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REACTION OF SODIUM BIS(2-ALKOXYETHOXY)ALUMINIUM HYDRIDES

V*. REDUCTION AND REDUCTIVE METHYLATION OF AROMATIC CONJUGATED HYDROCARBONS BY SODIUM BIS(2-METHOXYETHOXY)-ALUMINIUM HYDRIDE**

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Summary

Reduction (80°) and reductive methylation (160—175°) of some geminal diphenyl-substituted olefins and conjugated dienes by sodium bis(2-methoxyethoxy)aluminium hydride are described. 1,1-Diphenylethylene was reduced to give 1,1-diphenylethane as a sole product, while reductive methylation gave 2,2-diphenylpropane in high yield. Similarly, 1,2,2-triphenylpropane was obtained from 1,1,2-triphenylethylene. Reductive methylation of cyclohexylidene diphenylmethane took place with partial rearrangement of the exocyclic double bond to give 1-(1-cyclohexenyl)-1,1-diphenylethane as the main product, which was accompanied by cyclohexyldiphenylmethane and 1-cyclohexyl-1,1-diphenylethane. 1,1,4,4-Tetraphenyl-1,3-butadiene at 175° underwent a new type of a reductive C—C bond cleavage leading to a 88/12 mixture of 2,2-diphenylpropane and 2,2-diphenylbutane, both formed by methylation of cleavage fragments. The reduction of 6,6-diphenylfulvene afforded a mixture of isomers, which from the NMR and mass spectra, were identified as 1-(diphenylmethyl)-1,3-cyclopentadiene (47%), 2-(diphenylmethyl)-1,3-cyclopentadiene (47%) and 5-(diphenylmethyl)-1,3-cyclopentadiene (6%). Reductive methylation of this mixture or of 6,6-diphenylfulvene alone gave a mixture of 1-(1,3-cyclopentadien-1-yl)-1,1-diphenylethane, 1-(1,3-cyclopentadien-2-yl)-1,1-diphenylethane and 1-(1,3-cyclopentadien-5-yl)-1,1-diphenylethane in a similar ratio. When 9-hydroxy-9-methylfluorene was used in place of biphenylene ethylene, hydrogenolytic methylation by the hydride afforded 9,9-dimethylfluorene in high yield. In all cases the methylation reaction is regioselective, and takes place exclusively at the phenyl-activated benzylic carbon atom of acidic hydrocarbons.

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* For part IV see ref. 1.

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Introduction

We recently described the products obtained from the reaction of some diaryl ketones, polycyclic aromatic ketones, polycyclic quinones, or polycyclic aromatic hydrocarbons with sodium bis(2-methoxyethoxy)aluminium hydride, $NaAlH_2(OCH_2CH_2OCH_3)_2$, at elevated temperatures. In a one-step reaction of benzophenone with the hydride, 2,2-diphenylpropane was formed in high yield, in addition to 1,1-diphenylcyclopropane [2,3]; benzhydrol, diphenylmethane, 1,1,2,2-tetraphenylethane and 1,1-diphenylethane were found as intermediates in this reaction [3]. Similar reactions involving anthracene, 9,10-dihydroanthracene, or anthraquinone gave 9,9,10,10-tetramethyl-9,10-dihydroanthracene as the main product along with *spiro*-cyclopropane-1,9'-9',10'-dihydroanthracene and *spiro*-cyclopropane-1,9'-10'-methyl-9',10'-dihydroanthracene [1]. 9-Fluorenone gave a high yield of 9,9-dimethylfluorene, but instead of the expected *spiro*-cyclopropane derivative, 9-ethyl-9-methylfluorene was obtained as a by-product [3]. It is thought that methyl and 2-oxyethoxy radicals (generated by a thermally initiated cleavage of CH_3—O bond of the 2-methoxyethoxy group of the hydride molecule) and the corresponding intermediate aryl-activated benzylic anions participate in the formation of these methylated, cyclopropylated, or ethylated products [3]. The facile reduction of anthracene by sodium bis(2-methoxyethoxy)aluminium hydride, which takes place, as shown by the electronic spectra, via the formation of the corresponding radical anions, dianions, and finally 9-hydroanthracene anions [1] stimulated us to study the reactions of aromatic olefins with this hydride. We now report on the reduction and reductive methylation of geminal diphenyl-substituted olefins and conjugated diolefins, 1,1-diphenylethylene, 1,1,2-triphenylethylene, cyclohexylidene diphenylmethane, 1,1,4,4-tetraphenyl-1,3-butadiene, and 6,6-diphenylfulvene with sodium bis(2-methoxyethoxy)aluminium hydride.

Results and discussion

Rapid and quantitative reaction of 1,1-diphenylethylene (I) occurs with sodium bis(2-methoxyethoxy)aluminium hydride to give 1,1-diphenylethane (II) (eqn. 1); the reaction conducted in refluxing benzene (80°, 1.5 h) to complete consumption of the olefin is analogous to that between I and diisobutylaluminium hydride (114°, 6h) [4]. In the reaction of I with sodium bis(2-methoxyethoxy)-aluminium hydride at 160° (eqn. 2), however, II was formed as an intermediate and was methylated by the hydride exclusively at the phenyl-activated benzylic carbon atom to give 2,2-diphenylpropane (III) as the final product, isolated in 90% yield. In contrast to the methylation of diphenylmethane by the hydride which always gave, along with III and 1,1-diphenylcyclopropane, a certain amount of the corresponding dimer, i.e., *sym*-tetraphenylethane [2], reductive methylation of I gave no dimeric product, 1,1,4,4-tetraphenylbutane. The stepwise character of both the reduction and the methylation reaction, which presumably proceed through the intermediate state A, is clearly demonstrated by the time-concentration dependence of I, II and III during the early stages of the transformation of I. (Fig. 1). Similar course was observed with the reductive methylation of 1,1,2-triphenylethylene (IV), which proceeded under the same conditions but at a

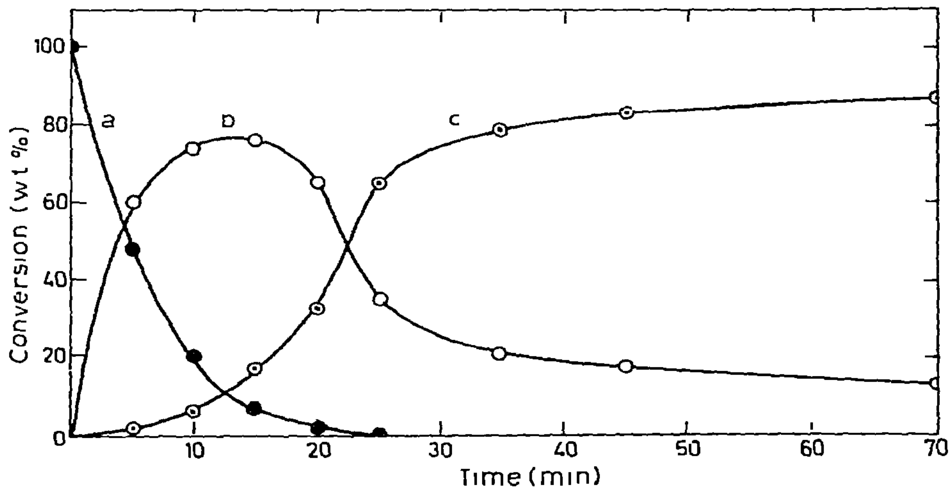
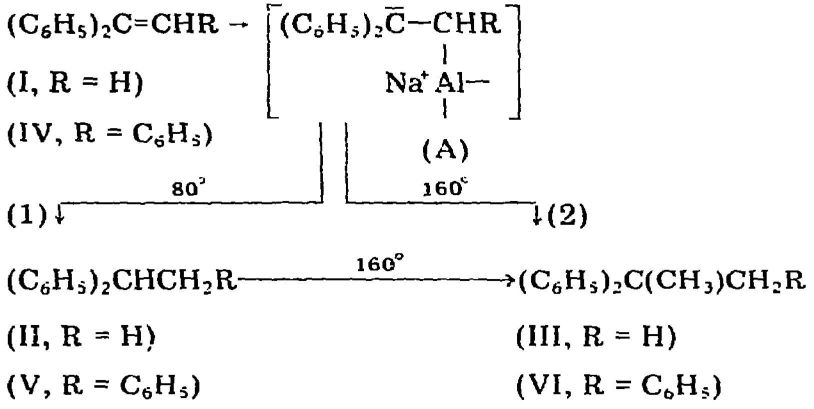
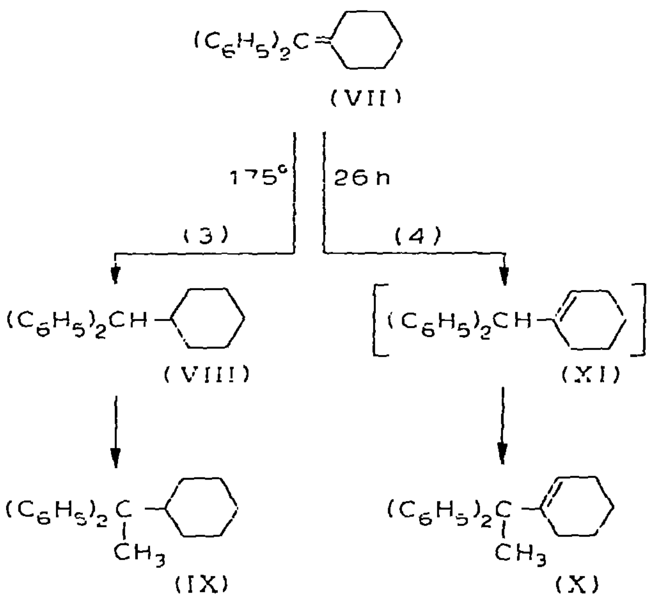


Fig. 1. Dependence on time of the concentration of 1,1-diphenylethylene (a), 1,1-diphenylethane (b) and 2,2-diphenylpropane (c) in the early stages of the reductive methylation of 1,1-diphenylethylene by sodium bis(2-methoxyethoxy)aluminium hydride (1/3 mole ratio) in n-propylbenzene at 160°.

somewhat lower rate, to give 1,2,2-triphenylpropane (VI) in 75% yield, along with the intermediate 1,1,2-triphenylethane (V) (10%).



Cyclohexylidene diphenylmethane (VII), for which, in contrast to I or IV, a C=C bond shift is possible, reacts in the presence of sodium bis(2-methoxyethoxy)aluminium hydride by two concurrent pathways. When the reaction in refluxing *p*-cymene was stopped at 97% conversion of VII and the products were analyzed by GLC—mass spectrometry, there was obtained, in addition to the expected cyclohexyldiphenylmethane (VIII) (31%) and 1-cyclohexyl-1,1-diphenylethane (IX) (7%), (eqn. 3), a 42% yield of a new compound, which on the basis of the mass, NMR, and IR spectra, was identified as 1-(1-cyclohexenyl)-1,1-diphenylethane (X). Both the hydrocarbons VIII and X were isolated by preparative GLC from the product mixture. There is no doubt that (1-cyclohexenyl)diphenylmethane (XI), although not detected in the product mixture, is the precursor of X, and thus rearrangement of the exocyclic C=C bond takes place (eqn. 4) along



with the expected reduction of the C=C bond in the early stage of the transformation of VII*.

The possibility that all of the VII is rearranged to XI, and the saturated hydrocarbon VIII is formed by subsequent reduction of XI, can be ruled out because of the known resistance of the isolated C=C bond to reduction by sodium bis(2-methoxyethoxy)aluminium hydride [5]. On the contrary, the fact that the amount of X is approximately equal to that of VIII plus IX indicates that the reduction of VII to VIII and the rearrangement of VII to XI are equally favoured.

The absence of XI from the product mixture, which contains 3% of the starting material VII, and the formation of IX and X, rule out the possibility that the rearrangement of VII to XI occurs upon hydrolysis of the reaction mixture; such a rearrangement was observed during the hydrolysis of product mixture resulting from the reaction of certain aryl olefins with diisobutylaluminium hydride [4].

Carbinols are frequently used as starting materials for the preparation of the corresponding arylolefins and so an attempt was made to obtain 9,9-dimethylfluorene (XII) directly by interaction of sodium bis(2-methoxyethoxy)aluminium hydride with 9-hydroxy-9-methylfluorene, (XIII) (eqn. 5), rather than with biphenylene ethylene (XIV). The reaction proceeded via hydrogenolysis of XIII and subsequent methylation of the intermediate 9-methylfluorene (XV); pure XII was isolated in 84% yield.

An unexpected course of reaction was observed when 1,1,4,4-tetraphenyl-1,3-butadiene (XVI) was allowed to react with sodium bis(2-methoxyethoxy)aluminium hydride in refluxing *p*-cymene. Instead of the expected reductive methylation of XVI to 2,2,5,5-tetraphenylhexane (XVII) or possibly to 2,2,5,5-tetraphenyl-

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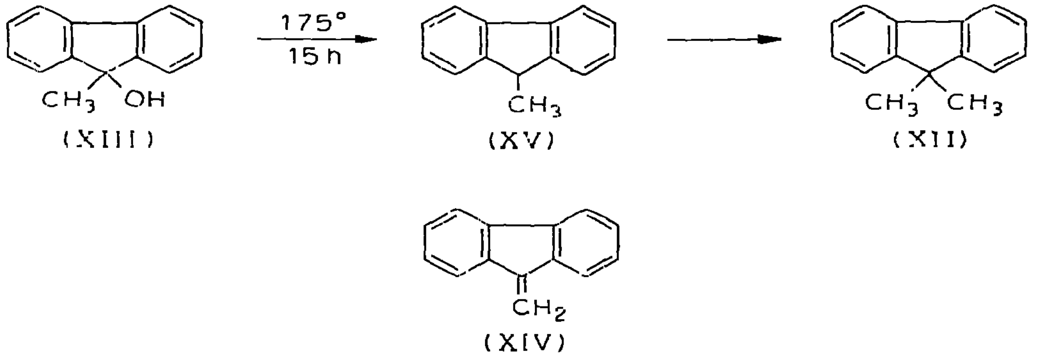
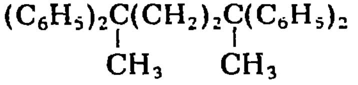
* While this work was in progress, Gold and Babad reported a similar C=C bond rearrangement: heating of β-methylstyrene with sodium bis(2-methoxyethoxy)aluminium hydride in refluxing toluene gave allylbenzene [5].



(5)

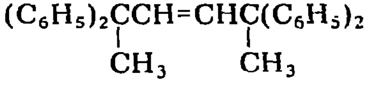
hex-3-ene (XVIII) there occurred a new type of reductive cleavage of the 1,3-diene system with simultaneous methylation of fragments, leading to a 88/12 mixture of III (50% yield) and 2,2-diphenylbutane (XIX) (6% yield) (eqn. 6). Approximately 50% of XVI was converted into undistillable polymeric products. Both III and XIX were isolated from the mixture by preparative GLC and unambiguously identified by GLC and IR spectra. Definite conclusions about the mechanism of the reaction of XVI with the hydride cannot yet be drawn, but by analogy to the other reactions considered above it can be assumed that the reduction of C=C

$$\underset{\text{(XVI)}}{(C_6H_5)_2C{=}CHCH{=}C(C_6H_5)_2} \xrightarrow[8\text{ h}]{175^\circ} \underset{\text{(III)}}{(C_6H_5)_2C(CH_3)_2} + \underset{\text{(XIX)}}{(C_6H_5)_2C(CH_3)C_2H_5} \qquad (6)$$



$$(C_6H_5)_2\underset{CH_3}{C}(CH_2)_2\underset{CH_3}{C}(C_6H_5)_2$$

(XVII)



$$(C_6H_5)_2\underset{CH_3}{C}CH{=}CH\underset{CH_3}{C}(C_6H_5)_2$$

(XVIII)

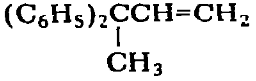
bonds is the initial step, and that 1,1,4,4-tetraphenylbutane (XX) is the intermediate undergoing the cleavage reaction. Thus XIX seems to arise from methylation of the fragment which is split off during the cleavage of the C_3—C_4 bond of XX, while III appears to be formed by C_2—C_3 bond cleavage of XX and subsequent methylation of the fragment; another source of III must be methylation of the diphenylmethine group [2, 3] resulting from the cleavage of the C_3—C_4 bond. The formation of III as the main product confirms the preferential cleavage of the C_2—C_3 bond.

If during the reaction of XVI with the hydride, 1,1,4,4-tetraphenyl-2-butene (XXI) were also formed, 3,3-diphenyl-1-propene (XXII) should also have been present among the intermediate products of its reductive cleavage; the methylation of XXII should then, by analogy to the formation of X from VII, give 3,3-diphenyl-1-butene (XXIII) as one of the cleavage products. However,

$$\underset{\text{(XX)}}{(C_6H_5)_2CH(CH_2)_2CH(C_6H_5)_2} \qquad \underset{\text{(XXI)}}{(C_6H_5)_2CHCH{=}CHCH(C_6H_5)_2}$$

$$(C_6H_5)_2CHCH{=}CH_2$$

(XXII)

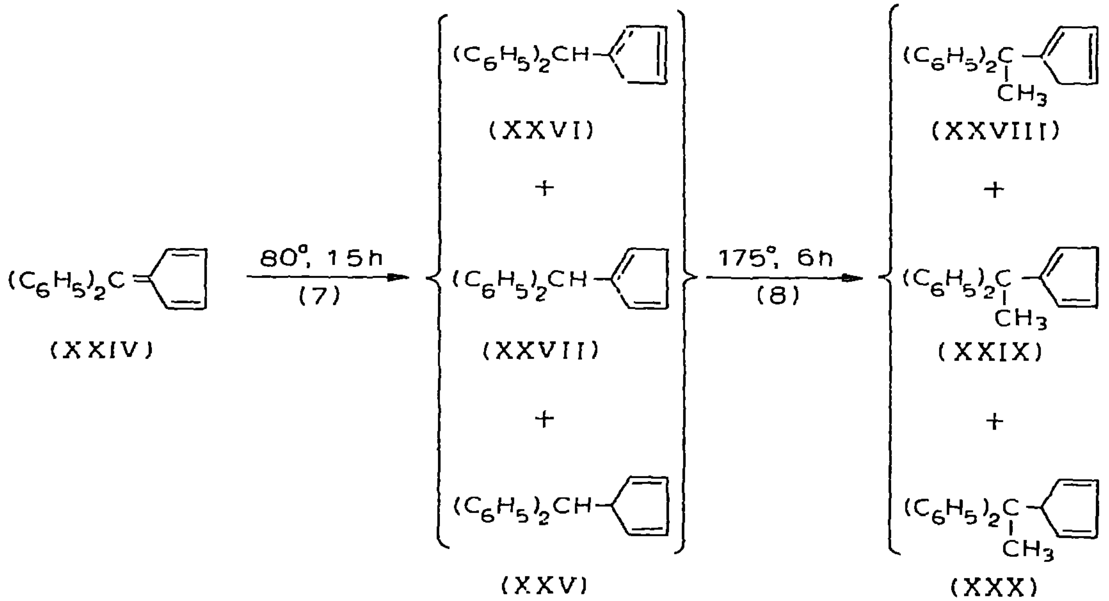


$$(C_6H_5)_2\underset{CH_3}{C}CH{=}CH_2$$

(XXIII)

XXIII has not been detected in the product mixture, and this suggests that XX is the sole product of the reduction in the early stages of the reaction of XVI with the hydride.

The smooth reduction of the exocyclic C=C bond in 6,6-diphenylfulvene (XXIV) (eqn. 7) by sodium bis(2-methoxyethoxy)aluminium hydride in refluxing benzene agrees well with the similar reaction of fulvene hydrocarbons with lithium aluminium hydride [6—8], diisobutylaluminium hydride [9] or sodium trimethoxyborohydride [10]. However, the melting point of our product (155.0—155.5°) differed significantly from that given for the compound (i) (m.p. 36.5°) prepared by the action of ethanol on 1,3-cyclopentadienylsodium [11], the compound (ii) (m.p. 36—38°) obtained by interaction of 1,3-cyclopentadienylsodium with diphenylmethyl bromide [12] and the compound (iii) (m.p. 124°) obtained by treatment of phenylnitromethylsodium with methiodide of *N,N*-dimethylaminomethylferrocene [13]. All the compounds (i), (ii) and (iii) were described in the literature as 5-(diphenylmethyl)-1,3-cyclopentadiene (XXV). The GLC of our product gave a single unsymmetrical peak and the mass spectrum (M^+ = 232 m/e) confirmed the reduction of the exocyclic C=C bond in XXIV. The NMR spectrum of our reduction product showed the presence of 10 aromatic, 1 methine and 5 cyclopentadienyl protons; the latter gave peaks at about τ 8.92, 7.22, 5.82 and 3.97, revealing the fluxional behaviour of the conjugated carbon—carbon double bond system in the substituted cyclopentadienes [14]. By comparison of the NMR spectrum with that of methylcyclopentadienes [15] our product is considered to be a mixture of three isomers differing in the position of the C=C bonds in the cyclopentadiene ring. The NMR spectrum indicates that 1-(diphenylmethyl)-1,3-cyclopentadiene (XXVI), 2-(diphenylmethyl)-1,3-cyclopentadiene (XXVII) and XXV are present in a ratio of 47/47/6. The vinylic isomers XXVI and XXVII present in a 1/1 ratio thus predominate, and the content of the thermodynamically unstable XXV does not exceed a few percent. A closely similar



ratio of analogous isomers was found in the equilibrated mixture of methylcyclopentadienes [14—17].

When the fulvene XXIV or the product mixture containing XXV-XXVII was subjected to methylation by the hydride in refluxing *p*-cymene (eqn. 8), a relatively unstable oily product was formed in 94% yield. The mass ($M^+ = 246$ *m/e*) and NMR spectra indicated that there was a mixture of isomers, identified as 1-(1,3-cyclopentadien-1-yl)-1,1-diphenylethane (XXVIII), 1-(1,3-cyclopentadien-2-yl)-1,1-diphenylethane (XXIX), and 1-(1,3-cyclopentadien-5-yl)-1,1-diphenylethane (XXX). The relative amounts of these isomers in the product of the methylation reaction, as indicated by the NMR spectrum, were approximately the same as those of the corresponding compounds XXV—XXVII in the product mixture resulting from reduction of XXIV by the hydride at 80° (eqn. 7).

The results discussed above show (a) a significant dependence of the course of the reduction by sodium bis(2-methoxyethoxy)aluminium hydride on the structure of the olefin or the conjugated diene hydrocarbons; (b) the high selectivity of the methylation reaction, leading in all cases to products exclusively methylated at the aryl-activated benzylic carbon atom.

The formation of s-butylbenzene and *p*-ethylisopropylbenzene from the n-propylbenzene and *p*-cymene, used as solvents in the reductive methylation reaction provides additional support for the previously proposed [1—3] homolytic character of the methylation reactions. The isolation of ethylene glycol from the products is in accordance with the expected cleavage of the CH_3—O bond of the 2-methoxyethoxy group of the hydride molecule in these reactions [3].

Experimental

General comments

The solutions of sodium bis(2-methoxyethoxy)aluminium hydride in n-propylbenzene and *p*-cymene were prepared from commercial benzene solution of the hydride (70%) (VCHZ-Synthesia, Kolín, Czechoslovakia) as previously described [3]. Hydrocarbon solvents were thoroughly dried over sodium wire and distilled immediately before use. The starting compounds I [18], IV [19], XVI [20], VII [21, 22] (NMR spectrum: CCl_4, HMDS reference: τ 2.64, 10H, phenyl protons; τ 7.52, 4H, $(CH_2)_2C=$; τ 8.17, 6H, $-CH_2-$), XXIV [23], and XIII [24], as well as II [3], III [3] and XIX [2] used as standards for GLC were synthesized by the published methods. The purity of all starting compounds, standards, and isolated products was checked by GLC. Infrared spectra were obtained on a Zeiss UR-20 spectrophotometer to an accuracy of ± 2 cm^{-1}. The NMR spectrum of X was measured on a Varian HA-100 instrument and the NMR spectra of other compounds on a Tesla BS 477 Model (60 MHz). Mass spectra were recorded on a MCH-1303 spectrometer. The product mixture from the reaction of VII with the hydride, as well as the n-propylbenzene/s-butylbenzene (2—3%) and *p*-cymene/*p*-ethylisopropylbenzene (2—4%) mixtures were analyzed on a Pye 104 Chromatograph (SE-30 columns) combined with an AEI M3902 mass spectrometer. Melting points were determined with a Kofler hot plate microscope, and are uncorrected.

General procedure for reduction and reductive methylation with sodium bis(2-methoxyethoxy)aluminium hydride

The olefin dissolved in a minimum amount of benzene, *n*-propylbenzene, or *p*-cymene was added in one portion to a solution of the hydride in the same solvent, and the homogeneous mixture was heated under reflux in an atmosphere of nitrogen for 6—26 h. The reactions were accompanied by hydrogen evolution. The ensuing red mixture was cooled to 0°, and the excess of the hydride destroyed by addition of 20% sulphuric acid with cooling. The aqueous layer was extracted with several portions of ether and the extracts were combined with the organic layer, which was then washed with an aqueous solution of sodium bicarbonate and then with water, and dried over sodium sulphate. The solvents were removed by distillation, and the products isolated by fractionation of the residue under vacuum or by crystallization. The optimum reaction time was determined in preliminary experiments, which were monitored by GLC analyses of aliquots (1—2 ml) taken at appropriate time intervals and treated as above. The GLC analysis and mass spectra showed that the reactions of the olefins with the hydride in n-propylbenzene as solvent were accompanied by formation of 2—3% s-butylbenzene; the peak for this compound was detected after 2—3 h reaction. With *p*-cymene as solvent, formation of *p*-ethylisopropylbenzene (2—4%) was similarly demonstrated.

Preparation of 1,1-diphenylethane (II)

The olefin I (2.7 g, 15 mmol) was added to a 70% solution of the hydride (6.06 g, 30 mmol) in benzene. After 1.5 h refluxing, the mixture was free of I (GLC; Apiezon L 25% on Celite, 200°). The usual work-up followed by distillation under reduced pressure gave a colourless oily product (2.4 g), b.p. 135.0—136.5°/12 mm (lit. [25] b.p. 136°/12 mm), whose NMR spectrum (neat; τ 2.85 s, 10H, aromatic protons; τ 8.45 d (J = 7.26Hz), 3H, CH_3; τ 5.81 q (J = 7.13 Hz), 1H, CH) (lit. [3] τ 2.86 s, 8.47 d and 5.80 q) and elemental analysis (found:C, 92.10; H, 7.70. $C_{14}H_{14}$ calcd.: C, 92.26; H, 7.74%) correspond to pure II (88% yield).

Preparation of 2,2-diphenylpropane (III)

The reaction between I (5.4 g, 0.03 mol) and the hydride (18.2 g, 0.09 mol) in 32.5 g n-propylbenzene at the reflux temperature gave a dark red solution. GLC analysis (Apiezon L 30000 on Celite, 130°), showed that olefin was absent after 25 min and the intermediate II after 6 h. Work-up and distillation gave an oil (5.3 g), b.p. 132—134°/12 mm, which was identified as pure III (lit. [26] b.p. 115—117°/2 mm) by GLC, IR [27], NMR ($CDCl_3$, TMS reference: τ 8.31 s, 6H, CH_3; τ 2.80 s, 10H, aromatic protons; lit. [28] τ 8.32, CH_3; τ 2.80, aromatic protons), and mass spectra (*m/e*) (M^+ 196, 181 (100%), 166, 165, 103, 91, and 77).

GLC analysis of the aqueous layer on hydrolysis of the reaction mixture with 20% sulphuric acid revealed, along with 2-methoxyethanol, ethylene glycol, formed to an extent of approximately 110%, with respect to the 2,2-diphenylpropane.

Preparation of 1,2,2-triphenylpropane (VI)

The olefin IV (2.56 g, 0.01 mol) was added to a solution of the hydride (6.1 g, 0.03 mol) in 18.3 g n-propylbenzene. The mixture was heated under reflux. The deep red mixture was free from olefin after 1 h (GLC; Apiezon L, 10% on Celite, 220°); the reaction was stopped when the conversion of V (GLC) reached 90% (6 h). The mixture was worked up as usual and the solvents were removed under reduced pressure; crystallization of the resulting mass from ethanol gave white crystals (1.93 g) of pure VI (GLC), m.p. 116—117° (lit. [29] m.p. 116—117°).

Heating of the olefin (1.28 g, 5 mmol) with the glassy hydride (3.05 g, 15 mmol) without solvent for 6 h gave (GLC) the same result.

The infrared spectrum of VI in tetrachloromethane and carbon disulphide showed absorptions (bands are ordered according to descending intensity) at 699; triplet at 756, 772, and 746; 1498, 1030; a doublet at 1445 and 1455; 3031, 3064, 577, 3088, 2977, 559, 537, 629, 2939, 1601, 1374; a doublet at 2864 and 2877; 1945, 1803; a triplet at 1074, 1083, and 1061 cm^{-1}.

Reaction of cyclohexylidene diphenylmethane (VII) with sodium bis(2-methoxyethoxy)aluminium hydride

The olefin VII (2.4 g, 0.01 mol) was added to a solution of the hydride (7.4 g, 0.037 mol) in *p*-cymene (14.4 g) and the mixture was refluxed for 18 h. Another quantity of the hydride (4.7 g, 0.023 mol) in *p*-cymene (9.1 g) was added, and the heating was continued for 8 h. The mixture was worked up as above, the solvents were evaporated, and the residue distilled to give an oily fraction 2.12 g), b.p. 115—122°/0.4—0.25 mm. A sample of this fraction was subjected to GLC (OV 17 on Diatomite Gas-Chrom Q (100—120 mesh), 180°, 1.5 m × 4 mm) combined with mass spectrometry, which showed, besides the starting compound VII (3%) (M^+ 248 (base peak), principal ions at *m/e* 205, 180, 91, 77), the presence (in the order of increasing retention times) of VIII (31%) (M^+ 250, base peak 167, principal ions at *m/e* 168, 165, 91, 77), of an unknown compound (*a*) (42%) (M^+ 262 (base peak), principal ions at *m/e* 247, 219, 205, 181, 117, 103, 91, 77), and of IX (7%) (M^+ 264, base peak 147, principal ions at *m/e* 249, 117, 91, 77). Another sample of the fraction was separated by preparative GLC (Silicone Elastomer 350, 3% on ground unglazed tiles (0.2—0.3 mm), 2.4 m × 6 mm, 210°) into a lower and higher boiling product. The lower boiling product solidified on standing and was recrystallized from methanol to give white crystals, m.p. 55°, the mass spectrum of which (vide supra) and NMR spectrum (CCl_4, HMDS reference: τ 2.93 s, 10H, phenyl protons; τ 6.65 d (J = 10.7 Hz), 1H, CH; τ 8.5 m, 11H, cyclohexyl protons) corresponded to VIII (lit. [30] m.p. 56.5°). The mass spectrum of the higher boiling product (viscous oil) was identical with that of the above compound (*a*); from the mass, NMR ($CDCl_3$, TMS reference: τ 8.17 s, 3H, CH_3 on tert. C; τ 4.81 m, 1H, trisubstituted double bond; τ 3.1—2.5, 10H, phenyl protons), and IR spectra [liquid film between KBr plates: 3100—3000 (4 bands: aromatic and olefinic = C—H), 2927 s (chain of $(CH_2)_n$ for $n > 2$), 1598 m and 708 vs (phenyl groups), and 1376 m cm^{-1} (CH_3—C); the absence of a band near 1650 cm^{-1} and the presence of an olefinic =C—H stretching band above 3000 cm^{-1} confirm the presence of tri- or tetra-substituted C=C bond; a great number of sharp medium bands between 1300 and 900 cm^{-1} indicates the presence of an alicyclic group], the compound (*a*) was identified as 1-(1-cyclohexenyl)-1,1-diphenylethane (X) (nc).

Preparation of 9,9-dimethylfluorene (XII)

To a solution of the hydride (14.08 g, 73 mmol) in *p*-cymene (25.9 g) the carbinol XIII (3.92 g, 20 mmol) was added and the mixture was heated under reflux. After 1h, GLC analysis (Apiezon L, 10% on Chromosorb W; 200°) showed that the dark red mixture contained 29 wt. % of XIII, 57 wt. % of XV, and 14 wt. % of XII. Heating for a further 14 h led to complete disappearance of XIII and the formation of 96 wt. % of XII and 4 wt. % of XV (GLC). The mixture was cooled to 0° and worked up as above; after removal of solvents, distillation of the residue gave an oily fraction, b.p. 75—80°/0.2 mm, which was dissolved in cold ethanol. A crystalline mass formed on standing, and the crude product was filtered off and recrystallised from aqueous ethanol to give 3.25 g of white crystals (84% yield), m.p. 94° (lit. [31] m.p. 95—96°); the elemental analysis (found: C, 92.80; H, 7.23. $C_{15}H_{14}$ calcd.: C, 92.73; H, 7.26%) and IR spectrum [31] corresponded to pure XII.

Reaction of 1,1,4,4-tetraphenyl-1,3-butadiene (XVI) with sodium bis(2-methoxyethoxy)aluminium hydride

XVI (1.79 g, 5 mmol) was heated under reflux with a solution of the hydride (6.1 g, 30 mmol) in 14.2 g *p*-cymene. After 8 h, the GLC analysis (Silicone Elastomer 350, 10.2% on ground unglazed tiles, 220°) showed the absence of XVI and formation of a higher boiling (*b*) (12 wt. %) and a lower boiling (*c*) (88 wt. %) product. After work-up of the dark red reaction mixture and removal of solvents, distillation gave an oily fraction, b.p. 120—140°/10 mm and an undistillable polymeric residue (0.89 g). The oily fraction was separated by preparative GLC (6 m × 8 mm column; AK 5000C, 6% on Chromosorb W; 145°) and two products (*b*) and (*c*) were obtained. Product (*b*) (6% yield) was found to be XIX by comparison of its GLC retention time to an authentic sample and by IR spectra [32]; product (*c*) (50% yield) was identified as III by GLC analysis and its IR spectrum [27].

Reduction of 6,6-diphenylfulvene (XXIV) with sodium bis(2-methoxyethoxy)aluminium hydride

A solution of XXIV (23 g, 0.1 mol) in 100 ml benzene was added during 5 min to a 70% solution of the hydride (38.9 g, 0.194 mol) in benzene and the mixture was heated under reflux for 1.5 h. GLC analysis (Silicone Elastomer E 302, 11.5% on Chromosorb W, 205°) of the mixture revealed it to be essentially free of XXIV and to contain a new component giving an unsymmetrical peak with lower retention time. The mixture was worked up as above, solvents were removed, and the residue was treated with petroleum ether; an insoluble and viscous oil was discarded, the petroleum ether solution was freed of solvent, and the residue subjected to a trap-to-trap distillation (105° to 138°/0.25 mm) to give 16.7 g (72%) of a crude product. This was dissolved in hot ethanol and on cooling gave white crystals; recrystallisation from ethanol gave a product melting at 155.0°—155.5°. (Found: C, 93.28; H, 7.03. $C_{18}H_{16}$ calcd.: C, 93.06; h, 6.94%). Mass spectrum: M^+ 232 (base peak), *m/e* (principal peaks in the order of decreasing abundance) 167, 91, 165, 152, 153, 128, 141, 115, 154, 191, 155. NMR spectrum (CCl_4, HMDS reference): τ 2.88 m, 10H, phenyl protons; τ 8.27 m, 1H, diphenylmethine proton; τ 8.92 m, < 1H on C_5 of XXV; τ 7.22 m and τ 5.82 m, > 2H on C_2—C_3 of XXVI or on C_1—C_2 of XXV; τ 3.97 m, > 2H on C_3—C_4 of XXVII or on C_3—C_4 of XXV. The total integral thus corresponds to the presence of 10 phenyl protons, 1 methine proton, and 5 cyclopentadienyl protons. According to the NMR spectrum the product was a 47/47/6 mixture of XXVI, XXVII and XXV.

Reductive methylation of 6,6-diphenylfulvene (XXIV) with sodium bis(2-methoxyethoxy)aluminium hydride

To a solution of the hydride (16.4 g, 0.081 mol) in 35.4 g *p*-cymene the fulvene XXIV (4.6 g, 0.02 mol) was added, and the mixture was heated under reflux for 6.5 h. The GLC (Silicone Elastomer 302, 11.5% on Chromosorb W, 205°) of the mixture indicated the absence of the starting XXIV and the formation of a product (94 wt. %) with a higher retention time, accompanied by small amounts of two other compounds (4 and 2 wt. %). The mixture was worked up as above, the solvents were evaporated, and the residue was distilled (114—122°/0.3 mm) to give 3.6 g of an oil, which was purified by preparative GLC (Silicone Elastomer 350, 3% on ground unglazed tiles (0.2—0.3 mm), 2.4 m × 6 mm, 205°). Mass spectrum: M^+ 246 (base peak), principal peaks at *m/e* 231, 181, 165; NMR spectrum: CCl_4, HMDS reference: τ 2.80 m, 10 H, phenyl protons: τ 8.30 d, 3H, methyl protons: signals at τ 8.85, 7.35, 5.75, and 3.76 were multiplets (5H) corresponding to different positions of C=C bonds in the cyclopentadiene ring, approximately in the same integral relations as for the unmethylated derivatives. From its mass and NMR spectra, the product is thought to be a mixture of the isomers XXVIII (nc), XXIX (nc), and XXX (nc). The reaction of the product mixture XXV—XXVII with the hydride under these conditions gave the same result.

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