# The Reduction of 1,2-Dihalo-3,4-bis(diphenylmethylene)cyclobutenes by Lithium Aluminum Hydride

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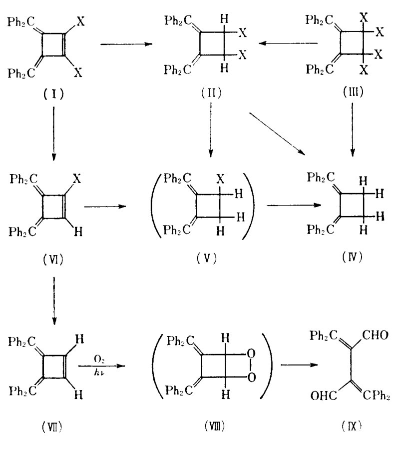
Even though its calculated delocalization energy (1.21$\beta$) is comparable to that of cyclobutenedione (1.24$\beta$),[1,2] it has been established[3,4] on the basis of ultraviolet spectral data that dimethylenecyclobutene is better viewed as a cross conjugated diene rather than as a conjugated triene. Since this is probably because of the *endo*-double bond's causing ring strain, an anomalous reaction of the bond can be expected.

In the course of our studies of the title compounds (I),[5] we have found that the *endo*-double bond of I is easily reduced by lithium aluminum hydride (LAH) to afford 1,2-bis(diphenylmethylene)cyclobutane (IV).[6,7] Since no LAH reduction of carbon-carbon double bond has yet been reported, except where the double bond is conjugated with an electronegative group such as carbonyl, nitro, or cyano, the present results would seem to show an anomalous reactivity of the *endo*-double bond of I.

A mixture of Ia[5] and three equivalents of LAH in ether-tetrahydrofuran (3 : 2 ratio) was heated under reflux in a nitrogen atmosphere for 2 hr. After cooling, the reaction mixture was decomposed with water and hydrochloric acid, and then extracted with ether. The ether layer was washed with water and dried over sodium sulfate. Fractional recrystallization from the acetone of the crude product obtained by the evaporation of the solvent afforded IV and 3,4-bis(diphenylmethylene)butanedial (IX) in 33 and 8% yields respectively. The spectral data of IV (mp 180°C); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 260 (23500), 357 nm ($\varepsilon$, 20900); NMR ($CDCl_3$) 2.89 (s, Ph, 10H), 3.30 (s, Ph, 10H), 7.16 $\tau$ (s, $CH_2$, 4H), and of IX (mp 208.5°C); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 300 (16100), 335 sh, nm ($\varepsilon$, 11600); IR ($CHCl_3$) 2870 and 2750 (CHO), 1670 and 1655 (CO), 1580 and 1555 cm$^{-1}$ (C=C); NMR ($CDCl_3$) 0.45 (s, CHO, 2H), 2.90 $\tau$ (m, Ph, 20H), were identical with those of the corresponding authentic samples prepared according to the previously-reported method.[7]



a: X=Br; b:X=Cl

Table 1. Yields (%) of the reduction products

| Product | Reactant | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ia | Ib | VIa | VII | IIa | IIIa | IIIb |
| IV | 33 | 41 | 30 | — | 78 | 71 | 67 |
| IX | 8 | 9 | 15 | 100 | — | — | — |

The yields of the reduction products, obtained by the same treatment as that employed for Ia, of 3,4-bis(diphenylmethylene)cyclobutenes (Ib,[5] VI[7] and VII[7]) and 3,4-bis(diphenylmethylene)-cyclobutanes (II[7] and III[8]) are summarized in Table 1.

The reduction of the cyclobutanes to afford IV may proceed by means of substitution processes. On the other hand, the reduction of the cyclobutenes into the two products can well be interpreted by two competing paths. One of them is the addition of hydride ion, followed by substitution, to afford IV finally. The other one is substitution to afford VII, which is photooxidized to IX, probably *via* VIII, during the course of isolation.

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