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The Preparation, Lithium Aluminum Hydride Reduction, and Electronic Spectra of Halogen-substituted 3,4-Bis(diphenylmethylene)-cyclobutenes and -cyclobutanes

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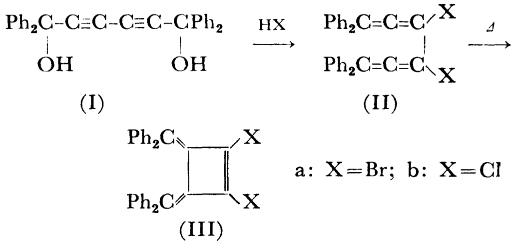
The title compounds were prepared, and their physical and chemical properties were investigated. The reduction of the cyclobutenes with lithium aluminum hydride afforded halogen-free cyclobutane. The mechanism of the reduction is discussed. The cyclobutenes showed their K-bands in a wavelength region *ca.* 100 nm shorter than in the cases of the corresponding cyclobutanes. Furthermore, the K-band of the cyclobutenes is comparable to that of 1-phenylbuta-1,3-diene. On the basis of the electronic spectral data, a puckered structure was postulated for the cyclobutenes.

Molecular orbital calculations have indicated that dimethylenecyclobutene has a delocalization energy of 1.21 β, which is almost equal to that of cyclobutenedione, 1.24 β.[1–3] Those calculated values, however, might not always show the stability or aromaticity of such a small-ring system, since calculations are carried out without consideration of any ring-strain factor.

Some anomalous ultraviolet spectral data of dimethylenecyclobutenes have been discussed. Since the two strong absorption bands of dimethylenecyclobutenes having no conjugated substituents, 209—213 and 245—249 nm, are comparable to those of 1,2-dimethylenecyclobutane, 237, 246, and 255 (sh) nm, it has been suggested that dimethylenecyclobutene is better viewed as a cross-conjugated diene rather than as a conjugated triene.[3–5] On the other hand, the absorption bands of 1,2-diphenyldimethylenecyclobutene, 237, 262, and 328 nm, are not derivable by the simple overlap of the spectra of dimethylenecyclobutane and *cis*-stilbene, 285 nm.[3,6,7]

The discrepancy of the calculated delocalization energy and the spectral data of dimethylenecyclobutene probable arises because of the *endo*-double bond's causing ring strain. In order to clarify the nature of such *endo*-double bonds, we have studied the electronic spectra and lithium aluminum hydride (LAH) reduction of the title compounds (III—X). Electronic spectral studies of those compounds have shown that bis(diphenylmethylene)cyclobutanes (IV, V, VII, IX and XII) absorbed at a much longer wavelength region, *ca.* 390 nm, than did bis(diphenylmethylene)-cyclobutenes (III, VIII and X) (*ca.* 290 nm). The reduction of the compounds of both series by LAH afforded bis(diphenylmethylene)cyclobutane (XII). Studies of the reduction mechanism, disclosed that the reduction of the *endo*-double bond of III and X to afford XII proceeds by way of competing addition and elimination processes.



Scheme 1

Preparation of Compounds. The treatment of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (I) with hydrohalogeno acid in acetic acid at about 0°C afforded 3,4-dihalo-1,1,6,6-tetraphenylhexa-1,2,4,5-tetraene (II).[*1] By heating a benzene solu-

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[1] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Amer. Chem. Soc.*, **74**, 4579 (1952).

[2] S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **34**, 1336 (1959).

[3] M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York and London (1967), pp. 157—179.

[4] A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, **1961**, 332.

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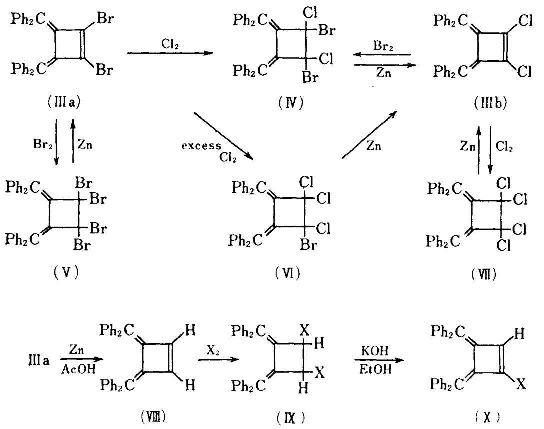
[6] A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

[7] A. T. Blomqist and Y. C. Meinwald, *ibid.*, **79**, 5317 (1957).

[*1] The preparation of IIa and its transformation to 2,5,6,6-tetraphenyl-3-bromofulvene by protonation, accompanied by the cyclization and migration of phenyl, have been reported in a preliminary communication: M. Higashi, F. Toda and K. Akagi, *Chem. Ind.* (London), **1969**, 491.

tion of II under reflux for 1 hr in a nitrogen atmosphere, a cyclization product, 1,2-dihalo-3,4-bis(diphenylmethylene)cyclobutene (III), was obtained in a quantitative yield. The IIIa and IIIb thus obtained showed the medium band of the *endo*-double bond at 1510 and 1530 cm^{-1} respectively, in addition to the weak band of the *exo*-double bond at 1660 cm^{-1}. The method of preparing III from II is comparable to that used for preparing dimethylenecyclobutene from 1,5-hexadiyne by pyrolysis at 350°C.[8] The reaction is believed to proceed through an intermediate diallene.[8]



a: X=Br; b: X=Cl

Scheme 2

The addition of bromine to IIIa and that of chlorine to IIIb in chloroform afforded tetrabromide (V) and tetrachloride (VII) respectively, in almost quantitative yields. Heating the tetrahalides with zinc powder in ethanol gave the corresponding dihalides (III) quantitatively. The action of chlorine on IIIa, which affords mainly monobromotrichloride (VI) (71%), is in contrast to that of bromine on IIIb, which gives dibromodichloride (IV). The addition of chlorine, however, under carefully-controlled conditions afforded mainly IV. Both IV and VI afforded IIIb when treated with zinc powder in boiling ethanol. Since the cross-addition reactions of IIIa and IIIb afforded the same product, IV, it is clear that the addition occurs on the *endo*-double bond. Furthermore, the structures of the tetrahalides (IV, V, VI, and VII) were determined on the basis of the electronic spectral data: those data showed that all the tetrahalides absorbed at nearly the same region, 400—388 nm (Table 2).

It has been reported[3,9] that the reduction with zinc powder of the tetrachloride (VII, mp 202°C) prepared by the thermal dimerization of 1,1-diphenyl-3,3-dichloropropadiene afforded benzophenone, but not cyclobutene (IIIb). This finding differs widely from the present observation that VII (mp 210—211°C) was easily dehalogenated with zinc powder to IIIb.

Bis(diphenylmethylene)cyclobutene (VIII), 3,4-dihalo-bis(diphenylmethylene)cyclobutane (IX). and 1-bromo-3,4-bis(diphenylmethylene)cyclobutene (X) were successively prepared from IIIa by the manner shown in Scheme 2. Adding an equimolar amount of bromine to a chloroform solution of VIII at room temperature afforded IXa in an 82% yield. The reaction of VIII with an excess of chlorine afforded IXb in a 36% yield, together with the tetrachloride (VII) and an unidentified tetrachloride (mp 183—184.5°C) in 18 and 26% yields respectively. The tetrachloride (VII) must be produced by the chlorine substitution on the IXb initially formed, since the same treatment of IXb with chlorine yielded VII.

The structure of IX was determined by comparing its NMR spectral data with those reported for the same compound which had been prepared by the dimerization of 1,1-diphenyl-3-halopropadiene.[10,11] The τ-values of the methyne proton signal of IXa (mp 145—146°C), 4.85, and of IXb (mp 189—190°C), 4.96, were almost the same as the reported values for IXa (mp 143—144°C), 4.87[10], and for the *cis*-isomer of IXb (mp 191—192°C), 4.98.[11] Since the *cis*-addition of halogen to olefin is unlikely, dihalide (IX) must have a *trans*-geometry. Therefore, the reported *cis*-geometry of the dichloride (IXb)[11] is doubtful. After our work had been finished, the fact that the *cis*-geometry of IXb is erroneous was reported.[12] Therefore, the reaction of IX with base to afford X proceeds by means of *cis*-elimination.

Few additions of halogen to the *endo*-double bond of dimethylenecyclobutene have been known. It has, however, been reported[13] that the addition of chlorine to 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene to afford perchloromethylenecyclopentene probably proceeds *via* the intermediate 1,1,2,2-tetrachloro-3,4-bis(dichloromethylene)-cyclobutane initially produced by the addition of chlorine to the *endo*-double bond.

Reduction by Lithium Aluminum Hydride. Heating a mixture of IIIa, IIIb or Xa, and LAH

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[8] W. D. Huntsman and H. J. Wristers, *ibid.*, **85**, 3307 (1963).

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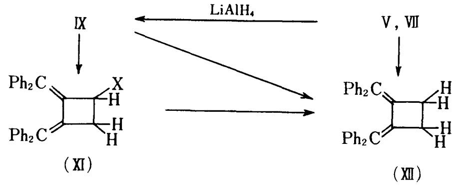
THF-ether under reflux for 2 hr afforded 1,2-bis-(diphenylmethylene)cyclobutane (XII) and 2,3-bis(diphenylmethylene)-1,4-butanedial (XVIII) in the yields summarized in Table 1. In order to clarify the reaction mechanism, V, VII, and IXa were also treated with LAH under the same conditions as above, but this yielded XII, not XVIII. By the same treatment, however, VIII afforded XVIII quantitatively. Those results are also shown in Table 1.

TABLE 1. YIELDS (%) OF THE REDUCTION PRODUCTS

Product	Reactant						
	IIIa	IIIb	Xa	VIII	V	VII	IXa
XII	33	41	30	—	71	67	78
XVIII	8	9	15	100	—	—	—

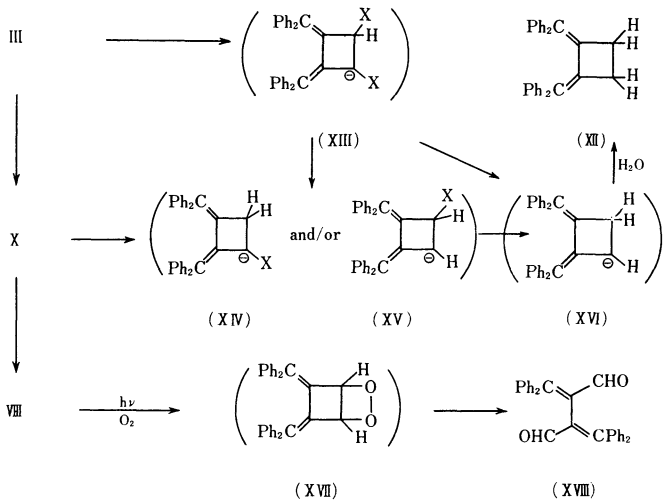
The transformation of V, VII, and IX into XII may be due to direct and/or successive substitution, as is shown in Scheme 3, since it has been well established[14,15] that halogen at an allylic position is easily reduced by LAH. On the other hand, the reduction of III and X to afford XII and XVIII must proceed by the following two competing paths. One consists of addition followed by substitution, such as III→XIII→XII and X→XIV (and/or XV)→XII. The other one consists of substitution, III→X→VIII, finally yielding the photooxidation product XVIII, probably *via* the cyclic intermediate (XVII). It is clear that the VIII formed initially by the substitution is converted to XVIII during the procedure of isolation, since it has been reported that VIII is easily photooxidized into XVIII even in the course of recrystallization from a usual organic solvent,[16] and since the same treatment of VIII with LAH afforded XVIII quantitatively. The above speculation on the two competing paths is further supported by the observation that the reduction of X afforded XVIII in a yield about twice that of the XVIII obtained from III, Table 1.



Scheme 3

Since no LAH reduction of carbon-carbon double bonds has yet been reported, except where the double bond is conjugated with an electronegative group, such as carbonyl, nitro, or cyano, the present results show an anomalous reactivity of the strained *endo*-double bond of III and X. However, the results of LAH reduction differ from those of the sodium borohydride reduction[16] of IIIa in ethanol to Xa by the addition-elimination process.

Electronic Spectra. The K-bands of the electronic spectra are summarized in Table 2. Those data show distinct difference in the absorption maxima between cyclobutene (III, VIII, or X) and cyclobutane (IV, V, VI, VII, IX, or XII). The former, formally conjugated triene, absorbs at a wavelength region shorter by about 100 nm than the latter, conjugated diene. It is



Scheme 4

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[14] R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3738 (1948).

[15] L. F. Hatch and R. H. Perry, *ibid.*, **71**, 3262 (1949).

[16] F. Toda, M. Higashi and K. Akagi, *Chem. Commun.*, **1969**, 1219.

TABLE 2. K-BANDS OF 3,4-BIS(DIPHENYLMETHYLENE)-CYCLOBUTENES AND -CYCLOBUTANES IN CHLOROFORM

K-Band	Cyclobutenes				Cyclobutanes					
	IIIa	IIIb	Xa	VIII	V	IV	VI	VII	IXa	XII
λ_{max} (nm)	290	285	285	280	400	395	390	388	378	357
$\varepsilon_{max} \times 10^{-2}$	364	364	306	287	162	140	159	159	145	209

very clear that the cyclobutene is not to be viewed as a conjugated triene, since the K-band of the cyclobutene differs widely from those of such conjugated trienes as *trans*-1,6-diphenyl-[17] and *trans*-1,1,6,6-tetraphenyl-hexa-1,3,5-triene.[18] 358 and 370 nm respectively.

Since the K-band of the cyclobutane, 357—400 nm, is comparable to those of 1,4-diphenyl-[19] and 1,1,4,4-tetraphenyl-buta-1,3-diene,[20] 328 and 342 nm, respectively, the cyclobutane can be considered as a conjugated diene. On the other hand, the K-band of cyclobutene, 284—290 nm, is comparable to that of 1-phenylbuta-1,3-diene,[21] 283 and 308 nm, rather than to those of 1,4-diphenyl- and 1,1,4,4-tetraphenyl-buta-1,3-diene.

The above data of cyclobutene can reasonably be interpreted by assuming the puckered structure shown in Fig. 1, in which one diphenylmethylene group is out of the plane containing the other diphenylmethylene and the *endo*-double bond. It is not unreasonable to assume that the four-membered ring with the large ring strain, which is due to the combination of the *endo*-double bond and to steric crowding among the four phenyl rings, is stabilized, with relaxation from the steric crowding among the four phenyl rings by means of the puckering. Recently, a similar puckered structure of a cyclobutenone derivative has been reported.[22]

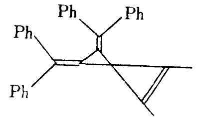

Fig. 1. Puckered structure of 3,4-bis(diphenylmethylene)cyclobutenes.

Experimental

All the melting points were uncorrected. The electronic spectra were measured in chloroform on a Hitachi spectrophotometer, model 124. The infrared spectra were recorded on a grating spectrophotometer, IR-G, of the Japan Spectroscopic Co. The NMR spectra were recorded in deuterochloroform on a Japan Electron Optics Laboratory H-100 spectrometer, TMS being used as the internal standard.

Thermal Isomerization of II into 1,2-Dihalo-3,4-bis(diphenylmethylene)cyclobutene (III). A solution of IIa* in benzene was heated under reflux in a nitrogen atmosphere for 1 hr. The crude crystals obtained by the subsequent evaporation of the solvent were recrystallized from ethyl acetate to afford IIIa as colorless needles in a practically quantitative yield; mp 190—191°C. IR (CHCl$_3$), 1510 cm^{-1} (C=C); the NMR spectrum showed only aromatic protons.

Found: C, 66.97; H, 3.49; Br, 29.41%; mol wt (benzene), 551. Calcd for $C_{30}H_{20}Br_2$: C, 66.67; H, 3.70; Br, 29.58%; mol wt, 540.

The chloro-analog (IIb) afforded IIIb quantitatively when treated like IIa; mp 195°C. IR (CHCl$_3$), 1530 cm^{-1} (C=C).

Found: C, 80.01; H, 4.25; Cl, 15.99%; mol wt (benzene), 455. Calcd for $C_{30}H_{20}Cl_2$: C, 79.84; H, 4.44; Cl, 15.72%; mol wt, 450.9.

Addition of Halogen to III. An equimolar amount of bromine was added to, or an equimolar amount of chlorine was bubbled through a stirred solution of III in chloroform at room temperature. After the subsequent evaporation of the solvent, curde crystals were recrystallized from ethyl acetate, affording the corresponding tetrahalide (IV, V or VII) almost quantitatively in all cases. All the tetrahalides are orange yellow prisms. The melting points and analytical data of those tetrahalides were as follows: IV, mp 208—209°C (dec).

Found: C, 58.86; H, 3.21%. Calcd for $C_{30}H_{20}Br_2Cl_2$: C, 58.92; H, 3.27%. V, mp 203—204°C (dec).

Found: C, 51.18; H, 2.73%. Calcd for $C_{30}H_{20}Br_4$: C, 51.43; H, 2.85%. VII, mp 210—211°C (lit[9], mp 202°C).

Found: C, 69.29; H, 3.60%. Calcd for $C_{30}H_{20}Cl_4$: C, 68.98; H, 3.87%. When IIIa was treated with an excess of chlorine, monobromotrichloride (VI) was obtained as the main product. An excess of chlorine was bubbled through a solution of IIIa (1.0 g, 1.85 mmol) in chloroform (10 m*l*) at room temperature. The residue obtained on evaporation was recrystallized from ethyl acetate to afford VI; 0.88 g (71%); mp 179—181°C.

Found: C, 63.51; H, 3.43%. Calcd for $C_{30}H_{20}BrCl_3$: C, 63.77; H, 3.54%.

The treatment of V and VII with zinc powder in boiling ethanol for 5 min afforded IIIa and IIIb respectively. By a similar treatment, both IV and VI afforded IIIb.

Preparation of 3,4-Bis(diphenylmethylene)-cyclobutene (VIII). A mixture of IIIa (1.08 g, 2 mmol), zinc powder (1 g), and glacial acetic acid (30 m*l*) was heated under reflux for 30 min. An insoluble

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[17] K. W. Hausser, R. Kuhn and A. Smakula, *Z. phys. Chem.*, **B29**, 384 (1935).

[18] F. Toda and H. Tani, This Bulletin, **37**, 915 (1964).

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[22] S. M. Krueger, J. A. Kapecki, I. C. Prul and J. E. Baldwin, *J. Chem. Soc.*, *B*, **1969**, 796.

solid was then removed by decantation. After the organic layer had been cooled, colorless needles which speararated out were collected by filtration, washed with water, and dried to give VIII; 0.61 g (80%); mp 182°C. NMR, 2.68 (m, Ph, 10H), 2.94 (s, =CH, 2H) and 3.16τ (m, Ph, 10H). The analytical sample was made by recrystallization from ethyl acetate in the dark, since VIII was easily photooxidized in daylight during the course of the recrystallization into the dialdehyde (XVIII). Upon the recrystallization, however, its mp did not change.

Found: C, 93.60; H, 5.68%. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

Photooxidation of VIII into 2,3-Bis(diphenylmethylene)-1,4-butanedial (XVIII). A solution of VIII (0.382 g, 1 mmol) in ethyl acetate (20 m*l*) was irradiated using a high-pressure Hg-lamp under oxygen for 1 hr. The curde product obtained on the evaporation of the solvent was recrystallized from ethyl acetate to yield XVIII, 0.29 g (70%), as pale yellow rhombs; mp 208.5°C. λ_{max}, 300 (16100) and 335 sh nm (ε, 11600); IR ($CHCl_3$), 2870 and 2750 (CHO), 1670 and 1655 (CO), and 1580 and 1555 cm^{-1} (C=C); NMR, 0.45 (s, CHO, 2H) and 2.90τ (m, Ph, 20H).

Found: C, 86.65; H, 5.39%. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%.

Addition of Halogen to VIII. An equimolar amount of bromine (0.38 g) was added to a solution of VIII (0.8 g, 2.1 mmol) in chloroform (15 m*l*) at room temperature. After the subsequent removal of the solvent by distillation, the crude crystals which remained were recrystallized from ethanol to afford IXa, 0.95 g (82%), as yellow rhombs; mp 145—146°C (lit,[10] mp 143—144°C). NMR, 2.64 (s, Ph, 10H), 3.12 (s, Ph, 10H) and 4.85τ (s, CH, 2H).

Found: C, 66.73; H, 4.15%. Calcd for $C_{30}H_{22}Br_2$: C, 66.42; H, 4.06%.

Through a solution of VIII (0.5 g, 1.3 mmol) in chloroform (30 m*l*) an excess of chlorine was bubbled at room temperature. The residue obtained by the evaporation of the solvent was fractionated into three components by means of fractional recrystallization from acetone. The orange-yellow crystals which separated out initially were collected by filtration and recrystallized from acetone. The product was VIIb, 0.12 g (18%), the structure of which was identified by a comparison of its spectral data with those of an authentic sample prepared by the addition of chlorine to IIIb. The second crop obtained from the above filtrate was recrystallized from acetone to afford IXb as pale yellow needles; 0.21 g (36%); mp 189—190°C (lit,[11] mp 191—192°C): NMR, 2.72 (s, Ph, 10H), 3.22 (s, Ph, 10H) and 4.90τ (s, CH, 2H).

The acetone mother liquor which remained after the removal of VIIb and IXb was concentrated to dryness, and the residue was recrystallized from ethyl acetate to give an unidentified tetrachloride ($C_{30}H_{20}Cl_4$) as pale yellow needles; 0.18 g (26%); mp 183—184.5°C. λ_{max}, 245 (25000) and 288 nm (ε, 28800).

Found: C, 68.42; H, 3.60%. Calcd for $C_{30}H_{20}Cl_4$: C, 68.97; H, 3.83%.

Preparation of 1-Bromo-3,4-bis(diphenylmethylene)cyclobutene (Xa). A mixture of IXa (0.54 g, 1 mmol), potassium hydroxide (0.3 g), and ethanol (20 m*l*) was heated under reflux for 10 min. After cooling, the reaction mixture was decomposed with water, and the solid formed was filtered and washed with water. The dried solid was recrystallized from ethyl acetate-ethanol to afford Xa as colorless needles; 0.45 g (97%), mp 172—173°C (lit,[16] mp 172—173°C). NMR, 2.67 (m, ph, 10H), 2.80 (s, =CH, 1H) and 3.15τ (m, Ph, 10H). The UV (Table 1) and NMR spectral data were identical with those of an authentic sample prepared by the sodium borohydride reduction of IIIa according to the reported method.[16]

LAH Reduction of Halogen-substiuted 3,4-Bis(diphenylmethylene)cyclobutanes (V, VII, and IXa). To a solution of LAH (0.11 g, 3 mmol) in ether (15 m*l*) under nitrogen, a solution of V (0.62 g, 1 mmol) in tetrahydrofuran (10 m*l*) was added, drop by drop, over a period of 1 hr. Then, the mixture was boiled under reflux for 2 hr in a nitrogen atmosphere. After cooling, the reaction mixture was decomposed with water and then with hydrochloric acid, and diluted with ether. The organic layer was repeatedly washed with water and dried over sodium sulfate. The crude product obtained on the evaporation of the solvent was recrystallized from acetone to give XII; 0.27 g (71%): mp 179.5—180°C. NMR, 2.89 (s, Ph, 10H), 3.30 (s, Ph, 10H) and 7.16τ (s, CH_2, 4H).

Found: C, 93.29; H, 6.36%. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

Upon similar treatment, VII and IXa also afforded XII; the yields are shown in Table 1.

LAH Reduction of Halogen-substituted 3,4-Bis(diphenylmethyene)cyclobutenes (IIIa, IIIb, and Xa). A solution of IIIb (1.0 g, 2.22 mmol) in tetrahydrofuran (20 m*l*) was treated with a solution of LAH (0.25 g, 6.66 mmol) in ether (30 m*l*) by the same procedure as that employed for V. After decomposition with water and then with hydrochloric acid, the product was taken up in ether. The ether layer was repeatedly washed with water and dried over sodium sulfate. The residue obtained on the evaporation of the solvent was fractionated into two compounds by fractional recrystallization from acetone. The yellow prisms which crystallized initially were recrystallized from acetone to afford XVIII; 0.74 g (8%); mp 208.5°C. The structure was determined by a comparison of its spectral data with those of an authentic sample prepared by the photooxidation of VIII. The pale yellow crystals obtained by the concentration of the acetone mother liquor remaining after the isolation of XVIII were recrystallized from acetone to give XII; 0.28 g (33%); mp 179.5—180°C. The structure was determined by a comparison of its spectral data with those of an authentic specimen.

Upon similar treatment, IIIa and Xa afforded XII and XVIII in the yields shown in Table 1.

LAH Reduction of 3,4-Bis(diphenylmethylene)cyclobutene (VIII). The treatment of a solution of VIII (0.9 g, 2.36 mmol) in tetrahydrofuran (20 m*l*) with a solution of LAH (0.27 g, 7.0 mmol) in ether (20 m*l*) under the conditions employed for V and IIIb afforded XVIII; 0.98 g (100%).

The authors wish to express their thanks to Mr. Shoichi Kato for his elemental analyses and to Miss Toshiko Matsutomo for the measurement of the electronic spectra and molecular weights.