

SIMULTANEOUS HYDROGENOLYSIS AND ALKYLATION OF AROMATIC KETONES BY SODIUM BIS(2-METHOXYETHOXY)ALUMINUM HYDRIDE AT ELEVATED TEMPERATURES*

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Benzophenone and 9-fluorenone were quantitatively hydrogenolyzed by sodium bis(2-methoxyethoxy)aluminum hydride in aromatic hydrocarbons at 110–170°C to diphenylmethane and fluorene, respectively, which by the action of the hydride immediately underwent consecutive alkylation and dimerization reactions and parallel cycloalkylation reactions. Final products of the reaction of benzophenone with the hydride were 2,2-diphenylpropane and 1,1-diphenylcyclopropane in 77 and 11% yield, respectively. The reaction course was dependent on the stoichiometry and the reaction temperature. At 110°C the reaction of benzophenone with the hydride could be stopped in the stage of monoalkylation, and the product of the reaction was exclusively 1,1-diphenylethane in 66% yield. The reaction of benzophenone was accompanied by the formation of 1,1,2,2-tetraphenylethane and of 9,10-diphenylanthracene. The reaction of 9-fluorenone with the hydride carried out in *p*-cymene at 170°C gave 68% of 9,9-dimethylfluorene, 20% of 9,9'-bifluorenyl and 10% of 9-ethyl-9-methylfluorene.

The course of the reduction and hydrogenolysis of arylalkyl- and diarylketones by complex metal hydrides is significantly dependent on the reactivity of the hydride and on the reaction conditions. The reaction of acetophenone with lithium aluminum hydride–aluminum trichloride complex was found to give either styrene¹ (40%), ethylbenzene in a mixture with styrene and 1-(chloroethyl)benzene², corresponding carbinol³ (93%), or ethylbenzene⁴ (94%). Similarly, hydrogenolysis of benzophenone with the same hydride complex in ether gave either diphenylmethane³ (95%), or, in dependence on the hydride to aluminum trichloride molar ratio and on the temperature⁵, diphenylmethanol (90%), diphenylmethane (90%), or a mixture of bis(diphenylmethyl) ether and α -chlorodiphenylmethane. In toluene, there occurs also arylation and one of the products is (4-methylphenyl)diphenylmethane⁶. Simple course and high yields are typical for hydrogenolysis by sodium bis(2-methoxyethoxy)aluminum hydride of aromatic ketones containing electron-donating substituents.

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tients in the *ortho* and/or *para* positions to the carbonyl group⁷⁻⁹. Effective hydrogenolytic reagents are also complexes of sodium borohydride with boron trifluoride and aluminum trichloride, or diborane, which react with benzophenone to give diphenylmethane¹⁰ (90%). Diphenylsilane yields with this ketone (diphenylmethoxy)-diphenylsilane (75%) or diphenylmethane^{11,12} (37%); 9-fluorenone is hydrogenolyzed by diphenylsilane to fluorene¹² (60%), while with lithium aluminum hydride-aluminum trichloride the ketone is reduced to 9-fluorenol³ (94%). In reactions of complex metal hydrides with aromatic ketones the alkylation at the carbon atom of the carbonyl group to give diarylalkylalkanes or alkyl-substituted condensed hydroaromatic hydrocarbons has not yet been reported. General method for preparing such compounds is the reaction of sodium or lithium salts of diarylalkanes¹³ or of fluorene¹⁴⁻¹⁸ with alkyl halides or dialkyl sulphates. 1,1-Diphenylmethane has recently been prepared from benzophenone also by the action of methyl lithium in ether and subsequent reduction of the formed intermediate product by lithium in liquid ammonia¹⁹.

With regard to the high hydrogenolytic ability of sodium bis(2-methoxyethoxy)-aluminum hydride which exceeds that of lithium aluminum hydride in the series of substituted aromatic ketones⁷⁻⁹, it was of interest to examine the behaviour of sodium bis(2-methoxyethoxy)aluminum hydride also toward unsubstituted aromatic ketones. In the first part of the Series we briefly reported on the reaction of benzophenone with the above hydride and with sodium bis(2-ethoxyethoxy)-aluminum hydride leading at elevated temperatures in one step to diphenylalkylmethanes and to diphenylcyclopropane²⁰. On the contrary, hydrogenolysis of 2-acetylnaphthalene by sodium bis(2-methoxyethoxy)aluminum hydride gave along with the expected 2-ethylnaphthalene also *meso*- and (\pm)-2,3-bis(2-naphthyl)butane as final products²¹. Unusual character of these reactions, which are unique in the chemistry of metal hydrides, initiated us to further study their course and the effect of reaction conditions upon the product formation. In the present work we discuss in detail the results of the reactions of sodium bis(2-methoxyethoxy)aluminum hydride with unsubstituted aromatic ketones, *i.e.* acetophenone, benzophenone, and 9-fluorene, at elevated temperatures.

EXPERIMENTAL

Compounds used. Sodium bis(2-methoxyethoxy)aluminum hydride was donated by the Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Prague-Řež as a 70% solution in benzene. The solutions of the hydride in other solvents were prepared by evaporating the benzene solutions at 10–15 Torr (bath temperature 50–70°C) and by dissolving the pasty residue in hot toluene, *o*-xylene, *m*-xylene, *n*-propylbenzene or *p*-cymene, to required concentration. The starting ketones, acetophenone, benzophenone, and 9-fluorenone, and the standards, ethylbenzene, diphenylmethane, and diphenylmethanol, were commercial preparations of analytical purity grade and were purified prior to using by crystallization or by fractional distillation until their chromatographic purity was established. *o*-Xylene, *m*-xylene, *n*-propylbenzene, and *p*-cymene

used as solvents were distilled prior to using in the presence of the hydride and were chromatographically pure.

Analysis. The purity of the starting compounds and of the solvents, as well as the intermediate and final compositions of the reaction mixture from the reduction and hydrogenolysis of acetophenone, benzophenone, and of 9-fluorenone, and from the hydrogenolytic alkylation of benzophenone and of 9-fluorenone were determined chromatographically, with the aid of Chrom I and Chrom III gas chromatographs equipped with a flame-ionization detector. Preparative gas chromatography was performed on an instrument equipped with a thermal conductivity detector (produced by Vývojové dílny, Czechoslovak Academy of Sciences, Prague). NMR spectra were taken on a modified Tesla BS 477 spectrometer and on a Varian 100 instrument. IR spectra were recorded with a Zeiss UR-20 spectrophotometer (calibration by polystyrene film; frequencies were read with an accuracy of $\pm 2 \text{ cm}^{-1}$) and mass spectra were measured on a MCh-1303 spectrometer. The products of hydrogenolytic alkylation of 9-fluorenone were analysed on a Pye 104 (flame ionization detector) instrument combined with an AEI, MS 902, mass spectrometer. Melting points were determined with a Kofler hot plate microscope and are uncorrected.

1-Phenylethanol and ethylbenzene. Acetophenone (6.01 g, 0.05 mol) was added to a solution of 20.2 g (0.1 mol) of sodium bis(2-methoxyethoxy)aluminum hydride in 36 g of *o*-xylene and the mixture was heated under nitrogen at 142°C for 5 h. The usual work-up followed by distillation gave 5.24 g (86%) of 1-phenylethanol, b.p. 92–93°C/14 Torr (ref.²² b.p. 93–95°C/15 Torr) and m.p. 21.4–21.5°C (ref.²³ m.p. 21.45°C). Gas chromatographic analysis of the *o*-xylene fraction showed that ethylbenzene was formed in 5% yield.

9-Fluorenone. A benzene solution of 7.2 g (0.04 mol) of 9-fluorenone was slowly added under nitrogen to a 70% benzene solution of 11.6 g (0.04 mol) of sodium bis(2-methoxyethoxy)aluminum hydride. The reaction mixture was heated at 80°C for 30 min, decomposed by ice and 20% sulphuric acid and worked up in the usual way. Crystallization of the crude product gave 7 g (95%) of 9-fluorenone, m.p. 157.5–158.0°C (ref.²⁴ m.p. 158°C).

Hydrogenolytic alkylation of benzophenone in *m*-xylene. To a boiling solution of 32.8 g (0.18 mol) of benzophenone in 89 g of *m*-xylene, 104 g of a 70% benzene solution of sodium bis(2-methoxyethoxy)aluminum hydride (0.36 mol) were slowly added under nitrogen atmosphere. After approximately half the amount of the hydride had been added, the colour of the reaction mixture had already turned to dark red. Then, 85 g of a benzene-*m*-xylene mixture were removed by distillation and the residual mixture was refluxed (140°C) for 2 h (hydrogen evolution), cooled to 0°C, diluted by ether, and decomposed by 20% sulphuric acid. The usual work-up and fractional distillation under reduced pressure yielded fraction I, b.p. 138–145°C/12 Torr (22.1 g), fraction II, b.p. 98–105°C/1 Torr (4.4 g), and fraction III containing higher boiling compounds (5.1 g). Fraction I was divided into four fractions by preparative gas chromatography (column 3 m \times 6 mm, Apiezon L 25% on Celite, column temperature 200°C, nitrogen as carrier gas). The first fraction was identified as pure diphenylmethane. The IR spectrum of the second fraction was identical with the spectrum of 1,1-diphenylethane²⁵, and the identity of the fraction with 1,1-diphenylethane was confirmed also by NMR spectrum (CDCl_3 , TMS as internal standard: singlet C_6H_5 (10H) τ 2.77; doublet CH_3 (3 H) τ 8.37, $J_{\text{H-C-CH}_3}$ 7.2 Hz; quadruplet CH (1 H) centered at τ 5.87) (ref.¹⁹ NMR(CCl_4): τ 8.46 (3 H, doublet, 7 Hz); τ 5.97 (1 H, quadruplet, 7 Hz); τ 2.88 (10 H, singlet)) and by mass spectrum (M^+ 182 (35%), m/e 167 (100%), 165 (27%), 152 (15.5%), 103 (6.3%), 77 (11%) (ref.¹⁹ M^+ 182 (32%), m/e 167 (100%)). For $\text{C}_{14}\text{H}_{14}$ (182.0) calculated: 92.26% C, 7.74% H; found: 92.42% C, 7.74% H. The third fraction was identified by IR spectrum (ref.²⁶), NMR spectrum (in CDCl_3 , with respect to TMS: CH_3 (6 H), τ 8.32; C_6H_5 (10 H), τ 2.76) (ref.²⁷), NMR spectrum: CH_3 τ 8.32, C_6H_5 τ 2.8) and by mass spectrum (M^+ 196 (30%), m/e 181 (100%), 166 (17%), 165 (14%), 103 (24%), 91 (12%), and 77 (15%)) as pure 2,2-diphenylpropane. For

$C_{15}H_{16}$ (196.28) calculated: 91.78% C, 8.22% H; found: 91.56% C, 8.13% H. The fourth fraction was found by NMR spectrometry (CCl_4 , with respect to HMDS: aromatic protons (10 H), singlet, τ 2.94; cyclopropane protons (4 H), singlet, τ 8.81) (ref.²⁸; NMR spectrum: (10 H), singlet, τ 2.95; (4 H), singlet, τ 8.76) and by mass spectrum (M^+ 194 and further ions m/e 151, 178, 179, 165, 116, and 117) to be pure 1,1-diphenylcyclopropane. For $C_{15}H_{14}$ (194.3) calculated: 92.74% C, 7.26% H; found: 92.60% C, 7.20% H. From fraction II, which solidified on standing, were obtained by crystallization from light petroleum 2.3 g of diphenylmethanol, m.p. 66.5–67.0°C (ref.²⁹ m.p. 68–69°C) (no depression of mixed melting point with an authentic sample). Fraction III, which solidified on standing, was crystallized from ethanol to give 1.8 g of yellow needle-like crystals, which after sublimation at 0.1 Torr had m.p. 244–247°C; the compound was shown by IR spectrum³⁰, mass spectrum (M^+ 330 (100%), m/e 252 (31.5%)) and by elemental analysis to be identical with 9,10-diphenylanthracene (ref.³¹ m.p. 247–248°C). For $C_{26}H_{18}$ (330.4) calculated: 94.51% C, 5.49% H; found: 94.33% C, 5.65% H. By evaporating the ethanol from the mother liquor after crystallization of 9,10-diphenylanthracene from fraction III, a substance was obtained, which after repeated crystallization from ethanol yielded white needle-like crystals melting at 215°C; by IR spectrum (ref.³²) and mass spectrum (fragments at m/e 167), the compound was identified as 1,1,2,2-tetraphenylethane (m.w. 334.4) (ref.³³ m.p. 214–215°C).

Hydrogenolytic alkylation of benzophenone in n-propylbenzene. To prove the formation of *sym*-tetraphenylethane already in the initial phase of the reaction, benzophenone (9.1 g, 0.05 mol) was reacted with sodium bis(2-methoxyethoxy)aluminum hydride (25.3 g, 0.125 mol) in *n*-propylbenzene (55.7 g) at 162°C. The reaction was stopped after 15 min. Solvent removal under reduced pressure and crystallization of the distillation residue (86 wt. % of diphenylmethanol, 11 wt. % of diphenylmethane, and 3 wt. % of 1,1-diphenylethane) from ethanol gave 100 mg of a substance melting at 215°C; its mass spectrum produced ions at m/e 167 and corresponds, as does its IR spectrum³², to 1,1,2,2-tetraphenylethane.

Preparation of 1,1-diphenylethane in o-xylene. Benzophenone (9.11 g, 0.05 mol) was mixed with sodium bis(2-methoxyethoxy)aluminum hydride (22.4 g, 0.11 mol) dissolved in 83.6 g of *o*-xylene, and the mixture was heated under nitrogen at 142°C. According to g.l.c. analysis, the reaction mixture did not contain the starting ketone already after 5 min. After 6 h the reaction mixture was cooled, worked up in the usual way, and the solvents were evaporated under reduced pressure. The product was distilled at 0.1 Torr and it contained 13.4 wt. % of diphenylmethanol (10% yield), 10.2 wt. % of diphenylmethane (8% yield), 76.4 wt. % of 1,1-diphenylethane (59% yield), and less than 1 wt. % of 2,2-diphenylpropane and of 1,1-diphenylcyclopropane (by g.l.c.). Crystallization of the distillation residue from a benzene-ethanol mixture and from chloroform gave 250 mg of a crystalline portion which according to its mass spectrum consisted of 9,10-diphenylanthracene and 1,1,2,2-tetraphenylethane.

Preparation of 1,1-diphenylethane in toluene. A solution of 50.6 g (0.25 mol) of sodium bis(2-methoxyethoxy)aluminum hydride in 110 g of toluene was mixed with 18.2 g (0.1 mol) of benzophenone and heated under reflux condenser in a nitrogen atmosphere to 108°C. By g.l.c. analysis it was found that benzophenone was quantitatively converted into diphenylmethane in 20 min. After 3 h the mixture contained 5 wt. % of diphenylmethane. After 9 h the reaction mixture did not contain diphenylmethanol and consisted of diphenylmethane (major product) and 3 wt. % of 1,1-diphenylethane. The amount of 1,1-diphenylethane increased after 18 h to 50 wt. %, and after 36 h, when the reaction mixture was practically free of diphenylmethane, the reaction was stopped. The reaction mixture was cooled to 0°C and decomposed first by dry ice and then by 20% sulphuric acid. The usual work-up followed by distillation under reduced pressure gave 12.1 g of colourless product, b.p. 136–137°C/13 Torr (ref.³⁴ b.p. 136°C/12 Torr), whose NMR spectrum (neat: quadruplet CH centered at 5.80 τ , ($J = 7.13$ Hz), doublet CH_3 (3 H), τ 8.47 ($J = 7.26$ Hz),

and singlet of aromatic protons (10 H, τ 2.86) corresponds to 1,1-diphenylethane (66.5% yield); the product contained less than 1 wt. % of diphenylmethane (by g.l.c.). The distillation residue (5 g) was repeatedly crystallized from ethanol to give 9,10-diphenylanthracene, m.p. 247–248°C (ref.³¹ m.p. 247–248°C) and 1,1,2,2-tetraphenylethane, m.p. 214–215°C (ref.³³ m.p. 214–215°C). Gas chromatographic analysis of the aqueous layer resulting from the decomposition of the reaction mixture by sulphuric acid revealed the presence of ethylene glycol, along with 2-methoxyethanol.

Effect of molar ratio of the hydride to benzophenone on the reaction course. Benzophenone (9.11 g, 0.05 mol) was reacted in 5 parallel experiments with 30% solutions of sodium bis(2-methoxyethoxy)aluminum hydride in *n*-propylbenzene which contained 10.17 g (0.05 mol), 15.25 g (0.075 mol), 20.35 g (0.10 mol) 25.45 g (0.125 mol), and 30.50 g (0.15 mol) of the hydride. In each experiment, the reaction mixture was refluxed (162°C) under nitrogen for 6–7 h and the changes in concentrations of diphenylmethanol, diphenylmethane, 1,1-diphenylethane, 2,2-diphenylpropane, and of 1,1-diphenylcyclopropane during the reaction were followed at fixed intervals by g.l.c. analysis (Apiezon L, 4% on ground unglazed tiles, column temp. 170°C, hydrogen as carrier gas, 40 ml per min flow rate) of the organic layer of the samples removed from the reaction mixture and decomposed by 20% sulphuric acid. The results of these experiments are summarized in Table I. According to g.l.c. analysis and to the mass spectrum, the reaction of the ketone with the hydride in a molar ratio $\geq 1 : 2$ in *n*-propylbenzene is accompanied by the formation of *sec*-butylbenzene (c. 2%); the peak of this compound can be detected on the chromatogram after 3 h of the reaction.

Hydrogenolytic alkylation of 9-fluorenone. To a boiling solution of 27.4 g (0.136 mol) of sodium bis(2-methoxyethoxy)aluminum hydride in 36.5 g of *p*-cymene were added under nitrogen in one portion 3.6 g (0.02 mol) of 9-fluorenone. The mixture was heated at 175°C for 15.5 h, cooled, decomposed by 20% sulphuric acid, and the sample of organic layer was analysed by g.l.c. (SE 30, column temperature 70°C, temperature program with speed 4°C/min, helium as carrier gas) combined with mass spectrometry. The main product of the reaction (76.5 wt. %) was, by its mass spectrum (M^+ 194, base peak at m/e 179 and ion at m/e 164), assigned the structure of 9,9-dimethylfluorene (m.w. 194.3; 68% yield); in accordance with their mass spectrum, side products of the reaction were identified as 9-ethyl-9-methylfluorene (m.w. 208.3) (M^+ 208, base peak at m/e 179 and ions at m/e 178 and 164) (14 wt. %; 10% yield) and 9-ethylfluorene (m.w. 194.3) (M^+ 194, base peak at m/e 165) (2 wt. %) as well as two additional substances (4.5 and 3 wt. %), whose retention times correspond to 9-methylfluorene and 9-fluorene. In addition to *p*-cymene, the solvent fraction distilled from the resulting reaction mixture also contained higher homologues of *p*-cymene having m.w. 148 (M^+ 148, base peak at m/e 133 and ions at m/e 119 and 105) and 162 (M^+ 162, m/e 133). The organic layer obtained by decomposition of the reaction mixture with sulphuric acid was combined with the ether extract of the water layer, washed with 10% sodium hydrogen carbonate and with water and dried over sodium sulphate. The solvents were removed by distillation at a temperature gradually raised to 100°C/12 Torr, the oily residue (4.02 g) was distilled *in vacuo* and the fraction boiling at 77–110°C/0.2 Torr was collected. Preparative gas chromatography of this fraction (Apiezon L 20% on Rysorb) yielded 9,9-dimethylfluorene, which after crystallization from ethanol had m.p. 94.5–95.0°C (ref.¹⁷ m.p. 95–96°C). Its NMR spectrum (in CCl_4 , relative to HMDS) shows an unresolved doublet in the region of aromatic protons (8 H) at 2.56–3.13 τ and a singlet due to the gem-dimethyl group (6 H) at 8.59 τ . The distillation residue obtained by distilling off the fraction boiling at 77–110°C/0.2 Torr was crystallized from ethanol and the crystalline substance obtained (0.66 g) had after repeated crystallization from this solvent a m.p. 245.5–246.0°C (20% yield); its mass spectrum (M^+ 330, base peak at m/e 165) and melting point correspond to 9,9'-bifluorenyl (m.w. 330.4) (ref.³⁵ m.p. 246–247°C).

RESULTS AND DISCUSSION

Unsubstituted aromatic ketones, such as acetophenone^{22,36}, 1- and 2-acetylnaphthalene²¹, benzophenone, and 9-fluorenone, undergo fast reduction, as do aliphatic ketones and cycloaliphatic ketones^{22,36}, by sodium bis(2-methoxyethoxy)aluminum hydride at a temperature below 80°C, to give high yields of corresponding alcohols. On the contrary, the main products of the reaction of benzophenone with excess hydride at 140°C are 2,2-diphenylpropane and 1,1-diphenylcyclopropane, accompanied by small amounts of 1,1,2,2-tetraphenylethane and 9,10-diphenylanthracene³⁷. Diphenylmethanol, 1,1-diphenylethane, and diphenylmethane, were isolated as intermediate products. The consecutive character of the hydrogenolytic and methylation reactions leading to 2,2-diphenylpropane, and parallel formation of 1,1-diphenylcyclopropane from diphenylmethane is evident from Fig. 1. From the practically instantaneous transformation of benzophenone to diphenylmethanol under the given conditions, it also follows that this alcohol may be the starting compound in the alkylation reaction.

The formation of 1,1-diphenylethane, 2,2-diphenylpropane, and of 1,1-diphenylcyclopropane is accompanied by an intense red colouration of the homogeneous reaction mixture and by an evolution of gaseous products. Alkylation and cycloalkylation are significantly dependent on the reaction temperature and stoichiometry. When benzophenone and the hydride were reacted at 110°C in toluene (36 h) using a molar ratio of 1 : 2.5, the main alkylation product was 1,1-diphenylethane (66% yield). By increasing the temperature to 140°C, the alkylation of diphenylmethane to 1,1-diphenylethane can be markedly increased (59% yield after 6 h). With a further increase to 162°C it is no longer possible to stop the reaction in the stage of monomethylation, and the reaction course is dependent upon relative concentrations of the hydride and the ketone (Table I). With molar ratio of the hydride to benzophenone equal to or less than 2, the equilibrium is already established after 2 h, and the composition of the reaction mixture does not change substantially even with prolonged heating at the above temperature. The complete transformation of diphenylmethane to 2,2-diphenylpropane and 1,1-diphenylcyclopropane (71% and 11% yield, respectively) may not be achieved with the molar ratio less than 3 : 1. From the dependence of the course of the reaction on the stoichiometry it also follows that only one of the two 2-methoxyethoxy groups of the hydride participates in the methylation reaction.

The reaction of benzophenone with the hydride gave the same diphenylmethane derivatives, whether the reaction was carried out in *o*-xylene, *m*-xylene or in *n*-propylbenzene, which indicates that there is no interaction of the solvent with benzylic hydrogen. Some aromatic hydrocarbons employed as solvents did undergo, however, transformations in the reaction medium. While *o*- and *m*-xylene were recovered from the reaction mixture unchanged, simultaneous hydrogenolysis and methylation

of benzophenone in *n*-propylbenzene at 162°C were accompanied after 3 h by the formation of 1–2% of *sec*-butylbenzene (with respect to *n*-propylbenzene). The formation of this hydrocarbon cannot be explained except by radical methylation of *n*-propylbenzene; the presence of *sec*-butylbenzene and comparative inertness of *o*- and *m*-xylene are, however, in agreement with the known four times greater relative reactivity in the abstraction of secondary benzylic hydrogen in solution relative to the reactivity of primary benzylic hydrogen^{38–40}, as well as with our assumption on the radical character of methylation reactions.

Another major product of the reaction of benzophenone with the hydride is 1,1-diphenylcyclopropane. As it is evident from Fig. 1, the formation of this hydrocarbon begins when the concentration of diphenylmethane in the reaction mixture is a maximum. The increase in its concentration parallels the increase in the concentration of 1,1-diphenylethane, and both hydrocarbons reach their concentration maxima almost simultaneously. This finding, together with the parallel character of the formation of both substances speaks for a close relationship between methylation and cyclization reactions.

The amount of *sym*-tetraphenylethane (approx. 5%), which accompanies the transformation of benzophenone to 2,2-diphenylpropane and 1,1-diphenylcyclopropane remains practically constant throughout the whole reaction. Further experimental data are needed to explain the mechanism of formation of this hydrocarbon, which may be regarded as the dimer of the diphenylmethyl radical, $(C_6H_5)_2\dot{C}H$. Nevertheless, preliminary experiments have already shown that the presence of this dimer also accompanies methylation of diphenylmethane by the hydride²⁰. The assumption that *sym*-tetraphenylethane is formed by recombination of two ketyl radicals of benzo-

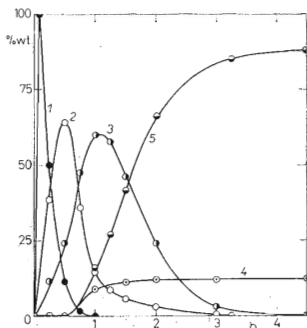


FIG. 1

Time Dependence of Concentrations of Diphenylmethanol 1, Diphenylmethane 2, 1,1-Diphenylethane 3, 1,1-Diphenylcyclopropane 4, and of 2,2-Diphenylpropane 5 in the Reaction of Benzophenone with Sodium Bis(2-methoxyethoxy)aluminum Hydride (1 : 3 Molar Ratio) in *n*-Propylbenzene at 162°C

Benzophenone was transformed into diphenylmethanol during first 5 min of the reaction.

phenone, $(C_6H_5)_2\dot{C}OH$, and by hydrogenolysis of the 1,1,2,2-tetraphenyl-1,2-ethanediol formed, can be then considered as improbable. Similarly to diphenylmethane, *sym*-tetraphenylethane gives by reaction with the hydride 2,2-diphenylpropane and 1,1-diphenylcyclopropane. The comparatively lower rate found in this reaction²⁰ may account for the presence of *sym*-tetraphenylethane in the final stage of the reaction of benzophenone with the hydride. Among the products of hydrogenolytic alkylation of benzophenone, we have not detected 2,2,3,3-tetraphenylbutane, $(C_6H_5)_2C(CH_3)C(CH_3)(C_6H_5)_2$, the dimer of 1,1-diphenylethyl radical, $(C_6H_5)_2\dot{C}CH_3$, which could have been formed by abstraction of hydrogen atom from 1,1-diphenylethane. Its absence is, however, in accordance with the observation by Ziegler and coworkers^{41,42}, that this dimer is unstable and suffers spontaneous decomposition at temperatures below 100°C.

Without entering into a detailed discussion of the mechanism of alkylation and cycloalkylation reactions, we believe that the results obtained are consistent with the assumption on the formation of diphenylmethyl radical anions by interaction of the hydride with diphenylmethane at elevated temperatures. Radical anions then react with methyl radicals, generated by cleavage of CH_3-O bond of the 2-methoxyethoxy group of the hydride molecule, $NaAl(OCH_2CH_2OCH_3)_2H_2$, to give 1,1-diphenylethane. Subsequent interaction of 1,1-diphenylethyl radical anions with methyl radicals leads analogously to 2,2-diphenylpropane. We believe that the 2-methoxy-

TABLE I

Effect of Molar Ratio of Sodium Bis(2-methoxyethoxy)aluminum Hydride to Benzophenone upon Composition of Reaction Mixture (%wt.) in *n*-Propylbenzene after 4 h of the Reaction at 162°C

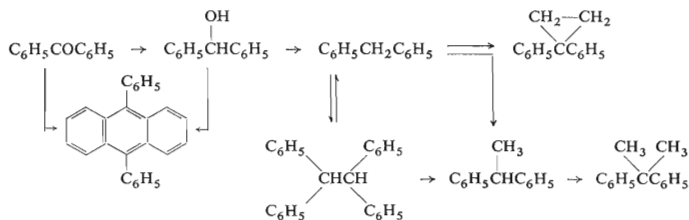
The data were obtained by g.l.c. analysis of volatile substances in the samples of the reaction mixture after their decomposition; the analysis does not include 1,1,2,2-tetraphenylethane and 9,10-diphenylanthracene.

Hydride/ketone mol. ratio	Diphenylmethanol ^a	Diphenylmethane	1,1-Diphenylethane	2,2-Diphenylpropane	1,1-Diphenylcyclopropane
1.0 ^b	35.0	24.5	33.0	5.0	2.5
1.5 ^b	14.0	13.0	41.0	20.5	11.5
2.0 ^b	—	4.0	32.5	51.5	12.0
2.5	—	—	9.5	78.5	12.0
3.0	—	—	—	88.0 ^c	12.0 ^c

^a All benzophenone reacted to form diphenylmethanol during first 5 min of the reaction; ^b at the given molar ratio, the composition presented was nearly achieved after 2 h of the reaction and this composition did not change during a further 4 h of heating at 162°C; ^c after work-up of the final reaction mixture the yield of both compounds was 77 and 11%, respectively.

ethoxy group of the hydride molecule should at a temperature higher than 110°C (heating of the hydride with benzophenone at 110°C does not induce cycloalkylation reaction), also be the source of a radical, which by interaction with diphenylmethyl radical anion yields first a transient organometallic derivative. Its further transformation, most likely of pyrolytic character, leads then to 1,1-diphenylcyclopropane. In accordance with this assumption, the intense red colour of the reaction mixture disappears only after the decomposition of this organometallic compound. Further support is provided by the formation of ethylene glycol and *sym*-tetraphenylethane, which were isolated from the reaction mixture, and by the formation of *sec*-butylbenzene in the case when *n*-propylbenzene was employed as solvent. A detailed discussion of the mechanism of alkylation and cycloalkylation reactions is the subject of a subsequent work.

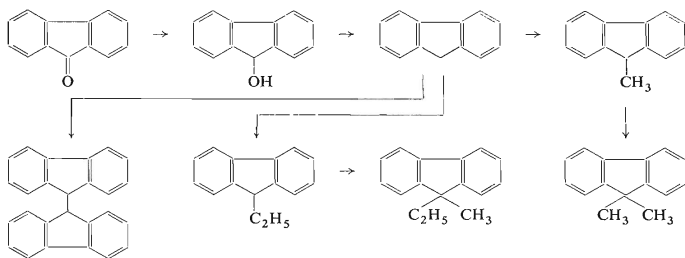
The formation of 9,10-diphenylanthracene in the reaction of benzophenone with the hydride is not surprising, and it is obviously an analogy to an intramolecular condensation of benzophenone or of diphenylmethanol by the action of calcium hydride at high temperatures⁴³. We believe that on the basis of available experimental data the hydrogenolytic alkylation of benzophenone may be described by Scheme 1.



SCHEME 1

Hydrogenolytic alkylation of 9-fluorenone with sodium bis(2-methoxyethoxy)aluminum hydride³⁷, relative to benzophenone, is characterized by a slower reaction rate; at 175°C in *p*-cymene as solvent, more than a four-fold reaction time is needed for transformation of the ketone to alkylated products. The main product of the reaction, characterized by an intense red colouration of the reaction mixture, from the very beginning of the reaction, is 9,9-dimethylfluorene (68% yield), which is accompanied by 9,9'-bifluorenyl (20%), 9-ethyl-9-methylfluorene (10%), and by 9-ethylfluorene (2%). Intermediate products were identified as 9-fluorenone, fluorene, and 9-methylfluorene. The structures of the intermediate and final reaction products were unambiguously determined by mass and IR spectra and by gas chromatography.

graphic analysis. Based on these results, the course of hydrogenolytic alkylation of 9-fluorenone with the hydride may be depicted as follows (Scheme 2).



SCHEME 2

The transformation of 9-fluorenone differs in its course and in the composition of the products from the reaction of benzophenone with the hydride. The slowest reaction step is hydrogenolysis of fluorene to fluorene. On the other hand, the comparatively higher rate of methylation reactions, likely due to the greater migration ability of fluorene hydrogens on C₍₉₎, results in a low concentration of fluorene and of 9-methylfluorene in the reaction mixture throughout the whole course of the reaction.

Contrary to the reaction of the hydride with benzophenone, with 9-fluorenone we did not observe the formation of the expected cyclopropyl derivative, spiro(fluorene-9,1'-cyclopropane). Instead, 9-ethylfluorene is formed (in the amount corresponding to the formation of a cyclopropyl derivative from benzophenone), which is however preferentially further methylated by the hydride to 9-ethyl-9-methylfluorene. The fact that the above mentioned spirocyclopropane has not been found during the course of the reaction speaks against the assumption that the ethyl derivative is formed by reductive cleavage of the transiently formed three-membered ring⁴⁴. The 9-ethylfluorene may, however, be a product of a reaction alternative to the cyclization. In such a case, the ethylation reaction would be typical for the above reaction conditions (175°C) of hydrogenolytic alkylation and also for the reaction of 9-fluorenone with the hydride.

Also unusual is a comparatively high yield of 9,9'-difluorenyl, which is comparable *e.g.* with the yield of the reaction of lithium aluminum hydride with 9-bromofluorene⁴⁵. It is noteworthy that 9,9'-bifluorenyl is obtained also by the reaction of lithium aluminum hydride with fluorene. The intermediate product in this case is an organo-

metallic compound, whose formation is characterized by red colouration of the reaction mixture (after 26 h in tetrahydrofuran) and by the evolution of gas^{4,5}, similar to the reaction of fluorene with sodium bis(2-methoxyethoxy)aluminum hydride.

In analogy with the formation of *sec*-butylbenzene in the reaction of benzophenone with the hydride in *n*-propylbenzene, the hydrogenolytic alkylation of 9-fluorenone in *p*-cymene solution is also accompanied by alkylation of the solvent to give several percent of homologous hydrocarbons which are methylated in the side chain.

The results reported previously^{20,21} and discussed in the present work indicate the general character of the reaction of sodium bis(2-methoxyethoxy)aluminum hydride with diaryl ketones and with ketones derived from condensed hydroaromatic hydrocarbons. The dependence of the course of the reactions of the hydride on the structure of the ketones makes it possible to assume that hydrogenolytic alkylation of ketones proceeds more easily with an increasing extent of conjugation of the corresponding aromatic system. Furthermore, alkylation would be made more difficult by the higher acidity of the benzylic hydrogen of the transiently formed nonalkylated or monoalkylated hydrocarbons in hydroaromatic condensed systems. The reactions with some other compounds of this type and the discussion of their mechanism will be the subject of a subsequent work.

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