

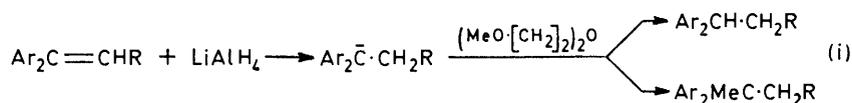
Lithium Aluminium Hydride-mediated Methylation of Diphenylmethane and Allied Compounds by Bis-2-(methoxyethyl) Ether

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Diphenylmethane (1) yields mainly 1,1-diphenylethane or 2,2-diphenylpropane (10) upon heating with lithium aluminium hydride in bis-(2-methoxyethyl) ether, depending on the reaction conditions. Cyclic analogues of diphenylmethane are $\alpha\alpha$ -dimethylated much faster than diphenylmethane itself under the same conditions. 1,1-Diphenylcyclopropane (11) is reduced to 2,2-diphenylpropane by lithium aluminium hydride on prolonged heating in bis-(2-methoxyethyl) ether. Evidence for the formation of the cyclopropane (11) as a by-product from diphenylmethane, bis-(2-methoxyethyl) ether, and lithium aluminium hydride is presented.

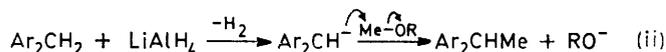
In a previous communication¹ we described the reaction of 1,1-diphenylethylene with lithium aluminium hydride in tetrahydrofuran which affords 1,1-diphenylethane (6) as the major product, accompanied by 2,2,3,3-tetraphenylbutane. An extension of this study^{2,3} revealed that similar reactions executed in bis-(2-methoxyethyl) ether

1,1-diphenylethane (6) in 16 h at 150 °C, whereas xanthen (2) yields 9,9-dimethylxanthen (7) in 1 h under the same conditions. Similarly, 9,10-dihydroanthracene (obtained *in situ* from anthracene and lithium aluminium hydride) affords 9,10-dihydro-9,9,10,10-tetramethylanthracene (9) fast enough to prevent isolation, or even



might lead to either protonation or methylation of the intermediate carbanions according to equation (i). Similar, but somewhat different, findings have been recently reported for sodium dihydridobis-(2-methoxyethoxy)aluminate and some aromatic olefins,⁴ ketones,⁵ and diarylmethanes.^{6,7}

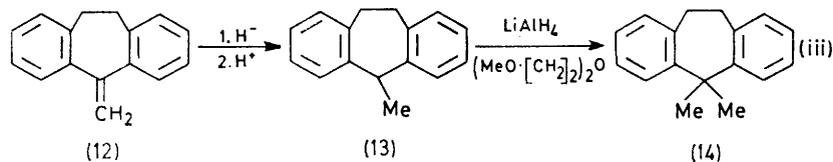
We report now a simple and synthetically useful methylation of diphenylmethane (1) and related compounds, which appears to be mechanistically associated with the above mentioned reactions. Diarylmethanes are deprotonated by lithium aluminium hydride in bis-(2-methoxyethyl) ether yielding diarylmethanide ions which are methylated by the solvent [equation (ii)].



The starting materials and the products obtained by this method are listed in the Table. The stability of the intermediate carbanions (or anion radicals^{5,8,9}), which

detection of intermediates. In contrast, 9,10-dihydrophenanthrene (5) is not methylated even after 46 h under the same conditions. This last observation indicates that the methylation is not only regioselective at the α -carbon atom, but also selectively applicable to a benzylic α -position in the presence of a benzylic site. Indeed, 10,11-dihydro-5-methyl-5H-dibenzo[*a,d*]cycloheptene (13)³ is methylated only at the benzylic position [equation (iii)].

Two by-products were identified in the reaction of diphenylmethane (1) with lithium aluminium hydride and bis-(2-methoxyethyl) ether: 2,2-diphenylpropane (10) and 1,1-diphenylcyclopropane⁵ (11) [$\delta(\text{CH}_2)$ 1.21] in *ca.* 1 : 1 ratio, as shown by the ¹H n.m.r. spectrum. The cyclopropane (11) could have been formed as shown by equation (iv). This mechanism is supported by the observation that the cyclopropane (11) is not formed during the methylation of 1,1-diphenylethane (6) under the same conditions, indicating that (11) is formed



are intensely coloured, appears to be related to both the degree of methylation and the reaction rate. Thus, diphenylmethane (1) is mainly monomethylated to give

¹ I. Granoth and Y. Segall, *J.C.S. Chem. Comm.*, 1974, 887.

² I. Granoth, R. Alkabets, Y. Segall, E. Rachaman, and H. Leader, *J.C.S. Chem. Comm.*, 1975, 348.

³ I. Granoth, Y. Segall, E. Rachaman, and R. Alkabets, 25th IUPAC Congress, Jerusalem, July 1975.

⁴ J. Malek and M. Cerny, *J. Organometallic Chem.*, 1975, **84**, 139.

⁵ J. Malek, M. Cerny, and R. Rericha, *Coll. Czech. Chem. Comm.*, 1974, **39**, 2656.

directly from (1). Furthermore, the dimeric species (15) and (16) have been obtained as by-products in the preparation of compounds (7) and (8), respectively. The fast monomethylation of xanthen (2), for example,

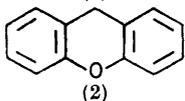
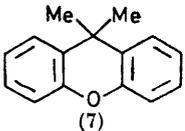
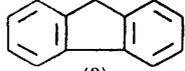
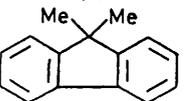
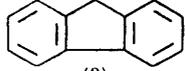
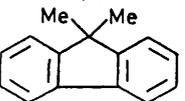
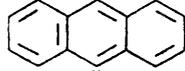
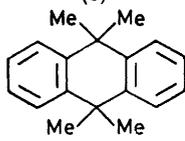
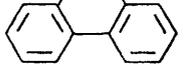
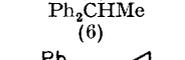
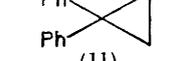
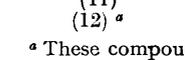
⁶ M. Cerny and J. Malek, *Tetrahedron Letters*, 1972, 691.

⁷ M. Cerny and J. Malek, *Coll. Czech. Chem. Comm.*, 1976, **41**, 119.

⁸ M. Cerny and J. Malek, *Coll. Czech. Chem. Comm.*, 1974, **39**, 842.

⁹ H. O. House and P. D. Weeks, *J. Amer. Chem. Soc.*, 1975, **97**, 2785.

Products obtained in bis-(2-methoxyethyl) ether at 150 °C from diarylmethane and related compounds in the presence of lithium aluminium hydride

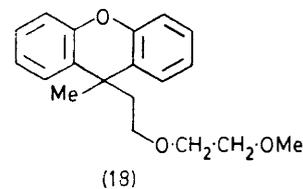
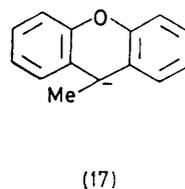
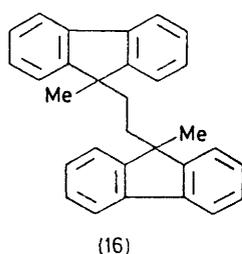
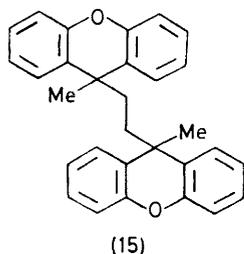
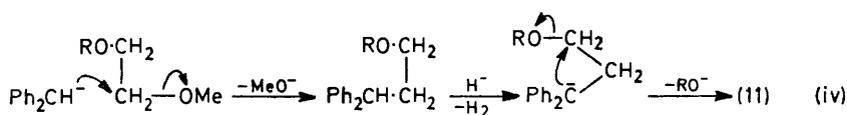
Starting material Ph ₂ CH ₂ (1)	Reaction time (h)	Product (6)	Yield (%)	B.p. (°C) [Torr] or m.p. (°C)	δ(CH ₃)	Ref.
	16		70	85 [0.3]	1.53	5
	1		60	104 [0.1]	1.52	†
	1.5		50	100 [0.1]; 92	1.41	5
	4		50	166—167	1.64	3, ‡
	46	Nil				
	48	Ph ₂ CMe ₂ (10)	80	90 [0.3]	1.61	5
	55	(10)	76	90 [0.3]	1.61	5
	5	(14) ^δ	82	120 [0.1]	1.85	3

^a These compounds are reduced ^{2,3} to 9,10-dihydroanthracene and (13) [equation (iii)], respectively, faster than the methylation in bis-(2-methoxyethyl) ether. I. Granoth, Y. Segall, R. Alkabetz, and H. Leader (*J. Org. Chem.*, in the press) give a detailed report on H⁻ addition to aromatic olefins. ^δ Purified by column chromatography (neutral alumina) with n-hexane as eluant.

† J. B. Chazan and G. Ourisson, *Bull. Soc. chim. France*, 1968, 1384. ‡ V. N. Ipatieff, H. R. Appel, and H. Pines, *J. Amer. Chem. Soc.*, 1951, **73**, 5507.

is probably followed by a ready deprotonation giving the carbanion (17), which might either be further methylated according to equation (ii), or ethylated in analogy to equation (iv), giving the ether (18). The

The solution of the carbanion formed upon addition of hydride to 1,1-diphenylethane is red, whereas diphenylmethane and the hydride produce a yellow solution in bis-(2-methoxyethyl) ether. Moreover, in



intermediate (18) might react with the anion (17) thus producing (15). These latter reactions would be slower than the methylation [equation (ii)] because of the greater steric hindrance associated with the side-reaction, involving nucleophilic attack at CH₂ rather than at CH₃ in bis-(2-methoxyethyl) ether.

spite of the formation of 2,2-diphenylpropane (10) as a by-product in the latter reaction, the yellow colour persists only during the monomethylation stage. The relatively difficult proton abstraction from 1,1-diphenylethane (6) by lithium aluminium hydride appears to be due to steric factors, since the cyclic, relatively rigid,

compounds studied (Table) are easily deprotonated, yield intensely red solutions of the appropriate carbanions, and are fully methylated at the α -position. Furthermore, orthogonal alignment of the aromatic ring with respect to the generated carbanion,¹⁰ stabilizing the latter, is better achieved with the cyclic compounds (2)—(4) and (12) than with diphenylmethane (1) and, especially, 1,1-diphenylethane (6). However, compounds (6) and, more interestingly, (11) are methylated and reduced, respectively, giving 2,2-diphenylpropane (10) upon prolonged heating with lithium aluminium hydride in bis-(2-methoxyethyl) ether. The reduction of (11) by hydride is reminiscent of the addition of hydride to 1,1-diphenylethylene,^{1,4} though the latter reaction is much faster than the former.

EXPERIMENTAL

All starting materials were either commercially available or prepared as described elsewhere.^{11,12} Products were characterized by comparison of their physical constants and ¹H n.m.r. data with those of authentic samples or with literature values. The ¹H n.m.r. spectra were determined at 60 MHz with a JEOL C-60 HL spectrometer for solutions in CCl₄ with Me₄Si as internal standard.

The progress of each reaction and the time needed for its completion were determined as follows. At various time intervals, a sample (0.5 ml) of the reaction mixture was pipetted into ice-cold N-HCl (20 ml). Extraction with CCl₄, drying over neutral alumina, and concentration to 0.5 ml, were followed by a ¹H n.m.r. analysis.

Lithium Aluminium Hydride-mediated Methylation by Bis-(2-methoxyethyl) Ether. General Procedure.—A mixture of dry bis-(2-methoxyethyl) ether (50 ml), lithium aluminium hydride (2.0 g), and the appropriate substrate (5.0 g) were heated under dry nitrogen at 150 °C for the time specified (Table). The mixture was cooled and ethyl acetate (10 ml) was carefully added, followed by N-HCl (300 ml). Extraction with CHCl₃ (100 ml), thrice washing the organic solution with water (100 ml), drying over neutral alumina (20 g), and evaporation gave the crude product. Fractional distillation, usually needed to remove some bis-(2-methoxyethyl) ether, or recrystallization from ethanol, or both, led to the pure products described in the Table.

1,2-Bis-(9-methylxanthen-9-yl)ethane (15). This compound was obtained, in 7% yield, by three recrystallizations (EtOH) of the residue left from the distillation of crude (7), m.p. 173°; δ 1.33 (6 H, s, CH₃), 1.48 (4 H, s, CH₂), and 6.70—7.15 (16 H, m, ArH); *m/e* 418 (2%, M⁺) and 195 (100, [M - C₁₆H₁₅O]).

1,2-Bis-(9-methylfluoren-9-yl)ethane (16). This was obtained in 10% yield, by a procedure analogous to that for (15), from the residue left after distillation of crude (8), m.p. 183°; δ 1.07 (6 H, s, CH₃), 1.20 (4 H, s, CH₂), and 6.85—7.70 (16 H, m, Ar-H); *m/e* 386 (17%, M⁺), 207 (25, [M - C₁₄H₁₁]⁺), 179 (100, C₁₄H₁₁⁺), and 178 (32, C₁₄H₁₀⁺).

[6/776 Received, 21st April, 1976]

¹⁰ M. J. Jorgenson and A. F. Tacher, *Chem. Comm.*, 1969, 1290.

¹¹ J. L. Kice and F. Taymoorian, *J. Amer. Chem. Soc.*, 1959, **81**, 3405.

¹² M. J. Jorgenson and A. F. Tacher, *Org. Synth.*, 1968, **43** 75.