Reduction of 3,4-Bisdiphenylmethylene-1,2-dibromocyclobutene by Sodium Borohydride

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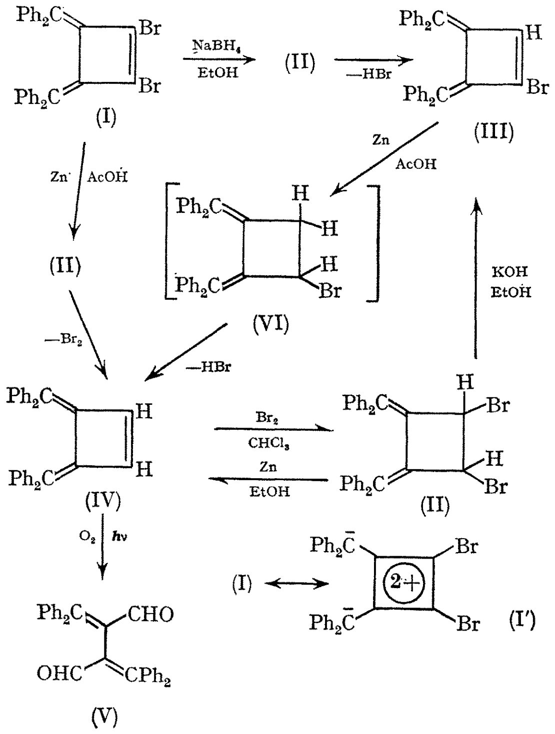
Summary The *endo*-double bond of the title compound is reduced on treatment with sodium borohydride in alcohol.

No sodium borohydride reduction of carbon–carbon double bonds has been reported, except where the double bond is conjugated with a carbonyl group.[1] We now report sodium borohydride reduction of the *endo*-double bond of the title compound (I).

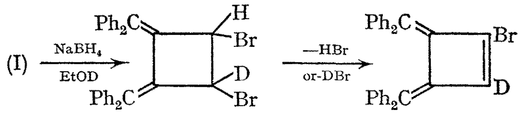
Heating (I)[2] and sodium borohydride in alcohol for 1 hr. afforded 3,4-bisdiphenylmethylene-1-bromo-cyclobutene (III) in quantitative yield as colourless leaflets [m.p. 172—173°; λ_{max} ($CHCl_3$) 285 (25,500) and 315 sh nm. (ϵ 17,300); n.m.r. ($CDCl_3$) τ 2·67 (m, Ph, 10H), 2·80 (s, =CH, 1H), and 3·15 (m, Ph, 10H)]. The reaction can be interpreted by assuming that the dihydro-derivative (II) is an intermediate.

Boiling a mixture of (I), zinc powder, and acetic acid for 30 min. afforded 1,2-bisdiphenylmethylenecyclobutene (IV) in quantitative yield as colourless needles [m.p. 182°; λ_{max} ($CHCl_3$) 280 (30,800) and 305 sh nm. (ϵ 24,600); n.m.r. ($CDCl_3$) τ 2·68 (s, Ph, 10H), 2·94 (s, =CH, 2H), and 3·16 (m, Ph, 10H)]. Further structural evidence for (IV) was provided by photo-oxidation in benzene to 2,3-bisdiphenylmethylenebutanedial (V) in 70% yield as pale yellow rhombs [m.p. 208·5°; λ_{max} ($CHCl_3$) 300 (16,100) and 335 sh nm. (ϵ 11,600); ν_{max} ($CHCl_3$) 2870 and 2750 (CHO), 1670 and 1655 (CO), and 1580 and 1555 cm.$^{-1}$ (C=C); n.m.r. ($CDCl_3$) τ 0·45 (s, CHO, 2H) and 2·90 (m, Ph, 20H)]. Addition of bromine to (IV) in chloroform at room temperature yielded 3,4-bisdiphenylmethylene-1,2-dibromocyclobutane (II) (82%) as pale yellow rhombs [m.p. 145—146°; λ_{max} ($CHCl_3$) 262 (24,500) and 378 nm. (ϵ 14,500); n.m.r. ($CDCl_3$) τ 2·64 (s, Ph, 10H), 3·12 (s, Ph, 10H), and 4·78 (s, CH, 2H)]. Martinet and Doupeux have reported[3] only a singlet signal at τ 4·87 for (II) (m.p. 143—144°) prepared by the thermal dimerisation of 3-bromo-1,1-diphenylpropadiene.



When (II) was heated in alcohol with potassium hydroxide for 5 min., (III) was produced quantitatively; hence, the reaction of (I) with sodium borohydride yielding (III) may proceed *via* (II). Further evidence for the intermediacy of (II) was obtained by the following experiment: the product obtained by sodium borohydride reduction of (I) in C_2H_5OD (99%) was shown to be a mixture of 60% (III) and 40%

[$^2H_1$]-(III) by quantitative analysis of the signal of olefinic proton at τ 2·80. This is the first observation of sodium borohydride reduction of carbon–carbon double bond. It is not unreasonable to consider that the contribution of cyclobutadiene dication (I′) to the resonance of (I) favours reduction by hydride ion. The overall reaction of (I) with sodium borohydride to (III) also represents a novel reduction of vinylic bromide to olefin. However, neither (III) nor (IV) was reduced by sodium borohydride under the same reaction conditions employed for (I).



[$^2H_1$]-(III)

+(III)

The reaction of (I) with zinc in acetic acid yielding (IV) can also be interpreted as reduction followed by debromination, since the heating (II) with zinc in alcohol readily afforded (IV). The same treatment of (III) with zinc in acetic acid yielded (IV). A possible mechanism is the dehydrobromination of (VI) produced by the reduction of (III).

On the other hand, the hydrogenation of (I) over Raney nickel at room temperature afforded 1,2-bisdiphenylmethylenecyclobutane as colourless needles [m.p. 180°; n.m.r. ($CDCl_3$) τ 2·89 (s, Ph, 10H), 3·30 (s, Ph, 10H), and 7·16 (s, CH_2, 4H) and 2,3-bisdiphenylmethylenebutane as colourless needles [m.p. 151°; n.m.r. ($CDCl_3$) τ 3·00 (m, Ph, 20H) and 8·04 (s, CH_3, 6H)] in various yields depending on the reaction condition employed.

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[1] For a review see E. Schenker, "Newer Methods of Preparative Organic Chemistry", ed. W. Foerst, vol. IV, Academic Press, New York, 1968, p. 247.

[2] F. Toda, H. Ishihara, and K. Akagi, *Tetrahedron Letters*, 1969, 2531.

[3] P. Martinet and H. Doupeux, *Compt. rend.*, 1965, **261**, *C*, 2498.