclopropene.—Lithium metal (1.0 g., 0.144 g.-atom) was added with a small amount of ferric chloride to 40 ml. of freshly distilled (from sodium-potassium alloy) *n*-propylamine. After refluxing for 60 hr., the lithium had all reacted and the solution gave a positive test (deep red color) with triphenylmethane. A solution of 1.019 g. (0.0038 mole) of triphenylcyclopropene in 10 ml. of dimethoxyethane was added and the solution was stirred for 90 min. at room temperature. A deep brown-red color formed immediately and persisted until the reaction was quenched with water (exothermic reaction). The reaction mixture was extracted with ether and the ether layer dried and evaporated to give an orange oil which still contained some amine. This oil was dissolved in *n*-pentane and treated with 10% aqueous hydrochloric acid, resulting in the formation of a heavy oil in the aqueous layer. When this oil was dissolved by adding methanol, white crystals appeared in the interface. The solid was filtered off, giving 0.685 g. of white needles, m.p. 116–120°. Further solid clinging to the flask and filter was dissolved in ether. Evaporation of the ether gave 0.172 g. of solid, m.p. 102–108°. Finally, extraction of the aqueous acid layer with ether and evaporation of the ether gave 0.208 g. of yellow, oily solid. All this material was combined and recrystallized from 95% ethanol, giving 0.480 g. of benzyldeoxybenzoin, m.p. 120–121°, m.m.p. with an authentic sample of benzyldeoxybenzoin 119–121°. Chromatography of the mother liquor on 100 g. of Merck acid-washed alumina and elution with 50% benzene in hexane gave, after one recrystallization from 95% ethanol, 0.105 g. of benzyldeoxybenzoin, m.p. 120–122°, also identified by direct comparison with an authentic sample, m.m.p. 119–120°; total yield of benzyldeoxybenzoin: 0.585 g., 54%. The chromatography has shown that less than 1% of dimer Ia is present.

Reaction of 1,2,3-Triphenylcyclopropene with Sodium Methoxide in Dimethyl Sulfoxide.—Dimethyl sulfoxide was dried for 24 hr. over anhydrous sodium sulfate and distilled at 55° (4 mm.).

A solution of 0.434 g. (0.0016 mole) of triphenylcyclopropene in 25 ml. of dimethyl sulfoxide was added to 10 g. (0.185 mole) of sodium methoxide in 25 ml. of dimethyl sulfoxide. The deep yellow reaction mixture was stirred at room temperature for 24 hr., quenched with water (exothermic reaction), and extracted with ether. The ether was dried and evaporated, giving 0.612 g. of yellow, oily material which was dissolved in a few ml. of cyclohexane and chromatographed on 30 g. of Merck acid-washed alumina. Elution with *n*-hexane yielded 0.141 g. (34.5%) of white crystalline solid, m.p. 90–92°. Three recrystallizations from 95% EtOH, then sublimation at 83° (0.05 mm.) gave white material, m.p. 91.5–93.5°.

Anal. Calcd. for C₂₂H₂₀O: C, 87.96; H, 6.71. Found: C, 87.73; H, 6.58.

The spectral and chemical properties of this compound are in good agreement with those expected for Δ^1 -1-methoxy-1,2,3-triphenylpropene (IV). The ultraviolet spectrum (95% ethanol) shows a broad band at 270 $m\mu$ (ϵ 16,400) and the n.m.r. spectrum (CS₂) shows a 10-proton aromatic band at 2.95 τ , a 5-proton aromatic band at 3.2 τ , a 2-proton aliphatic singlet at 6.14 τ , and a 3-proton singlet at 6.66 τ , which is due to the methoxyl. The infrared spectrum (KBr) shows a prominent band at 6.2 μ which may be ascribed to the carbon-carbon double bond stretching vibration.

The compound is quantitatively hydrolyzed with acid to benzyldeoxybenzoin (see below).

Further elution with *n*-hexane gave 0.311 g. (62%) of solid material, m.p. 100–140°. One recrystallization from *n*-hexane gave 1-methoxy-1,2,3-triphenylcyclopropane (III), m.p. 149–152°.

(32) V. Meyer and L. Oelkers, *Chem. Ber.*, **21**, 1300 (1888).

Two further recrystallizations from *n*-hexane raised the m.p. to 150–151.5°. This compound has only weak absorption in the ultraviolet (cyclohexane) above 225 μ . The n.m.r. spectrum (CS₂) shows a 15-proton aromatic multiplet at 2.9 τ , a 2-proton aliphatic doublet at 7.0 τ , and a sharp, 3-proton singlet at 7.24 τ , due to the methyl ether.

Anal. Calcd. for C₂₂H₂₀O: C, 87.96; H, 6.71; mol. wt., 300. Found: C, 87.52; H, 6.61; mol. wt., 331 (Rast, camphor), 310 (osm., benzene).

When the dimethyl sulfoxide reaction was repeated using 1.006 g. (0.0038 mole) of triphenylcyclopropene, 10 g. of sodium methoxide, and 50 ml. of dimethyl sulfoxide, a slightly different reaction was observed. Whereas the previous reaction was yellow, this one went through a variety of color changes from yellow to brownish gray to purple to brown-gray to green. It remained green until it was quenched with water. Work-up and chromatography gave the same products as before in addition to 0.005 g. (0.25%) of hexaphenylbenzene.²⁵

Hydrolysis of 1-Methoxy-1,2,3-triphenylpropene-1 (IV) to Benzyl-desoxybenzoin.—A solution of 0.100 g. (0.00033 mole) of IV in 10 ml. of 95% ethanol and 3 ml. of concentrated hydrochloric acid was refluxed on the steam bath for 1 hr. At the end of this time, the reaction was cooled and extracted with ether. The ether was dried over anhydrous sodium sulfate and evaporated to give 0.105 g. of slightly tan solid, m.p. 117–119°. One recrystallization from 95% ethanol gave 0.088 g. (92%) of benzyl-desoxybenzoin, m.p. 118.5–121°, m.m.p. 117–119°.

Reaction of 1,2,3-Triphenylcyclopropene with Sodamide in 1,2-Dimethoxyethane.—Sodamide was prepared in the usual way, using 1.277 g. (0.055 g.-atom) of sodium metal in 50 ml. of dry ammonia. When the Birch complex had decomposed to sodamide, the ammonia was allowed to evaporate and the reaction flask to come to room temperature. A solution of 0.619 g. (0.0023 mole) of triphenylcyclopropene in 30 ml. of dimethoxyethane was added and the mixture was stirred at room temperature for 14 hr. After 30 min. the reaction was a deep blue-green; it remained this color until it was quenched with water. The reaction mixture was extracted with ether and 10% hydrochloric acid. The ether was dried with brine and 0.054 g. of an insoluble solid was filtered off. Evaporation of the ether layer and trituration with *n*-hexane gave 0.555 g. of white solid, m.p. 115–220°. This material was dissolved in 5 ml. of hot cyclohexane and chromatographed on 40 g. of Merck acid-washed alumina.

Elution with *n*-hexane yielded 0.014 g. (2.2%) of diphenyl-ethane whose infrared spectrum (CHCl₃) was identical with that of an authentic sample.

Further elution with 20% benzene in hexane gave solid material which when recrystallized from benzene gave 0.040 g. (6.5%) of hexaphenylbenzene.²⁵ From the mother liquor more crystalline material appeared, m.p. 210–225°. Four recrystallizations from cyclohexane gave 0.050 g. (8%) of 1,4-dihydrohexaphenylbenzene (VII), m.p. 224–226°. This compound has only end absorption in the ultraviolet (cyclohexane). The n.m.r. shows a 30-proton aromatic multiplet at 3 τ and a 2-proton singlet at 5.33 τ .

Anal. Calcd. for C₁₂H₁₂: C, 93.99; H, 6.01. Found: C, 93.71; H, 6.56.

A thin layer chromatoplate of the crude reaction product showed only three major components (identified by direct comparison with authentic samples): hexaphenylbenzene, 1,4-dihydrohexaphenylbenzene (VII), and the *cis* dimer Ia. The poor yields reflect difficulties encountered in separating these compounds.

Treatment of 1,4-Dihydrohexaphenylbenzene (VII) with Bromine.—A solution of 0.044 g. (0.00008 mole) of dihydrohexaphenylbenzene in 2 ml. of hot cyclohexane was treated with an excess of bromine. A heavy precipitate came out and hydrogen bromide was given off. After 5 min. no more hydrogen bromide could be detected; the solid material was centrifuged and the mother liquor drawn off. The solid was triturated twice with hot *n*-hexane and recrystallized once from chloroform-hexane, giving 0.035 g. (80%) of hexaphenylbenzene.²⁵

Preparation of Tritium-Labeled Triphenylmethane.—A mixture of 8.5 ml. of acetic acid, 1.0 ml. of acetic anhydride, and 0.1 ml. of tritiated water (100 mcuries/g., New England Nuclear Corp.) was refluxed for 2 hr. After the solution was cool, 1.06 g. of triphenylmethyl chloride was added, followed by 3.018 g. of zinc dust. The resulting mixture was stirred at room temperature for 11 hr. when water was added and the reaction mixture extracted with ether. Unlabeled triphenylmethane, 0.470 g., was added as carrier, and the ether evaporated to give 1.2 g. of white solid, m.p. 84–86°.

This solid was chromatographed on 30 g. of Merck acid-washed alumina and eluted with *n*-hexane, giving 1.1 g. of material, which was combined with 4.192 g. more unlabeled triphenylmethane. The total material was recrystallized six times from 95% ethanol, giving shiny, white platelets, m.p. 92.5–94°. After recrystallizations 5 and 6, material was taken and dried under vacuum over P₂O₅ at 65°. A sample, 0.100 g., of each was dis-

solved in 25 ml. of scintillating solution and counted for constant activity.³³

	Av. activity, c./min.	No. times counted	Standard deviation, c./min.
5	612,168	5	1220
6	605,960	5	1440

Thus the two samples differed by 1% and the activity was judged to be constant.

Treatment of Tritium-Labeled Triphenylmethane with Potassium *t*-Butoxide.—After 2.79 g. (0.072 g.-atom) of potassium metal was refluxed for 7 hr. in 50 ml. of dry *t*-butyl alcohol, giving a saturated solution of potassium *t*-butoxide, the above-labeled triphenylmethane (0.962 g., 0.0039 mole) was added as a solid, and the mixture³⁴ was refluxed for 8 hr. (oil bath at 130°) when the reaction was quenched with water and extracted with ether. Evaporation of the ether yielded a slightly brown solid which was chromatographed on 30 g. of Merck acid-washed alumina. Elution with *n*-hexane yielded 0.935 g. of white triphenylmethane which after being recrystallized three times from 95% ethanol had m.p. 92–93.5°.

Samples were taken from recrystallizations 1, 2, and 3 and dried over phosphorus pentoxide. Counting of 0.100 g. of each sample dissolved in 25 ml. of scintillating solution gave these results:

	Av. activity, c./min.	No. times counted	Standard deviation, c./min.
1	106,112	5	988
2	131,060	5	1100
3	130,396	5	968

These samples were counted at the same time as the starting material above. Background was negligible, averaging about 50 c./min.

Preparation of Tritium-labeled Triphenylcyclopropene.—A solution of 8 ml. of acetic acid, 1.0 ml. of acetic anhydride, 0.1 ml. of tritiated water (100 mcuries/g., New England Nuclear Corp.) and 5 drops of concentrated sulfuric acid was refluxed for 30 min.

sym-Triphenylcyclopropenyl bromide, 1.060 g., was added, followed by 2.563 g. of zinc dust, and the mixture was stirred at room temperature. The reaction mixture was extracted with ether and water and 0.468 g. of unlabeled triphenylcyclopropene added as carrier. Evaporation of the ether gave 0.87 g. of solid material which was chromatographed on 30 g. of Merck acid-washed alumina. Elution with *n*-hexane gave 0.627 g. of solid material which was combined with 5.42 g. of unlabeled cyclopropene. The total material was recrystallized five times from 95% ethanol, giving a m.p. of 111–113°. Samples from each of the last three crystallizations were taken and dried. Each was counted by dissolving 0.100 g. of sample in 25 ml. of scintillating solution.

	Av. activity, c./min.	No. times counted	Standard deviation, c./min.
3	647	6	24
4	656	7	34
5	674	8	27

Treatment of Labeled Triphenylcyclopropene with Potassium *t*-Butoxide.—A solution of 2.69 g. (0.069 g.-atom) of potassium metal in 50 ml. of *t*-butyl alcohol was refluxed for 48 hr., giving a saturated solution of potassium *t*-butoxide. At the end of this time, 1.017 g. (0.0039 mole) of labeled cyclopropene was added as a solid and the mixture³⁴ refluxed for 242 hr. (oil bath at 125°). The reaction was quenched with water and extracted with ether. Evaporation of the ether layer gave 1.144 g. of white solid, m.p. 90–103°, which was chromatographed on 30 g. of Merck acid-washed alumina. Elution with *n*-hexane gave 0.483 g. of triphenylcyclopropene which was recrystallized three times from 95% ethanol, giving shiny white platelets, m.p. 111–113.5°.

Samples were taken from the last two crystallizations for counting and the starting material was recounted for comparison.

	Av. activity, c./min.	No. times counted	Standard deviation, c./min.
Starting material	500	5	23
2	515	5	14
3	527	5	13

Background was 65 c./min.

(33) Tritium analyses were performed using a Packard Tri-Carb semi-automatic liquid scintillation counter. Scintillating solution was prepared by dissolving 4 g. of 2,5-diphenylloxazole (PPO) and 0.03 g. of *p*-bis-(2-(5-phenylloxazolyl)-benzene) (POPOP) in 1 l. of toluene. In exchange experiments starting materials were recounted along with products to minimize variations in counting efficiency.

(34) The organic compound was completely in solution and an excess of solid potassium *t*-butoxide guaranteed that the solution remained saturated in base.