

METHYLATION AND ETHYLATION OF THE ARYL-ACTIVATED BENZYLIC GROUP AND FORMATION OF GEM-DIARYLCYCLOPROPANES BY MEANS OF BIS(2-ALKOXYETHOXY)ALUMINUM HYDRIDES*

M. ČERNÝ and J. MÁLEK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

Received December 27th, 1974

1,1-Diphenylethane, 1,1-diphenylpropane and triphenylmethane were methylated with sodium bis(2-methoxyethoxy)aluminum hydride at 162–183°C to give 2,2-diphenylpropane, 2,2-diphenylbutane and 1,1,1-triphenylethane, respectively, in essentially quantitative yields. Diphenylmethane reacted with sodium bis(2-methoxyethoxy)aluminum hydride under formation of 1,1-diphenylcyclopropane, 1,1,2,2-tetraphenylethane and 2,2-diphenylpropane as the main product; fluorene gave 9,9-dimethylfluorene and 1,2-bis(9-methyl-9-fluorenyl)ethane. Sodium bis(2-ethoxyethoxy)aluminum hydride, which did not react with diaryl-substituted methine group, converted diphenylmethane to 1,1-diphenylcyclopropane as the main product and to 1,1-diphenylpropane. Sodium bis(2-n-propoxyethoxy)aluminum hydride and sodium bis(2-n-butoxyethoxy)aluminum hydride reacted with diphenylmethane in a similar way.

In previous works of this series it has been established that diaryl ketones, aromatic cyclic ketones and quinones react with sodium bis(2-methoxyethoxy)aluminum hydride at elevated temperatures to give corresponding dimethyl derivatives and gem-diarylcyclopropanes or the monoethylated products¹⁻³. Corresponding diarylmethanes or condensed aromatic hydrocarbons with activated methylene group, such as fluorene or 9,10-dihydroanthracene, and their monomethylated derivatives were intermediates of these reactions. Hydrogenolysis and alkylation of the hydrogenolytic products proceed as consecutive reactions. It was therefore of interest to examine the course of the alkylation of diarylmethanes and of the above-mentioned condensed aromatic hydrocarbons with sodium bis(2-alkoxyethoxy)aluminum hydrides separately from the hydrogenolytic reaction. In addition to this, the results of the alkylation of gem-diaryl olefins⁴ have offered the possibility to obtain the monomethylated products with high selectivity by the reaction of 1,1-diarylanthanes of the type R_2CHR' ($R = \text{aryl}$, $R' = \text{alkyl}$) with sodium bis(2-methoxyethoxy)aluminum hydride. Also the reactivity of the hydrides $NaAlH_2(OCH_2CH_2OR)_2$, where R is an alkyl group other than methyl, has not yet been examined in these reactions. As preliminary experiments have indicated, the reactions of 1,1-diarylmethanes with sodium bis(2-ethoxyethoxy)aluminum hydride¹ produce cyclopropanes in higher yields than the analogous reactions with sodium bis(2-methoxyethoxy)aluminum hydride. It seemed therefore useful to get more detailed information about the conditions of this novel reaction that leads to formation of diaryl-substituted

* Part VI in the series Reactions of Sodium Bis(2-alkoxyethoxy)aluminum Hydrides; Part V: *J. Organometal. Chem.* **84**, 139 (1975).

cyclopropanes and to compare this reaction with the known syntheses of cyclopropane derivatives. In addition to the well-known Simmons-Smith reaction^{5,6}, cyclopropanes have been synthesised by reactions of allyl alkyl ethers with dialkylaluminum hydride⁷, allyl alcohols with trialkylaluminum⁸ and lithium aluminum hydride⁹, by reduction of aromatic α,β -unsaturated esters with lithium aluminum hydride¹⁰⁻¹³ and generally by reduction of aromatic α,β -unsaturated carbonyl compounds with this hydride^{14,15}. Formation of 1,1-diphenylcyclopropane in small amounts has been observed in the reactions of benzophenone and 1,1-diphenylethylene with a methylsulphonyl carbanion^{16,17}. A cyclopropane derivative is also the product of γ -elimination reactions of some quarternary ammonium salts^{18,19} or 3-phenylpropyl halogenides¹⁹; also thermolysis of pyrazolines²⁰ and the reaction of azines of some ketones with trimethylsulphonium iodide²¹ leads to cyclopropanes.

In this paper we summarize the results of the study of the reactions of diphenylmethane, 1,1-diphenylpropane, triphenylmethane, 1,1,2,2-tetraphenylethane, fluorene and indene with sodium bis(2-methoxyethoxy)aluminum hydride, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$. With the aim to determine the reactivity of this hydride toward the monoaryllkanes used as solvents in these reactions, also the alkylation of *n*-butylbenzene at elevated temperatures has been investigated. The alkylation ability of sodium bis(2-ethoxyethoxy)aluminum hydride, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5)_2$, sodium bis(2-*n*-propoxyethoxy)aluminum hydride, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OC}_3\text{H}_7\text{-}n)_2$ and sodium bis(2-*n*-butoxyethoxy)aluminum hydride, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OC}_4\text{H}_9\text{-}n)_2$, and formation of cyclopropanes have been studied in the reaction of these hydrides with diphenylmethane and 1,1-diphenylpropane. In order to elucidate further the mechanism of the alkylation and cyclisation reactions of hydrocarbons with the hydrides we have examined also the reactions of diphenylmethane with aluminum sesqui(2-methoxyethoxy) hydride^{22,23}, $\text{Al}_2\text{H}_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, sodium aluminum 2-methoxyethoxide²⁴, $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$, and aluminum 2-methoxyethoxide^{23,24}, $\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$.

EXPERIMENTAL

Compounds used. Solutions of the hydrides and 2-methoxyethoxides in aromatic hydrocarbons (25–45%) were prepared by evaporating benzene solutions of sodium bis(2-methoxyethoxy)aluminum hydride (VCHZ-Synthesia, Kolín), sodium bis(2-ethoxyethoxy)aluminum hydride, sodium bis(2-*n*-propoxyethoxy)aluminum hydride, sodium bis(2-*n*-butoxyethoxy)aluminum hydride, aluminum sesqui(2-methoxyethoxy) hydride, aluminum 2-methoxyethoxide and sodium aluminum 2-methoxyethoxide (all supplied by the Institute of Inorganic Chemistry, Prague-Řež) *in vacuo* (10–15 Torr; bath temperature 60–80°C) and mixing the distillation residue with *n*-propylbenzene (b.p. 162°C), mesitylene (b.p. 164°C), *p*-cymene (b.p. 177°C) or *n*-butylbenzene (b.p. 182°C) (Fluka A.G.). Solutions of sodium bis(2-methoxyethoxy)aluminum hydride in *n*-butylbenzene were homogeneous only at the boiling point of this hydrocarbon. Fluorene (Koch-Light, Co.), m.p. 116–117°C (ref.²⁵ m.p. 116–117°C), was used without further purification. Indene (VÚOS Rybitví) was fractionated under nitrogen and the fraction boiling at 182.0–182.5°C (ref.²⁶ b.p. 182.2–182.5°C) was used. 1,1-Diphenylethane, 2,2-diphenylpropane, 1,1-diphenylcyclopropane and 9,9-dimethylfluorene, all used to identify the products and reaction intermediates by comparing gas chromatographic retention times, were of chromatographic

purity; their synthesis was reported in previous works of this series^{1,2}. *sym*-Tetraphenylethane, used in mixed melting point determinations, was of the same provenience. Diphenylmethane²⁷ (m.p. 24–25°C, b.p. 137°C/16 Torr), 1,1-diphenylpropane^{28–30} (b.p. 138°C/10 Torr) and triphenylmethane³¹ (b.p. 188°C/10 Torr, m.p. 93.5–94°C) were prepared by reported procedures and their purity was checked by gas chromatography. Melting points were determined with a Kofler hot stage microscope and are uncorrected.

Analytical methods. The purity of the starting compounds and solvents as well as the running and final compositions of the reaction mixtures were determined with the aid of Chrom I and Chrom II gas chromatographs equipped with flame-ionisation detector. Preparative gas chromatography was made on a chromatograph (Vývojové dílny, ČSAV, Prague) equipped with a thermal conductivity detector. The IR spectra were measured with Zeiss, Model UR 20, spectrophotometer (Jena), the mass spectra were recorded with MCH – 1303 spectrometer, and the NMR spectra were recorded with Tesla BS 477 (modified model) and Varian HA 100 instruments. The intermediate products and the final products of the alkylation of fluorene and indene with the hydride were identified with the aid of Pye 104 chromatograph (flame ionisation detector) connected with AEI, Type MS 902, mass spectrometer. Thermal stabilities of the hydrides were measured by a thermogravimetric method on quartz McBain-Baker torsion balances.

General procedure. A solution of the hydrides (25–45% wt.) in *n*-propylbenzene, mesitylene, *p*-cymene or *n*-butylbenzene was mixed at room temperature in an appropriate ratio with the hydrocarbon substrate and the mixture was heated under nitrogen to the boiling point; in all cases, except the reaction of *n*-butylbenzene with sodium bis(2-methoxyethoxy)aluminum hydride, the outset of the reaction was accompanied by intense red colouration of the reaction mixture (on mixing triphenylmethane with sodium bis(2-methoxyethoxy)aluminium hydride the solution has turned blood-red already at room temperature) and by hydrogen evolution. In parallel experiments by which the optimum reaction temperature and the hydride to substrate molar ratio were sought for and in which the concentration changes of the starting compounds, intermediates and products were followed, samples of the homogeneous reaction mixture were taken by a hypodermic syringe (1 ml) at fixed time intervals, decomposed with 20% sulphuric acid, and the organic layer was analysed by gas chromatography. After completion of the reaction, the reaction mixture was cooled to 0°C and decomposed with 20% sulphuric acid-ice mixture, the aqueous layer was extracted with ether, the extract combined with the organic layer, washed successively with 10% sodium hydrogen carbonate solution and water, and then dried with sodium sulphate. The solvents were removed by distillation under reduced pressure and the products were isolated from the distillation residue by the procedures described below.

2,2-Diphenylpropane and 1,1-diphenylcyclopropane. In samples of the reaction mixture taken during the reaction of diphenylmethane (5.04 g, 30 mmol) with sodium bis(2-methoxyethoxy)aluminum hydride (19.5 g, 96 mmol) in *n*-propylbenzene, the presence of 1,1-diphenylethane, 2,2-diphenylpropane and 1,1-diphenylcyclopropane was confirmed by gas chromatographic analysis (AK 30000, 140°C, nitrogen as a carrier gas) and by comparison their retention times with those of authentic samples. The work-up of the final reaction mixture afforded a fraction (5.44 g), b.p. 139–142°C/10.5 Torr, which was subjected to preparative gas chromatography (3 m × 6 mm column, Apiezon L 25% on Cellite, 200°C, nitrogen as a carrier gas) to yield two products. 2,2-Diphenylpropane: NMR spectrum (in CDCl₃, tetramethylsilane as a reference compd.): CH₃(s), 6 H, 8.33τ; C₆H₅ (s), 10 H, 2.76τ (ref.³² NMR spectrum: CH₃ (s), 8.32τ; C₆H₅ (s), 2.8τ). Mass spectrum: M⁺ 196 (30.5%), *m/e* 181 (100%), 166 (17.5%), 165 (14.5%), 103 (24.5%), 91 (12%), 77 (15%) (ref.³³ M⁺ 196, *m/e* 181, 166, 119, 103, 91, 77). The IR spectrum was identical with that reported in the literature³⁴. 1,1-Diphenylcyclopropane: NMR spectrum (in CCl₄, hexamethyldisiloxane as a reference compd.): C₆H₅ (s), 10 H, 2.94τ; cyclopropane protons (s), 4 H, 8.81τ; (ref.¹⁷

NMR spectrum: C_6H_5 (s), 2.87 τ ; cyclopropane protons (s), 8.78 τ . Mass spectrum: M^+ 194 (100%), m/e 151 (45%), 178 (32%), 179 (31%), 165 (28%), 116 (27%), 117 (15%). In parallel experiments in which the reaction of diphenylmethane with sodium bis(2-methoxyethoxy)aluminum hydride (162°C) was stopped after 20 min, the work-up of the reaction mixture and the solvent removal by distillation afforded a white crystalline product (2.4%) which precipitated from the distillation residue and after recrystallisation from ethanol it had m.p. 213–214°C. On the basis of its IR³⁵ and mass spectrum (fragments at m/e 167) it was assigned the structure of 1,1,2-tetraphenylethane (ref.³⁶, mp. 214–215°C). 9,10-Diphenylanthracene^{1,2} was not found among the reaction products. A similar product distribution was obtained in the reaction of diphenylmethane with the hydride, *i.e.* in the absence of benzene hydrocarbons as solvents. The products of the reaction of 1,1,2,2-tetraphenylethane (1.67 g, 5 mmol) with sodium bis(2-methoxyethoxy)aluminum hydride (4.04 g, 20 mmol) carried out in a *n*-butylbenzene–*n*-propylbenzene mixture were identified by gas chromatography in a similar way.

1,1-Diphenylcyclopropane and 1,1-diphenylpropane. A gas chromatographic analysis (4% Apiezon L on porous ground unglazed tiles, 170°C, nitrogen as a carrier gas) showed that the distillation residue (5.18 g) obtained by the work-up of the reaction product of diphenylmethane (5.32 g, 31.6 mmol) with sodium bis(2-ethoxyethoxy)aluminum hydride (21.80 g, 94.8 mmol) in boiling *p*-cymene (51.6 g) contained (in the sequence of their increasing retention times) the unreacted diphenylmethane (1.5%), an unidentified substance (6%), 1,1-diphenylpropane (34%) and 1,1-diphenylcyclopropane (58%). Pure 1,1-diphenylcyclopropane was isolated by preparative gas chromatography (4 m \times 6 mm column, Apiezon L 20% on Rysorb BLK 0.2–0.3 mm), 190°C, nitrogen as a carrier gas). Its NMR and mass spectra agreed with the above-mentioned data. The IR spectrum was identical with that reported in the literature³⁷. For $C_{15}H_{14}$ (194.3) calculated: 92.74% C, 7.26% H; found: 92.66% C, 7.21% H. The second product was 1,1-diphenylpropane: NMR spectrum (in CCl_4 , tetramethylsilane as a reference compd.: CH_3 , triplet centered at 9.10 τ , (3 H); CH_2 , triplet centered at 6.25 τ , (1 H); CH_2 , quintet centered at 7.95 τ , (2 H); aromatic protons, 2.90 τ , (10 H) (ref.³⁸ NMR spectrum: 9.11 τ (t), 6.29 τ (t), 7.97 τ (q), 2.89 τ). Mass spectrum: M^+ 196 and m/e at 167 ($-C_6H_5$). For $C_{15}H_{16}$ (196.3) calculated: 91.78% C, 8.22% H; found: 91.69% C, 8.18% H. The same products were obtained by the reactions of diphenylmethane with sodium bis(2-*n*-propoxyethoxy)aluminum hydride and sodium bis(2-*n*-butoxyethoxy)aluminum hydride and were identified in a similar way.

2,2-Diphenylbutane. The product (2.4 g), b.p. 145–146°C/11 Torr, obtained by the reaction of 1,1-diphenylpropane (2.6 g, 13.2 mmol) with sodium bis(2-methoxyethoxy)aluminum hydride (8.1 g, 40 mmol) in *n*-propylbenzene (19.5 g) at 162°C was freed of the starting 1,1-diphenylpropane (6%) by preparative gas chromatography (6 m \times 8 mm column, AK 30000, 180°C, nitrogen as a carrier gas) and 2,2-diphenylbutane was isolated as a sole product. NMR spectrum (neat, hexamethyldisiloxane as a reference compd.): C_6H_5 (s), 10 H, 3.04 τ ; CH_3CH_2 (quadruplet), 2 H, 8.04 τ ; CH_3 (s), 3 H, 8.61 τ ; CH_3CH_2 (t), 3 H, 9.42 τ (ref.³⁹ NMR spectrum: 8.01 τ (q), 8.47 τ (s), 9.30 τ (t)). Mass spectrum: M^+ 210 and m/e at 181 ($-C_2H_5$). For $C_{16}H_{18}$ (210.3) calculated: 91.37% C, 8.63% H; found: 91.30% C, 8.69% H.

1,1,1-Triphenylethane. The reaction mixture obtained by the methylation of triphenylmethane (3.7 g, 15 mmol) with sodium bis(2-methoxyethoxy)aluminum hydride (6.1 g, 30 mmol) in *p*-cymene (14.1 g) was decomposed by water and the aqueous layer was extracted with ether. According to gas chromatographic analysis (Tween 9.2% – Poropak, 175°C, nitrogen as a carrier gas and 1,4-butandiol as an internal standard), the extract of the aqueous layer contained 2.70 g of 2-methoxyethanol and 1.175 g (0.019 mol) of ethylene glycol, which corresponds to formation of 1.26 equiv. of ethylene glycol with respect to triphenylmethane and 0.83 equiv. with respect to the hydride used, provided that only one of the two 2-methoxyethoxy groups of the

hydride molecule participated in the methylation reaction². The organic layer obtained by decomposition of the reaction mixture was worked-up in the usual way and the distillation residue was crystallised from ethanol to give the chromatographically pure (Apiezon L 4% on porous ground unglazed tiles (0.6 mm), 210°C, nitrogen as a carrier gas) 1,1,1-triphenylethane (3.8 h, 98%), m.p. 94–95° (ref.⁴⁰ m.p. 95°C), b.p. 113–114°C/0.1 Torr; $\nu(\text{CH}_3)$: 1376 cm^{-1} .

2-Phenylpentane. n-Butylbenzene (18.4 g, 110 mmol) was heated in a nitrogen atmosphere with sodium bis(2-methoxyethoxy)aluminum hydride (6.4 g, 32 mmol) under reflux for 14 h, then 5.4 g (27 mmol) of the hydride were added and the mixture was refluxed for 23 h. Preparative gas chromatography of the product (6 m × 6 mm, Apiezon L 25% on Celite, 160°C, nitrogen as a carrier gas) gave the pure 2-phenylpentane: NMR spectrum (in CS_2 , hexamethyldisiloxane as a reference compd.): C_6H_5 (s), 5 H, 2.98 τ ; CHCH_3 , 1 H, quintet in the region 7.71–7.24 τ ; CHCH_2 , 3 H, two singlets at 8.78 and 8.89 τ ; $\beta\text{-CH}_2$, 2 H, unresolved multiplet centered at 8.30 τ ; $\gamma\text{-CH}_2$, 2 H, unresolved multiplet centered at 9.10 τ . IR spectrum (700 cm^{-1} (C_6H_5); 760 cm^{-1} ($-\text{CH}_2\text{CH}_2-$); one band at 1380 cm^{-1} ($\alpha\text{-CH}_3$)) agreed with the reported spectra of 2-phenylpentane^{41,42}. Parallel experiments showed that mesitylene does not undergo alkylation by the hydride in contrast to n-butylbenzene, n-propylbenzene and *p*-cymene.

Products of the alkylation of indene. Indene (3.55 g, 31 mmol) was added to a solution of sodium bis(2-methoxyethoxy)aluminum hydride (19.85 g, 98 mmol) in *p*-cymene (35.5 g) and the mixture, which became gradually homogeneous and turned brown-red, was refluxed under nitrogen. After 10 h, when about 50% of indene was converted to higher boiling products (by gas chromatography on 20M Carbowax, 110°C, nitrogen as a carrier gas), the reaction mixture was cooled to 0°C and worked-up in the usual way. The residue obtained by distilling off the solvent was freed of traces of polymeric substances by trap-to-trap distillation and the distillate was analysed by a gas chromatograph (Silicone elastomer SE-30) connected with a mass spectrometer. The product contained 1,1-dimethylindane (9% yield) (M^+ 146, base peak 145, *m/e* 115, 116, 91) 1,1,2- or 1,1,3-trimethylindane (11%) (M^+ 160, base peak 145, *m/e* 117), 1,1,2- or 1,1,3-trimethylindene (9%) (M^+ 158, base peak 143, *m/e* 115) and presumably also spiro(cyclopropane-1,1',3',3'-dimethylindane) (7%) (M^+ 172, base peak 144, *m/e* 157, 129), along with three unidentified substances (2–4%) (M^+ 158; M^+ 172; M^+ 186). In *p*-cymene as a solvent, *p*-ethylisopropylbenzene was formed (with respect to *p*-cymene) in about 2% (M^+ 148, base peak 133, *m/e* 119, 117, 115, 105).

9,9-Dimethylfluorene and 1,2-bis(9-methyl-9-fluorenyl)ethane. The product of the reaction of fluorene (6.65 g, 40 mmol) with sodium bis(2-methoxyethoxy)aluminum hydride (24.3 g, 120 mmol) in n-propylbenzene (56 g) was worked up as usually, freed of the solvents at 100°C/12 Torr and the residue was mixed with 50 ml of ethanol; after standing for 3 days, the white crystalline product (2.12 g) was recrystallised from ethanol and light petroleum; m.p. 199.0–199.5°C. NMR spectrum (in CDCl_3 , hexamethyldisiloxane as a reference compd.): aromatic protons, 16 H, unresolved multiplet at 2.16–3.21 τ , CH_3 (s), 6 H, 8.96 τ ; CH_2CH_2 (s), 4 H, 8.83 τ . IR spectrum (KBr): the two absorption bands at 3000–2900 cm^{-1} were taken as indicative of the presence of methyl and methylene groups, the latter forming the chain $-\text{CH}_2\text{CH}_2-$. The absence of a doublet around 1380 cm^{-1} indicates that the methyl groups are not geminal. One CH_3 band was found at 3000–2900 cm^{-1} . The substance was assigned the structure of 1,2-bis(9-methyl-9-fluorenyl)ethane (M^+ 386) (ref.⁴³ m.p. 194–195°C). A brown oil remaining after crystallisation of this compound and free of 9-methylfluorene (Carbowax M 20 20% on Chromosorb, 190°C, nitrogen as a carrier gas) was distilled and the fraction with b.p. 77–110°C/0.2 Torr was collected; preparative gas chromatography of the distillate gave 9,9-dimethylfluorene which after crystallisation from ethanol had m.p. 94.5–95.0°C (ref.⁴⁴ m.p. 95–96°C); NMR spectrum (in CCl_4 , hexamethyldisiloxane as a reference compd.): aromatic protons, 8 H, unresolved

doublet at 2.56–3.13 τ ; gem-(CH₃)₂ (s), 6 H, 8.59 τ (ref.⁴⁵ NMR spectrum (CDCl₃): CH₃ (s), 8.55 τ). The IR spectrum was identical with that of 9,9-dimethylfluorene⁴⁴; the better resolved bands at 1200–1100 cm⁻¹ indicate a higher purity of our product.

RESULTS AND DISCUSSION

Diphenylmethane reacts with sodium bis(2-methoxyethoxy)aluminum hydride (*I*) at elevated temperatures in benzene hydrocarbons as solvents to give 2,2-diphenylpropane as the main product, 1,1-diphenylcyclopropane and a small amount of 1,1,2,2-tetraphenylethane. The reaction in the absence of solvents proceeds in the same way. The reaction is typical by evolution of hydrogen from the very beginning of the reaction and by formation of intense red coloured solutions which are characteristic of diphenylmethyl carbanions and differs thus from the hydrogenolytic alkylation of benzophenone with the hydride *I* (refs^{1,2}) only by the absence of 9,10-diphenylanthracene among the reaction products. In contrast to 1,1-diphenylethane whose concentration passes through a maximum (Fig. 1), the concentration of 1,1,2,2-tetraphenylethane acquires a value of 2–4% which is essentially constant throughout the

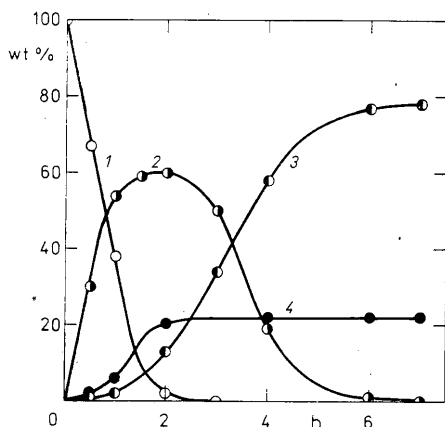


FIG. 1

Time Dependence of Diphenylmethane 1, 1,1-Diphenylethane, 2, 2,2-Diphenylpropane 3 and 1,1-Diphenylcyclopropane 4 Concentrations in the Reaction of Diphenylmethane with Sodium Bis(2-methoxy)aluminum Hydride (1 : 3.2 initial molar ratio) in *n*-Propylbenzene at 162°C

The formation and changes in the concentration of 1,1,2,2-tetraphenylethane (2–4%) are not depicted.

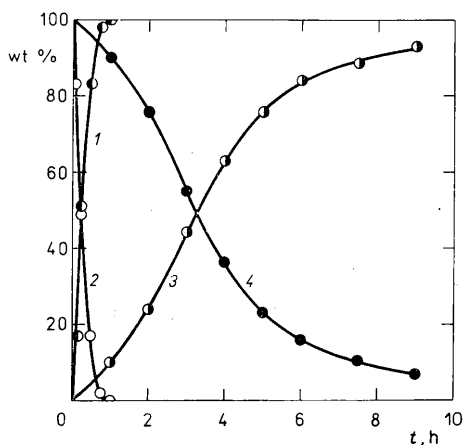


FIG. 2

Time Dependence of 1,1,1-Triphenylethane 1 and 2,2-Diphenylbutane 3 Concentrations in the Selective Methylation of Triphenylmethane 2 and 1,1-Diphenylpropane 4 with Sodium Bis(2-methoxyethoxy)aluminum Hydride (1 : 3 initial molar ratio) in *p*-Cymene at 177°C or in *n*-Butylbenzene at 183°C

reaction. 1,1,2,2-Tetraphenylethane reacts with the hydride *I* similarly as does diphenylmethane, but at a substantially slower rate and with lower selectivity; the side product of the reaction is also 2,2-diphenylbutane which is formed by additional methylation of 1,1-diphenylpropane (see later). The alkylation reaction and formation of the cyclopropane ring seem to be preceded in this case by the cleavage of the central C—C bond of 1,1,2,2-tetraphenylethane. The cleavage of this hydrocarbon was effected earlier with lithium biphenylide and the intermediate diphenylmethyl lithium was trapped in the form of diphenylacetic acid⁴⁶. Reasoning by analogy with a similar cleavage of 1,2-di(α -naphthyl)ethane by sodium biphenylide⁴⁷, we believe that also in our case the reaction intermediate is the corresponding dianion, $[(C_6H_5)_2C—C(C_6H_5)_2]^{2-}$, which decomposes in the rate-determining step of the reaction to give diphenylmethyl anions. These anions are most likely the key intermediates undergoing methylation with the hydride *I* to give 1,1-diphenylethane, rather than diphenylmethyl radical-anions² which are unstable at higher temperatures⁴⁸. 1,1-Diphenylethyl anion would then react analogously, giving 2,2-diphenylpropane. The absence of the corresponding dimer, 2,2,3,3-tetraphenylbutane, in the reaction of 1,1-diphenylethane with the hydride *I* was explained in a previous work². On the other hand, the formation of 1,1,2,2-tetraphenylethane in small amounts during the methylation of diphenylmethane with the hydride *I* speaks for a certain, but limited, existence of diphenylmethyl radical-anions as the intermediate products of this reaction. The hydride *I* acts in this reaction not only as an alkylating agent but also as a nucleophile which is able to abstract the acidic hydrogen from gem-diarylalkanes, condensed aromatic³ or condensed hydroaromatic hydrocarbons³ as well as to cleave polyarylalkanes of the 1,1,2,2-tetraphenylethane type. The presence of sodium and hydrogen atoms in the molecule of this hydride is a prerequisite. This conclusion is supported by our finding that diphenylmethane is recovered unchanged after prolonged heating at 140–177°C in the presence of aluminum sesqui(2-methoxyethoxy) hydride, sodium aluminum 2-methoxyethoxide or aluminum 2-methoxyethoxide. The above results give support to the reaction scheme proposed in the previous work for the hydrogenolytic alkylation of benzophenone and the methylation and cyclopropylation of diphenylmethane by the hydride *I*^{1,2}.

Fluorene radical-anions, which are relatively stable at temperatures around -70°C , decompose at higher temperatures to fluorenyl anions^{49,50}. It can be therefore assumed that also in our case the fluorenyl anion is the intermediate which reacts with the hydride *I* to form alkylated derivatives. Similar to the hydrogenolytic alkylation of 9-fluorenone², the main product of this reaction is 9,9-dimethylfluorene; however, instead of 9,9'-bifluorenyl, 1,2-bis(9-methyl-9-fluorenyl)ethane was isolated from the reaction mixture in relatively high yield, this substance being the product of the intermediate 1,2-di(9-fluorenyl)ethane. Contrary to diphenylmethane and fluorene whose alkylation took place exclusively on the methene group, *i.e.* on the site of the highest electron density, the reaction of indene with the hydride *I* showed only low

TABLE I
Methylation and Ethylation of Aromatic Hydrocarbons and Formation of gem-Diarylcyclopropanes by the Action of the Hydrides at Elevated Temperatures

Hydrocarbon	Reagent M ^a	Temperature °C	Time h	Products	Yield % ^b
Diphenylmethane	NaAlH ₂ (OC ₂ H ₄ OCH ₃) ₂ (1:3:2)	162	7.5	2,2-diphenylpropane ^c	72
				1,1-diphenylcyclopropane ^c	20
				<i>sym</i> -tetraphenylethane ^{c,d}	2
1,1-Diphenylethane	NaAlH ₂ (OC ₂ H ₄ OC ₂ H ₅) ₂ (1:3)	177	23.25	1,1-diphenylcyclopropane	58
				1,1-diphenylpropane	34
				unidentified substance ^e	6
1,1-Diphenylethane	NaAlH ₂ [OC ₂ H ₄ O(n-C ₃ H ₇)] ₂ (1:2)	183	6.75	1,1-diphenylcyclopropane	39
				1,1-diphenylpropane	14
				unidentified substance ^e	8
1,1-Diphenylethane	NaAlH ₂ [OC ₂ H ₄ O(n-C ₄ H ₉)] ₂ (1:2)	183	6.75	1,1-diphenylcyclopropane	37
				1,1-diphenylpropane	14
				unidentified substance ^e	10
1,1-Diphenylethane	NaAl(OC ₂ H ₄ OCH ₃) ₄ (1:1)	177	6.5	no reaction	—
	Al ₂ H ₃ (OC ₂ H ₄ OCH ₃) ₃ (1:3)	140	6.5	no reaction	—
	Al(OC ₂ H ₄ OCH ₃) ₃ (1:1)	177	6.5	no reaction	—
1,1-Diphenylethane	NaAlH ₂ (OC ₂ H ₄ OC ₂ H ₅) ₂ (1:3)	177	7	no reaction	—

1,1-Diphenylpropane	$\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_2$ (1:3)	183	9	2,2-diphenylbutane	93
	$\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_2$ (1:3)	162	23	2,2-diphenylbutane	94
	$\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OC}_2\text{H}_5)_2$ (1:2)	162	7.5	no reaction	—
Triphenylmethane	$\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_2$ (1:2)	177	1	1,1,1-triphenylethane	98 ^f
<i>sym</i> -Tetraphenylethane	$\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_2$ (1:4)	170	6	2,2-diphenylpropane	57
				1,1-diphenylcyclopropane	18
				2,2-diphenylbutane	8
				1,1-diphenylethane	7
Fluorene	$\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_2$ (1:3)	177	14	9,9-dimethylfluorene	66
				1,2-bis(9-methyl-9-fluorenyl)-ethane ^c	32 ^f
<i>n</i> -Butylbenzene	$\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_2$ (2:1)	183	37	2-phenylpentane ^g	30

^a The substrate to reagent initial mol. ratio; ^b determined by gas chromatography unless otherwise stated; ^c heating for another 5 h did not affect the composition of the reaction mixture; ^d the product was isolated from the nonvolatile portion of the reaction mixture; ^e unidentified substance had retention time between diphenylmethane and 1,1-diphenylpropane; ^f the yield of the isolated product; ^g gas chromatographic analysis showed the presence of two additional products (4 and 2 wt. %) with longer retention times.

selectivity; as confirmed by mass spectrometric analysis, the reaction mixture contained the indanes and indenenes methylated and ethylated in the 1-, 2- and 3-positions of the five-membered ring, along with the methyl and ethyl derivatives of spirocyclopropane (1,1')indane. Of all the benzene hydrocarbons used as solvents, only xylenes² and mesitylene resist alkylation with the hydride *I*. In the other cases *p*-ethylisopropylbenzene and sec-butylbenzene were formed in 2–4% from *p*-cymene, and from *n*-propylbenzene, as confirmed by mass spectra. Prolonged heating of *n*-butylbenzene with the hydride *I* leads to formation of 2-phenylpentane in 30% yield. The hydride *I* is thus capable, even though to a limited extent, to abstract protons from the benzylic group nonactivated by aryl group. As to the basicity of the hydride *I* it lies between sodium anthracenide, which catalyses also alkylation of toluene⁵¹, and sodium biphenylide, which abstracts the acidic hydrogen from triphenylmethane quantitatively but does not react with toluene⁵².

High selectivity was observed in the reaction of the hydride *I* with hydrocarbons containing the diaryl-activated methine group; the reaction of 1,1-diphenylpropane with the hydride *I* gave 2,2-diphenylbutane as a sole product (Fig. 2). 1,1,1-Triphenylethane was obtained similarly from triphenylmethane in essentially quantitative yield; the highest reaction rate was observed in this case, obviously owing to the relatively high acidity of the methine proton (pK_a 28–33)⁵³. Ethylene glycol was isolated

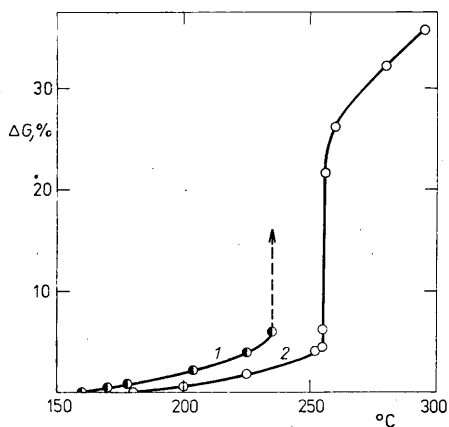


FIG. 3

Determination of Thermal Stability of Sodium Bis(2-methoxyethoxy)aluminum Hydride 1 and Sodium Bis(2-ethoxyethoxy)aluminum Hydride 2

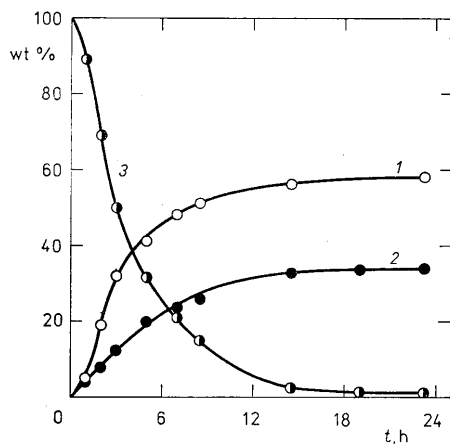


FIG. 4

Time Dependence of 1,1-Diphenylcyclopropane 1 and 1,1-Diphenylpropane 2 Concentrations in the Reaction of Diphenylmethane 3 with Sodium Bis(2-ethoxyethoxy)aluminum Hydride (1 : 3 initial molar ratio) in *p*-Cymene at 177°C

from the reaction mixture in an amount corresponding to 1.26 equivalents based on the triphenylmethane reacted; this finding confirms our assumption¹² that the cleavage of the $\text{CH}_3\text{—O}$ bond of the 2-methoxyethoxy group of the hydride *I* is a source of the methyl fragments participating in the methylation reactions.

When compared to the hydride *I* (ref.²⁴), sodium bis(2-ethoxyethoxy)aluminum hydride (*II*) exhibits somewhat higher thermal stability; as follows from thermogravimetric analysis, the hydride *II* is slowly decomposed at 180°C and rapidly only at 255°C (Fig. 3). The main product of the reaction of diphenylmethane with the hydride *II* is 1,1-diphenylcyclopropane; a competition reaction produces, likely *via* the same organometallic intermediate, 1,1-diphenylpropane as a side product (Fig. 4) and a small amount of an unidentified substance. Formation of 1,1-diphenylpropane by the cleavage of the cyclopropane ring is little probable, because of the inertness of 1,1-diphenylcyclopropane towards the hydrides *I* and *II* under the conditions of the cyclization reaction. 1,1-Diphenylcyclopropane and 1,1-diphenylpropane were also the products of the reaction of diphenylmethane with sodium bis(2-n-propoxyethoxy)aluminum hydride (*III*) and sodium bis(2-n-butoxyethoxy)aluminum hydride (*IV*). This provides support for our assumption that the fragments $\text{>AlOCH}_2\text{CH}_2\text{—}$ or $\text{>AlOCH}_2\text{CH}_2\text{O—}$ resulting from the thermal decomposition of the $\text{>AlOCH}_2\text{CH}_2\text{OR}$ ($\text{R} = \text{ethyl, n-propyl, n-butyl}$) group of the hydrides *II—IV* participate both in the cyclization and ethylation reactions. Also closely related to the mechanism of the reaction is the fact that the hydride *II* reacts only with hydrocarbons containing the methene group to form cyclopropyl and monoethyl derivatives. 1,1-Diphenylethane, 1,1-diphenylpropane and triphenylmethane were recovered unchanged when subjected to the reaction with the hydride *II*.

The authors thank Dr B. Čázenský, Institute of Inorganic Chemistry, Prague - Řež, for the kind gift of the hydride samples, Dr V. Hanuš, the J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Prague, for mass spectra measurements, Dr L. Dolejš, Institute of Organic Chemistry and Biochemistry, Prague, for gas chromatographic analyses combined with mass spectra measurements and Dr R. Řeřicha and Mr M. Pultr, this Institute, for IR and NMR measurements.

REFERENCES

1. Černý M., Málek J.: *Tetrahedron Lett.* 1972, 691.
2. Černý M., Málek J.: *This Journal* 39, 842 (1974).
3. Málek J., Černý M., Řeřicha R.: *This Journal* 39, 2656 (1974).
4. Málek J., Černý M.: *J. Organometal. Chem.* 84, 139 (1975).
5. Simmons H. E., Smith R. D.: *J. Amer. Chem. Soc.* 81, 4256 (1969).
6. Denis J. M., Girard C., Conia J. M.: *Synthesis* 1972, 549.
7. Zakharkin L. I., Savina L. A.: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1963, 1693.
8. Zakharkin L. I., Savina L. A.: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1962, 824.
9. Jorgenson M. J., Thacher A. F.: *Org. Syn.* 48, 75 (1968).
10. Jorgenson M. J., Fried A. W.: *J. Amer. Chem. Soc.* 87, 1815 (1965).

11. Jorgenson M. J., Thacher A. F.: *J. Chem. Soc., Chem. Commun.* 1969, 1290.
12. Ueda R. T., Cram D. J.: *J. Org. Chem.* 30, 2083 (1965).
13. Oullette R. J., Robins R. D., Smith A. jr. *J. Amer. Chem. Soc.* 90, 1619 (1968).
14. Zakharkin L. I., Savina L. A.: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1965, 1508.
15. Zakharkin L. I., Savina L. A.: *Zh. Obshch. Khim.* 37, 2565 (1967).
16. Walling C., Bollyky K.: *J. Org. Chem.* 28, 256 (1963).
17. Chaykovsky M., Corey E. J.: *J. Org. Chem.* 28, 254 (1963).
18. Bumgardner C. L., Iwerks H.: *J. Chem. Soc., Chem. Commun.* 1968, 431.
19. Bumgardner C. L.: *J. Chem. Soc., Chem. Commun.* 1965, 374.
20. Eberhard P., Huisgen R.: *J. Amer. Chem. Soc.* 94, 1345 (1972).
21. Elmes B. C.: *Tetrahedron Lett.* 1971, 4139.
22. Kříž O., Čásenský B., Štrouf O.: *This Journal* 38, 842 (1973).
23. Kříž O., Trška P., Čásenský B.: *This Journal* 39, 2559 (1974).
24. Čásenský B., Macháček J., Abrham K.: *This Journal* 36, 2648 (1971).
25. *Handbook of Chemistry and Physics* (D. Hodgman, Ed.), p. C-324. Chemical Rubber Publishing Co., Cleveland 1968.
26. Ref. 25, p. C-375.
27. Hartman W. W., Phillips R.: *Org. Syn; Coll. Vol. II*, p. 232. Wiley, New York 1959.
28. Nesmeyanov A. N., Sazonova V. A.: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1941, 499.
29. Wittig G., Gauss W.: *Chem. Ber.* 80, 363 (1947).
30. Klages A., Heilman S.: *Chem. Ber.* 37, 1450 (1904).
31. Norris J. F.: *Org. Syn., Coll. Vol. I*, p. 548. Wiley, New York 1961.
32. Bumgardner C. L.: *Tetrahedron Lett.* 1966, 5499.
33. Gelin R., Chantegrel B.: *Bull. Soc. Chim. Fr.* 1971, 2527.
34. *Sadtler Standard Spectra, Infrared Spectrogram* No 219. Philadelphia, USA.
35. *Sadtler Standard Spectra, Infrared Spectrogram* No 9509 CA. Philadelphia, USA.
36. Reinsdorf D., Normant H.: *Organometal. Chem. Syn. I*, 375 (1972).
37. Simmons H. E., Blanchard E. P., Hartzler H. D.: *J. Org. Chem.* 31, 295 (1966).
38. Jung A., Brini M.: *Bull. Soc. Chim. Fr.* 1965, 587.
39. Ransley D. L.: *J. Org. Chem.* 31, 3595 (1966).
40. Ref. 25, p. C-309.
41. Pines H., Huntsman W. D., Ipatieff V. N.: *J. Amer. Chem. Soc.* 73, 4344 (1951).
42. Cram D. J.: *J. Amer. Chem. Soc.* 74, 2154 (1952).
43. Coombs M. M.: *J. Chem. Soc.* 1958, 345.
44. Scherf G. W. H., Brown R. K.: *Can. J. Chem.* 38, 697 (1960).
45. Chazan J. B., Ourisson G.: *Bull. Soc. Chim. Fr.* 1968, 1384.
46. Eisch J. J.: *J. Org. Chem.* 28, 707 (1963).
47. Lagendijk A., Szwarc M.: *J. Amer. Chem. Soc.* 93, 5359 (1971).
48. Gerson F., Martin W. B. Jr.: *J. Amer. Chem. Soc.* 91, 1883 (1969).
49. Casson D., Tabner B. J.: *J. Chem. Soc. B* 1969, 887.
50. Casson D., Tabner B. J.: *J. Chem. Soc. B* 1970, 1565.
51. Pines H.: *Synthesis* 1974, 309.
52. Eisch J. J., Kaska W. C.: *J. Org. Chem.* 27, 3745 (1962).
53. House H. O.: *Modern Synthetic Reactions*, p. 494. Benjamin, New York 1972.

Translated by J. Hettflejš.