A sample of diketo sulfone V (m.p. 124–125°) was analyzed.

Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.61. Found: C, 63.52; H, 4.76; S, 10.54.

Although diketo sulfone IV was known,[4,5] a sample of it (m.p. 107–108.5°) was analyzed.

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54.52; H, 5.08; S, 16.18. Found: C, 54.32; H, 5.04; S, 15.97.

Measurement of Hydrogen Evolution.—In a 500-ml. two-necked flask equipped with a tightly fitting addition funnel (with a pressure equalizing side arm) and an efficient reflux condenser was placed 50 ml. of purified monoglyme and 0.25 mole of sodium hydride.[9] The upper end of the condenser was fitted with a gas take-off which was connected to an American Meter Company wet test meter filled with water. The system was flushed with dry nitrogen, and a solution of 0.05 mole of a β-keto sulfone in 100 ml. of monoglyme was placed in the addition funnel. The system was closed, and the flask was placed on the steam bath. When thermal equilibrium was established, an initial reading was taken on the test meter. The solution in the funnel was then added during 10–12 min. After the solution had been added, readings were taken periodically until the hydrogen evolution ceased. This required 30–40 min. The system was opened, and a solution of 0.075 mole of methyl benzoate in 50 ml. of monoglyme was placed in the addition funnel. The apparatus was closed, equilibrium was established, an initial reading was taken, and the ester solution was added during a period of 5–7 min. Readings were then taken periodically until gas evolution was no longer detectable. The values were corrected for temperature, pressure, and water vapor pressure. The results were summarized in Table II.

Diphenylcyclobutadienoquinone. III.[1] Attempted Synthesis of 1,2-Diphenylcyclobutadiene[2]

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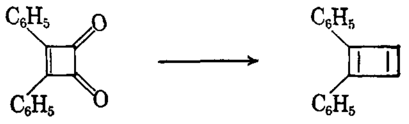
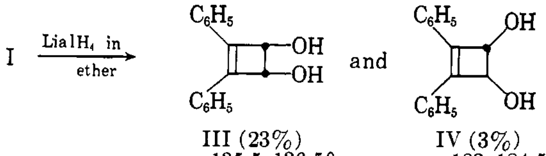
With the object of realizing a synthesis of 1,2-diphenylcyclobutadiene, further study has been made of diphenylcyclobutadienoquinone as a suitable precursor. Lithium aluminum hydride reduction of this diketone in ether gives mainly *cis*-1,2-diphenylcyclobutene-3,4-diol (23%) as well as some (3%) of the corresponding *trans*-diol. Reaction of the *cis*-diol with phosphorus tribromide affords smoothly (73%) *cis*-3,4-dibromo-1,2-diphenylcyclobutene. All efforts to prepare and isolate (or trap) the desired cyclobutadiene *via* debromination of the *cis*-dibromide with lithium amalgam, zinc dust, or nickel carbonyl have given only intractable polymeric organic products. Infrared studies of the *cis* and *trans* isomers of 1,2-diphenylcyclobutene-3,4-diol suggest that in the *cis*-1,2-diol there is intramolecular OH · · · π-electron hydrogen bonding with the cyclobutene double bond. Evidence that similar hydrogen bonding obtains for the *trans*-diol as well is not conclusive.

A considerable effort has been made in recent years by many investigators to prepare and isolate, or trap, *bona fide* cyclobutadienes. With diphenylcyclobutadienoquinone (I) readily available in the Cornell Laboratories,[1b] studies of this diketone as a precursor for the possible synthesis of 1,2-diphenylcyclobutadiene (II) were encouraged. The present report presents results of these investigations that supplement those presented earlier.[1b] In particular, this article describes efforts to realize the diene II *via* debromination of 3,4-dibromo-1,2-diphenylcyclobutene. Since this approach to a cyclobutadiene, *i.e.*, dehalogenation of 3,4-dihalo-1-cyclobutenes, has been widely and successfully used by many investigators to prepare cyclobutadienes *transiently*,[4] the method merited consideration for specific application to the 1,2-diphenyl-1-cyclobutene system.



I II

Lithium aluminum hydride reduction of the dione I in solvent ether gave *cis*-1,2-diphenylcyclobutene-3,4-diol (III), m.p. 135.5–136.5°, in 23% yield, and the corresponding *trans*-diol IV (3%), as well as products from expected ring-opening side reactions.[5] Only the *trans*-diol IV (5.5%), m.p. 183–184.5°, was formed upon $LiAlH_4$ reduction in tetrahydrofuran.[7] The two diols showed the following ultraviolet absorption maxima: the *cis*-diol III at 227 (ε 16,500) and 292 mμ (12,000); the *trans*-diol IV at 228 (ε 15,800) and 292 mμ (12,500). Unlike *cis*-tetramethylcyclobutenediol,[8]



III (23%)
m.p. 135.5–136.5°

IV (3%)
m.p. 183–184.5°

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[1] (a) For the preceding paper in this series, see A. T. Blomquist and P. R. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962). (b) For papers closely related to this study, *i.e.*, "Diphenylcyclobutadienoquinone I and II," see A. T. Blomquist and E. A. LaLancette, *ibid.*, **83**, 1387 (1961), and **84**, 220 (1962).

[2] For preliminary portions of this study, see (a) Abstracts of Papers, the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 54-0; (b) Abstracts of Papers, presented at the 16th National Organic Chemical Symposium of the American Chemical Society, Seattle, Wash., June 15-17, 1959, p. 11.

[3] Supported by funds from the Sage Fellowship, summer, 1957; Procter and Gamble Fellow, summer, 1958; American Cyanamid Fellow, summer, 1959; Allied Chemical and Dye Fellow, 1959-1960.

[4] R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959); M. Avram, E. Marica, and C. D. Nenitzescu, *Chem. Ber.*, **92**, 1088 (1959); M. Avram, E. Marica, J. Pogany, and C. D. Nenitzescu, *Angew. Chem.*, **71**, 626 (1959); C. D. Nenitzescu and M. Avram, *ibid.*, **72**, 39 (1960); M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957); C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957); M. Avram, D. Dinu, and C. D. Nenitzescu, *Chem. Ind.* (London), 257 (1959); M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1789 (1960).

[5] Reaction of the compound I with aqueous methanolic sodium hydroxide results in cleavage of the cyclobutene ring to give, as isolable products, benzaldehyde and α-keto-βγ-diphenyl-γ-butyrolactone. Similarly, ring cleavage occurs in the reaction of the diketone I with *o*-phenylenediamine to produce 3-phenylacetyl-2-phenylquinoxaline.[1b] The reduction of the related phenylcyclobutadienoquinone with either sodium borohydride or lithium aluminum hydride is reported[6] to yield intractable products. See also M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Am. Chem. Soc.*, **85**, 2076 (1963).

[6] J. D. Roberts, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **17**, 104 (1956).

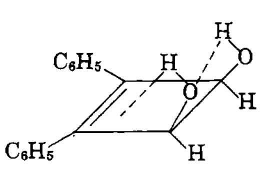
[7] Oily products obtained in the reductions were not characterized. However, both reductions afforded a solid crystalline accessory product of m.p. 196–197°, having λ_{max}^{KBr} 5.95 μ and indicative of the occurrence of ring opening.

[8] R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).

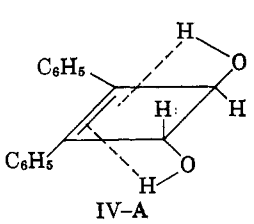
the *cis*-diol III failed to isomerize when treated with acid.

The above assignments of configuration to the two diols, III and IV, were made on the basis of infrared analysis[9] and reaction with potassium triacetyl osmate. The diol obtained as the major product in the $LiAlH_4$ reduction of the diketone I in ether showed infrared absorption maxima, in carbon tetrachloride solution, at 3602 and 3557 cm.$^{-1}$; correspondingly, the diol isolated from reduction in tetrahydrofuran (insoluble in carbon tetrachloride) has only a single absorption maximum (OH region) at 3603 cm.$^{-1}$ in chloroform solution. Since *cis*-1,2-diols inevitably show two infrared maxima in the OH region and *trans*-1,2-diols but one,[10] the diol of m.p. 135.5–136.5° is assigned the *cis* configuration III and the one of m.p. 183–184.5°, the *trans* configuration.

Information pertinent to the nature of OH hydrogen bonds in the *cis*- and *trans*-diols III and IV was also provided by infrared analysis after an appropriate correction had been made to adjust the observed OH band for the *trans*-diol IV, measured in chloroform, to a value which would have been observed had it been possible to examine the *trans*-diol in carbon tetrachloride solution. Since it has generally been found that alcohols show OH absorption bands some 10 to 21 cm.$^{-1}$ higher in carbon tetrachloride solution than in chloroform,[11] an approximate average of this increase, 15 cm.$^{-1}$, was added to the observed value for the *trans* isomer to give an "adjusted" value of 3618 cm.$^{-1}$ for the OH infrared band for the *trans*-diol IV. Further, saturated alcohols generally do not absorb[12] much below 3520 cm.$^{-1}$. Accordingly, the more intense, higher frequency band at 3602 cm.$^{-1}$ observed for the *cis*-diol III is considered not to arise from the presence of a "free OH" but is assigned to an OH$\cdots\pi$-electron hydrogen bond[13] that probably involves the cyclobutene double bond; and the band at 3557 cm.$^{-1}$ is assigned to the normal —O—H$\cdots$O— hydrogen bond present in *cis*-1,2-diols.[14] The need for applying a correction factor to the observed band of the *trans*-diol (chloroform solution) makes for some ambiguity with this isomer. It is probable that much weaker OH$\cdots\pi$-electron bonding obtains here owing to availability of two OH groups for such bonding. Based on the above, the *cis*- and *trans*-diols are represented by the formulations III-A and IV-A, respectively.



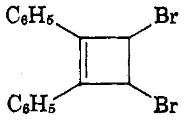
III-A



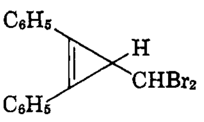
IV-A

In accord with the above infrared studies, the lower melting glycol III obtained from reduction of the diketone I in ether gave a positive test with potassium triacetyl osmate, indicative of a *cis*-1,2-diol, whereas the higher melting isomer formed by reduction in tetrahydrofuran gave a negative test with the reagent, indicative of a *trans*-1,2-diol.[8,15]

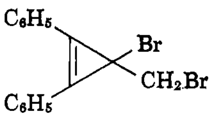
Reaction of the *cis*-diol III with phosphorus tribromide gave a white, crystalline dibromide (V, 73%), m.p. 115–116°, which had the molecular formula $C_{16}H_{12}Br_2$. Although this dibromide V gave an immediate precipitate with alcoholic silver nitrate, it failed to undergo solvolysis under conditions used successfully by Criegee and Louis[16] to effect solvolysis of 1,2,3,4-tetramethyl-1,2-dichlorocyclobutene; the starting dibromide V was recovered together with a small amount of an oil that presumably resulted from ring opening. Although this dibromide V was thought to be the desired 3,4-dibromo-1,2-diphenylcyclobutene (V), the cyclopropene derivatives VI and VII were also considered as other possible structures for the dibromide; the latter could arise *via* pinacol-type rearrangements. Since the n.m.r. spectrum[17] of the dibromide shows a singlet at 5.28 p.p.m. and a multiplet centered at 7.43 p.p.m. in a 1:5 ratio (relative to an internal tetramethylsilane standard at 60 Mc./sec.) the cyclopropene structure VI can be eliminated. Choice between the two remaining structures V and VII could be made on the basis of the ultraviolet spectrum observed in ethanolic solution for the dibromide at hand. This spectrum showed two principal maxima at 238 mμ (ε 26,000) and 303 (19,500) with a shoulder at 230 (23,300). This spectrum compares favorably with those observed for other closely related diphenylcyclobutene systems prepared at Cornell.[1b,18]



V



VI



VII

Although the ultraviolet spectrum of the dibromide in question shows a 10-mμ bathochromic shift relative to the cyclobutene diols III and IV, it is in even greater variance with that expected for a compound of structure VII. Breslow and co-workers[19] have found that 1,2-diphenylcyclopropenes absorb at about 306 and 320 mμ (ε *ca.* 28,000) and at 225 and 230 (*ca.* 20,000); *i.e.*, the strongest absorption is at higher wave lengths. In contrast, the reverse is true for 1,2-diphenylcyclobutene systems. In addition, the spectra of diphenylcyclopropenes show more fine structure than diphenylcyclobutenes. All of the foregoing suggests that the dibromide in question is in fact V and not VII. Finally, if the structure VII were the correct structure of the "di-

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[9] Through the agency of Dr. E. J. Moriconi we are indebted to Dr. Paul von R. Schleyer for the infrared studies which were made with a Perkin-Elmer Model 21 spectrometer equipped with a lithium fluoride prism.

[10] F. A. Smith and E. C. Creity, *J. Res. Natl. Bur. Std.*, **46**, 145 (1951); L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).

[11] J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **A162**, 419 (1937); A. V. Stuart, *J. Chem. Phys.*, **21**, 1115 (1953); A. R. H. Cole and A. J. Michell, *J. Chem. Soc.*, 2005 (1959).

[12] P. von R. Schleyer, private communication; see P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

[13] For other examples, see A. W. Baker and A. T. Shulgin, *ibid.*, **80**, 5358 (1958); **81**, 4524 (1959).

[14] For the interpretation of results obtained from similar systems, see E. J. Moriconi, W. T. O'Connor, L. P. Kuhn, E. A. Keneally, and F. T. Wallenberger, *ibid.*, **81**, 6475 (1959).

[15] R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 99 (1942).

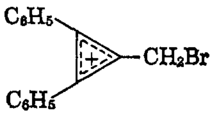
[16] The conditions used were those described by Criegee and Louis to effect readily the solvolysis of *cis*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene to the corresponding *cis*-diol (ref. 8).

[17] The spectrum was determined by Varian Associates, Palo Alto, Calif., using a deuteriochloroform solution.

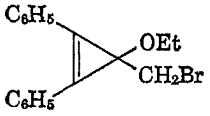
[18] A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **79**, 5317 (1957); **81**, 667 (1959).

[19] R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958); R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

bromide," it should form the corresponding diphenylcyclopropenyl cation VIII quite readily. However, the ultraviolet spectrum of the dibromide in acetonitrile–10% ethanol (conditions favorable for the presence of the ether IX) showed maxima at 238 mμ (ϵ 26,400) and 303 (20,400) with a shoulder at 230 (23,800). Also, the ultraviolet spectrum of the dibromide in acetonitrile–10% ethanol–0.1 *N* hydrochloric acid (conditions favorable for the cyclopropenium ion) revealed no shift with respect to the position or intensity of the absorption maxima. These results are in marked contrast to the reported behavior of diphenylcyclopropene systems, where appreciable changes occur under similar conditions.[20,21] Thus, structure VII for the dibromide can be eliminated and, accordingly, the dibromide must be 3,4-dibromo-1,2-diphenylcyclobutene (V).



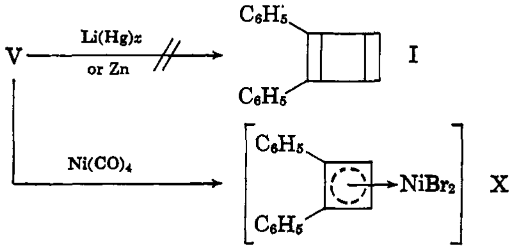
VIII



IX

The stereochemistry of the dibromide V is not known with complete certainty but it is probably *cis*. A chloroform solution of 3,4-dibromo-3,4-bis(bromomethyl)-1,2-diphenyl-1-cyclobutene,[18] which probably has a *trans* configuration, shows an ultraviolet maximum at 288 mμ (ϵ 19,500), but the long wave-length maximum of the dibromide V (in chloroform solution) remains at 303 mμ. It is probable, therefore, that the bathochromic shift observed for the compound V is a consequence of interactions of cisoid bromine atoms.[22]

Dehalogenation of the dibromide V with 0.5% lithium amalgam[16,24] failed to give 1,2-diphenylcyclobutadiene (II) or to generate such an intermediate which could be trapped by the diene cyclopentadiene. Instead, only an intractable polymeric crimson oil could be isolated which resisted all attempts at characterization. The infrared spectrum of this oil closely resembled the spectrum of a polystyrene film. Similar results were obtained in the zinc dust debromination of compound V.



Finally, the dibromide V reacted very slowly with nickel carbonyl. The amount of unchanged dibromide recovered and nickel bromide formed (up to 100%) varied with reaction conditions. The polymeric organic product formed could not be characterized. The nickel complex X, if formed, apparently decomposed readily to release nickel bromide and afforded a polymeric organic product. These results contrast markedly with those reported by Freedman for the stable tetraphenylcyclobutadiene–nickel bromide complex.[25]

Experimental[26]

***cis*-1,2-Diphenylcyclobutene-3,4-diol** (III).—A solution of 4.96 g. (21.1 mmoles) of unrecrystallized diketone[1b] in 13 ml. of dry benzene was added over a 10-min. period to a stirred slurry of 0.46 g. of lithium aluminum hydride in 90 ml. of dry ether. The mixture was stirred at 25° for 1 day, cooled to −6°, and then treated by the dropwise addition of 25 ml. of water followed by the addition of 50 ml. of 10% sulfuric acid. The aqueous acid layer was extracted with three 25-ml. portions of ether, and the combined organic solutions were washed successively with 25 ml. of saturated sodium bicarbonate solution, 50 ml. of water, and 25 ml. of saturated aqueous sodium chloride solution. Concentration of the dried organic solution gave, in two crops, an impure sample of the *cis*-1,2-diol III which, after recrystallization from carbon tetrachloride, afforded 1.14 g. (23%) of the pure diol III, m.p. 135.5–136.5°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.75; H, 5.68.

Further concentration of the carbon tetrachloride mother liquor gave 80 mg. of a white crystalline solid, m.p. 193–196°, λ_{max}^{KBr} 5.95 μ (indicative of a ring-opened product). A very slow evaporation of the original ether–benzene solution at room temperature deposited 0.16 g. (3%) of impure *trans*-diol IV.

Variations in the above procedure, *i.e.*, inverse addition of reactants or neutral conditions in the hydrolysis step, failed to increase the yield of the diol III.

***trans*-1,2-Diphenylcyclobutene-3,4-diol** (IV).—During a 10-min. period, 4.2 g. of the diketone I in 50 ml. of freshly purified tetrahydrofuran (THF)[27] was added to a cold (0°), stirred solution of 0.374 g. of $LiAlH_4$ in 50 ml. of dry THF. The mixture was stirred at room temperature for 21 hr. and then treated, by slow addition, with ethyl acetate to consume unchanged $LiAlH_4$. After the subsequent addition of water, the mixture was filtered from the insoluble granular salts, and the aqueous filtrate was extracted with ether. A solution of the inorganic salts, in a minimum amount of 10% hydrochloric acid, was also extracted with ether. The combined ether extract was washed with a saturated sodium bicarbonate solution, dried, and taken to dryness. The oil thus obtained crystallized from carbon tetrachloride to give 0.46 g. of a white solid (very impure diol IV) as well as a trace of a solid which had m.p. 273–275°. Fractional crystallization of the above impure diol IV from 1:1 ethanol–ethyl acetate effected a partial separation into approximately equal amounts of the *trans*-diol IV, m.p. 183–184.5°, and an unknown compound, m.p. 196–197°, λ_{max}^{KBr} 5.95 μ. This sample of the diol IV was analyzed.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.87; H, 5.84.

Infrared Studies of the Diols III and IV.—In a 1-cm. cell a carbon tetrachloride solution of the *cis*-diol III at a concentration of 6.5 mg./ml. showed two infrared bands at 3604 and 3559 cm.$^{-1}$. In a 5-cm. cell the bands were observed to be 3601 and 3555 cm.$^{-1}$. The assignments, that were based on average values, were made as follows: the more intense, higher frequency band at *ca.* 3602 cm.$^{-1}$ was attributed to an OH···π-electron bond with the cyclobutene double bond and the band at *ca.* 3557 cm.$^{-1}$ to the normal OH···O bond present in *cis*-1,2-diols.

The *trans*-diol IV, insoluble in carbon tetrachloride, is only slightly soluble in chloroform. Its infrared spectrum, in a saturated solution of chloroform, showed a weak band at 3603 cm.$^{-1}$. Since alcohols absorb at higher frequencies in carbon tetrachloride *vs.* chloroform, a correction of absorption was made in order to compare the observations made of the *cis*- and *trans*-diols. Suggested correction values[11] for this are 10, 15, and 21 cm.$^{-1}$. Accordingly, after application of the average correction

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

[21] R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

[22] Since the preparation of V, Criegee and Noll have noted[23] that only *cis*-3,4-dibromo-1,2,3,4-tetramethylcyclobutene was obtained when either the *cis* or *trans* isomer of 1,2,3,4-tetramethylcyclobutene-3,4-diol was treated with hydrogen bromide. Similarly, from either the *cis* or *trans* forms of Criegee's diol, reaction with either hydrogen chloride or thionyl chloride affords only *cis*-3,4-dichloro-1,2,3,4-tetramethylcyclobutene.

[23] R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959).

[24] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

[25] H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961); *J. Org. Chem.*, **27**, 2298 (1962).

[26] All melting points, taken with a Mel-Temp apparatus, are uncorrected. Ultraviolet spectra were determined with Beckman DK and Cary 14 instruments.

[27] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 292.

value of 15 cm.$^{-1}$, the *trans*-1,2-diol IV is predicted to show infrared absorption at 3618 cm.$^{-1}$ in carbon tetrachloride solution. This is indicative of an OH$\cdots\pi$-electron interaction that is much weaker than observed for the *cis*-diol III.

Reaction of the Diols III and IV with Potassium Triacetyl Osmate.[15]—The diol III reacted rapidly with triacetyl osmate, indicative of *cis*-1,2-diol configuration. The diol IV, however, was unreactive in this reaction in support of a *trans* arrangement of hydroxyl groups.

3,4-Dibromo-1,2-diphenylcyclobutene (V).—To a solution of the diol III (0.955 g., 4 mmoles) in a cooled (−50°) solution of chloroform, 1.11 g. (4.1 mmoles) of phosphorus tribromide was added. This mixture was allowed to stand at −50° for 5 hr., at 25° for 48 hr., and finally refluxed for 14 hr. After the addition of more chloroform, the mixture was poured carefully into an ice–water mixture. (The yellow solid deposited on the sides of the flask during the period of reflux was also dissolved in water and added to the chloroform solution.) After the chloroform solution had been separated, the remaining aqueous phase was extracted with additional chloroform. The combined chloroform solutions, after successive washings with saturated sodium bicarbonate and saturated aqueous sodium chloride, were dried ($MgSO_4$). Removal of the solvent *in vacuo* gave a crystalline residue which was recrystallized from 30–60° petroleum ether to give, in several crops, a total of 1.06 g. (73%) of the dibromide V. A sample of the compound V, m.p. 115–116° from petroleum ether, was analyzed.

Anal. Calcd. for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32; Br, 43.89. Found: C, 52.69; H, 3.34; Br, 43.91.

A crystalline modification of V, m.p. 103–104°, was isolated during the recrystallizations of the desired dibromide. The infrared spectrum of this dibromide was identical with the compound of m.p. 115–116°.

Attempted Solvolysis of the Dibromide V.—A solution of 64 mg. of V in 4 ml. of acetone was treated with 0.35 ml. of water and a "spatula tip" of sodium bicarbonate. The mixture was allowed to stand for 10 days at room temperature, the bicarbonate was filtered, and the acetone filtrate was taken to dryness. Extraction of the residue with petroleum ether gave a residual yellow oil (3 mg.) that was washed with water. The infrared spectrum of this oil showed λ_{max} 5.70 (C=O) and 2.72 μ (OH) which indicated that some ring opening had occurred even under these relatively mild conditions. The petroleum ether extract consisted of unchanged dibromide V.

Preparation of 0.5% Lithium Amalgam.[8,24]—The procedure described by Criegee and Louis[8] gave a nonhomogeneous mixture of solid and liquid amalgams. A more uniform product was obtained by shaking 2 g. of lithium with 400 g. of mercury for 4 hr. at 200–218° in an evacuated steel bomb. The solid amalgam thus obtained was separated from the liquid amalgam, which was discarded, and stored in a screw cap bottle.

Debromination of the 1,2-Dibromo Compound(V) with Lithium Amalgam.—A mixture of 0.50 g. (1.37 mmoles) of the dibromide V and 7.8 g. of 0.5% lithium amalgam (100% excess) in 80 ml. of anhydrous ether was shaken at room temperature for 20 hr. and then filtered; the mercury residue was also shaken with ether. The combined ether solutions, orange-red in color, were washed thoroughly with water, dried, and brought to dryness *in vacuo* at 25°. The residual, nonbromine-containing oil, 0.280 g. (100%), resisted all attempts to effect its purification. The infrared spectrum of this crude oil was very similar to that of a polystyrene film. Although the two spectra were identical in the 2.5–7-μ region, the product oil showed a few additional bands: 7.46 (m), 8.90 (s), 11.18 (w), and 11.49 μ (w). The ultraviolet spectrum of the oil showed maxima at 269 and 310 mμ.

The same oil was isolated when debromination was carried out in the presence of cyclopentadiene which was used as a reagent to trap any transiently formed 1,2-diphenylcyclobutadiene. Finally, similar results were again observed when debromination was carried out under the conditions used by Cava and Napier[28] to dehalogenate 1,2-dibromobenzocyclobutene.

Debromination of the Dibromide V with Nickel Carbonyl.—This experiment was carried out under a slow stream of dry nitrogen to remove carbon monoxide as liberated. Nickel carbonyl (0.7 ml.) was distilled into a cooled flask (−70°) that contained 0.7 g. (1.92 mmoles) of the dibromide V in 25 ml. of anhydrous ether. The reaction mixture was refluxed and became purple in color after 10 min. The red-brown mixture, formed after a reaction period of 101.5 hr., was filtered to separate a brown solid which was washed with ether. This solid (0.692 g.) failed to melt below 400°. The residual crimson oil obtained from the original filtrate was identical (infrared analysis) with the crimson oil (175 mg.) isolated by chloroform extraction of the original brown solid product. The purple solid (517 mg.) which remained after the chloroform extraction was partially soluble in water to give a green solution. Insoluble in water was 47 mg. of a black solid, m.p. 310–320° dec.

The green aqueous solution was shown to contain nickel bromide by positive tests with silver nitrate and dimethylglyoxime. Quantitative analysis of the aqueous solution (dimethylglyoxime reagent) showed that it contained 1.92 mmoles (100%) of nickel bromide.

Extraction of the combined fractions of crimson oil (described above) with petroleum ether gave a yellow solution and an insoluble red-brown solid. Attempted crystallization of the latter afforded only an oil. The yellow petroleum ether extract produced an intractable orange powder that showed strange behavior when a melting point determination was carried out; *i.e.*, it darkened and sintered at 100–120°, then melted at 165–180° and 250–260°.

Reaction of the dibromide V with nickel carbonyl for 65.5 hr. produced 74% of an equivalent of nickel bromide.

In contrast to the foregoing, reaction in a sealed tube of 1.24 g. of the dibromide V with 1 ml. of nickel carbonyl in 50 ml. of ether for 21 hr. at 25° and 42 hr. at 38–40° resulted in 89% recovery of unchanged dibromide and the formation of an intractable orange solid.

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(28) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1705 (1957).