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REACTIONS OF SODIUM BIS-(2-ALKOXYETHOXY)ALUMINOHYDRIDES. I. HYDROGENOLYSIS OF BENZOPHENONE AND ALKYLATION OF THE METHYLENE GROUP OF DIPHENYLMETHANE

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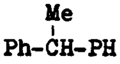
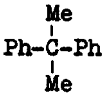
As previously noted, aromatic carbinols, aldehydes, ketones, carboxylic acids, their esters or sodium salts, with an electron-donating substituent on the ring facilitating the formation of a resonance-stabilized mesomeric carbonium ion, readily undergo hydrogenolysis on treatment with sodium bis-(2-methoxyethoxy)aluminohydride /$NaAlH_2(OCH_2CH_2CH_3)_2$/ (SMEAH) and give excellent yields of the corresponding substituted alkyl arenes or diarylmethanes[1-4]. In an extension of our study on the reducing and hydrogenolytic properties of the metal hydrides of this type, we wish to present our results on the one-step hydrogenolysis of benzophenone and on the selective alkylation of the intermediately formed diphenylmethane to diphenylalkylmethanes with SMEAH and sodium bis-(2-ethoxyethoxy)aluminohydride[5] /$NaAlH_2(OCH_2CH_2OC_2H_5)_2$/ (SEEAH). The ability of these hydrides to alkylate selectively an activated methylene group has no parallel in the complex metal hydride chemistry.

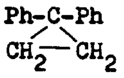
In a typical experiment, where benzophenone (0.05 mol) was heated with a solution of SMEAH (0.110 mol) in o-xylene (83.6g) at 142°, the reaction surprisingly did not stop at the diphenylmethane stage, as could be expected by analogy with the reaction of benzophenone and $LiAlH_4.AlCl_3$ [6-9]; during the course of the reaction the solution turned to deep red and after 6 hr refluxing and working up of the reaction mixture, the reaction yielded benzhydrol (10%), diphenylmethane (8%), 1,1-diphenylethane (I)(59%), and a small amount (<1%) of 2,2-diphenylpropane (II) and 1,1-diphenylcyclopropane (III) as volatile products [10,11]. From the distillation residue sym.tetraphenylethane (IV) and 9,10-diphenylanthracene [12](V) could be isolated by crystallization [11]. By using m- or p-xylene as solvents, the same products were obtained from benzophenone. This proved that the alkylaromatic solvents did not participate in the alkylation.


$\mathrm{Ph{-}\overset{Me}{C}H{-}PH}$

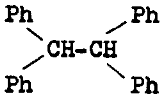
I


$\mathrm{Ph{-}\overset{Me}{\underset{Me}{C}}{-}Ph}$

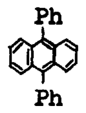
II



III



IV



V

If the reaction was repeated in n-propylbenzene (molar ration of benzophenone to SMEAH 1:3) at 162°, after 3.25 hr refluxing all diphenylmethane, and after 4.5 hr all I, were transformed into II and III as sole products in 71 and 11% yield, resp. The changes of concentration with time of all volatile compounds during the reaction are listed in Table I.

Table I

Composition of the Reaction Mixture (% wt.)[a] in the One-step Hydrogenolysis of Benzophenone and Methylation of Diphenylmethane by Sodium Bis-(2-methoxyethoxy)aluminohydride[b]

Compound	Reaction time (hr)					
	0.25	0.50	1.00	3.00	4.50	6.75
Benzhydrol[c]	50.0	11.4	-	-	-	-
Diphenylmethane	38.5	64.8	14.6	0.8	-	-
1,1-Diphenylethane	11.5	23.8	60.7	2.5	-	-
2,2-Diphenylpropane	-	-	15.7	84.9	88.2	88.2
1,1-Diphenylcyclopropane	-	-	9.0	11.8	11.8	11.8

[a] By g.l.c. of the reaction mixture after evaporation of solvents. [b] Molar ratio of benzophenone to SMEAH was 1:3; reaction temperature 162°. [c] Benzophenone was transformed into benzhydrol during 5 min of reaction.

The fact resulting from Table I that diphenylmethane was the intermediate product in the methylation occuring at the phenyl-substituted benzylic carbon was proved by a separate reaction of diphenylmethane (0.030 mol) as the starting compound with SMEAH (0.096 mol) in n-propylbenzene. Similarly as in the case of benzophenone, during the course of the reaction the solution turned from red to dark red and after 7.5 hr refluxing at 162°, the reaction gave II together with III as the sole products in 77 and 21% yield, resp. Practically the same result was obtained when the reaction was carried out with SMEAH solved in diphenylmethane and both reagents were allowed to react at the same temperature without the use of alkylaromatic solvents.

Refluxing of IV with SMEAH in a mixture of n-propylbenzene and n-butylbenzene at 170° for 6 hr yielded, although at a slower rate, the same products, e. g., II and III, in addition to small amounts of diphenylmethane and I.

In contrast to methylation with SMEAH, the reaction of SEEAH (0.042 mol) with diphenylmethane (0.021 mol) in n-propylbenzene did not afford the dialkylated product and after refluxing at 162° for 13.5 hr 1,1-diphenylpropane (VI) and the cyclopropylderivative III were obtained in 42 and 38% yield, resp., in addition to small amounts of I, 2,2-diphenylbutane (VII), an unknown compound, and of unreacted diphenylmethane.

$\text{Ph-}\overset{\text{Et}}{\overset{|}{\text{C}}}\text{H-Ph}$

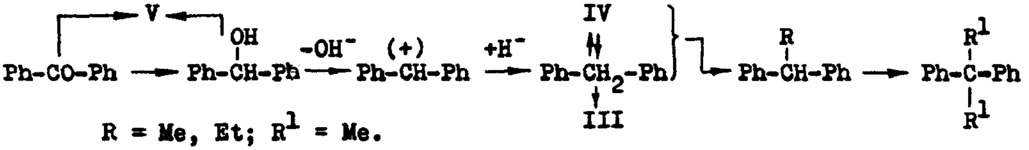
VI

$\text{Ph-}\underset{\text{Me}}{\underset{|}{\overset{\text{Et}}{\overset{|}{\text{C}}}}}\text{-Ph}$

VII

The results with SMEAH and SEEAH indicate that these hydrides act, under proper thermal conditions, not only as reducing but also as alkylating agents capable to replace hydrogen atoms, probably by a free radical mechanism, on the activated benzylic carbon by alkyls, generated by the fragmentation of the 2-alkoxyethoxy groups of the hydride molecule. Probably by an another mechanism, gem. diarylcyclopropanes are formed from diarylmethanes by a reaction parallel to alkylation.

Although the mechanism of both alkylation and cyclization has not yet been fully cleared, the formation of the products I-VI from benzophenone, diphenylmethane, and IV under the action of SMEAH or SEEAH, as well as the consecutive character of the alkylation (Table I), led us to postulate eq. 1 as the most likely reaction sequence:



$$\mathrm{Ph{-}CO{-}Ph} \longrightarrow \mathrm{Ph{-}\overset{OH}{CH}{-}Ph} \xrightarrow{-OH^-} \mathrm{Ph{-}\overset{(+)}{CH}{-}Ph} \xrightarrow{+H^-} \mathrm{Ph{-}\underset{III}{\overset{IV}{CH_2}}{-}Ph} \longrightarrow \mathrm{Ph{-}\overset{R}{CH}{-}Ph} \longrightarrow \mathrm{Ph{-}\underset{R^1}{\overset{R^1}{C}}{-}Ph} \quad \text{eq.1}$$

$R = Me, Et;\ R^1 = Me.$

The alkylation has been extended to other aromatic nonenolizable ketones and to quinones, such as fluorenone and anthraquinone, to other diarylmethanes, e.g., 1,1-diphenylpropane (with SMEAH), to fused compounds containing methylene group, e.g., 9H-fluorene and 9,10H-dihydroanthracene or 1H-indene, as well as to arylated ethylenes. Similar results obtained in the reactions of these compounds with sodium bis-(2-alkoxyethoxy)aluminohydrides proved the general character of this alkylation and will be published later in detail.

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10. According to g. l. p. c. of the volatile product fraction.
11. All the substances isolated had infrared, ultra-violet or nuclear magnetic resonance spectra and elemental analyses and/or mass spectra consistent with their assigned structures.
12. Benzophenone and benzhydrol have been reported to give V on treatment with CaH_2 at high temperatures (W. Schlenk and M. Karpus, Chem. Ber., 61, 1675 (1928).