739. *Hydrogenolysis of Aromatic Carbonyl Compounds and Alcohols with Aluminium Chloride and Lithium Aluminium Hydride.*

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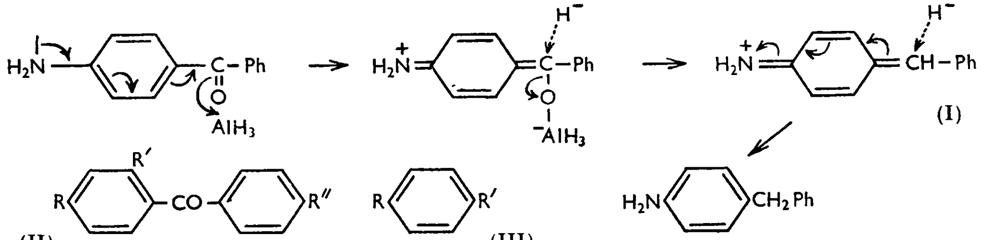
Aromatic ketones are smoothly hydrogenolysed by aluminium chloride and lithium aluminium hydride in ether. Benzaldehyde yields benzyl alcohol, but *p*-methoxy- and *p*-dimethylamino-benzaldehyde give the corresponding toluenes. These effects are interpreted as the result of the reduction of an intermediate carbonium ion.

The hydrogenolysis of amides ($NR_2{\cdot}COR' \longrightarrow NR_2{\cdot}CH_2R'$) and vinylogues of amides with lithium aluminium hydride has been extended to substituted aromatic carbonyl compounds by Conover and Tarbell[1] who used excess of lithium aluminium hydride at up to 90° for several days, obtaining yields of 30—80%. A mechanism was proposed, similar to that for amides,[2] the essential feature of which is the production and reduction of a

$$Ar{\cdot}CHR{\cdot}OH + A \longrightarrow Ar{\cdot}CHR^+ + HOA^-$$

mesomeric cation, *e.g.*, (I). This results from the attack of a Lewis acid on an alcohol, and this ionisation would be aided by use of a stronger Lewis acid (*e.g.*, aluminium chloride), presence of electron-donating groups in the *ortho*- or *para*-position of the benzene ring, or introduction of a group R capable of facilitating ionisation.

It has been reported[3, 4, 5] that such hydrogenolyses of allylic alcohols are promoted by aluminium chloride in the presence of lithium aluminium hydride. We now record the hydrogenolysis of a number of aldehydes, ketones, and alcohols according to the above scheme. Thus benzophenone, a number of substituted benzophenones (II; $R = R'' = NMe_2$, $R' = H$; $R = R'' = OMe$, $R' = H$; $R = R' = R'' = OMe$), and α-*p*-methoxyphenylbenzyl alcohol on brief treatment with aluminium chloride and lithium aluminium hydride (2 : 1 mol.) in ether gave the corresponding diphenylmethanes in yields of about 90%, and benzanthrone gave benzanthrene. Similarly acetophenone and substituted acetophenones (III; $R' = Ac$) yield ethylbenzenes. It thus appears that this is a general method for the hydrogenolysis of aryl ketones, though the use of a molar ratio of aluminium chloride to lithium aluminium hydride of less than 2 : 1 results in the production of styrene from acetophenone, presumably by reduction to the alcohol, replacement of the hydroxyl group by chlorine,[6] and loss of hydrogen chloride on distillation.[3] In contrast benzaldehyde, even with an aluminium chloride–lithium aluminium hydride ratio of 2 : 1, yields the normal lithium aluminium hydride reduction product, benzyl alcohol. Introduction of a *p*-methoxy- or *p*-dimethylamino-group, giving (III; R = OMe or



(I)

(II)

(III)

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[1] Conover and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 3586.
[2] Gaylord, *Experientia*, 1954, **10**, 166, 423.
[3] Broome and Brown, *Chem. and Ind.*, 1956, 1307.
[4] Birch and Slaytor, *ibid.*, p. 1524.
[5] Wheeler and Mateos, *ibid.*, 1957, 395.
[6] Cf. Broome, Brown, and Summers, *J.*, 1957, 2071.

NMe_2, R′ = CHO), results in 90% yields of the corresponding toluenes. Thus, for aryl aldehydes a structural requisite for hydrogenolysis is a *para*-group which is capable of donating electrons to facilitate the production of, and to stabilise sufficiently, the intermediate carbonium ion.

When this paper had been written, an abstract [7] reporting similar results became available.

EXPERIMENTAL

Light petroleum refers to the fraction of b. p. 40—60° unless otherwise stated. References given as " lit." are from Beilstein's " Handbuch."

General Method.—The reagent was prepared by the addition of lithium aluminium hydride (1·75 mol.) to a solution of aluminium chloride (3·5 mol.) in ether (1·33 mol.). After the vigorous reaction had subsided the alcohol, aldehyde, or ketone (1 mol.) was added, as solid or in ether, during 5—10 min. Each addition produced a vigorous reaction accompanied by a transient colour (usually orange). The reaction was completed by boiling the mixture under reflux for 20—30 min. Excess of methyl formate in ether was added at 0° to decompose excess of reducing agent, and the mixture was worked up in the usual way with 20% sulphuric acid or 20% aqueous sodium hydroxide (for basic products). Evaporation of the dried ether layer yielded the crude product which was purified and characterised as described below.

Specific Examples.—*Benzyl alcohol from benzaldehyde* (8·3 g.). Distillation gave a colourless oil (5·1 g.), b. p. 204°/765 mm., n_D^{18} 1·5367 (lit., b. p. 205°/760 mm., n_D^{20} 1·5395). The phenylurethane had m. p. 78° (lit., 78°).

p-*Methoxytoluene from* p-*anisaldehyde* (9·68 g.). The oil, in light petroleum, was filtered through alumina. *p*-Methoxytoluene (6·75 g.) was obtained having b. p. 172—173°/753 mm., n_D^{19} 1·5124 (lit., b. p. 177°/760 mm., n_D^{19} 1·5124).

p-*Dimethylaminotoluene from* p-*dimethylaminobenzaldehyde* (8·01 g.). Distillation gave a liquid (6·54 g.), b. p. 211°/765 mm., n_D^{16} 1·5486 (lit., b. p. 211°/760 mm., n_D^{20} 1·5470). The picrate separated from alcohol as yellow needles, m. p. 130°. von Braun [8] gives m. p. 130°.

Ethylbenzene from acetophenone (8·7 g.). Distillation gave ethylbenzene (7·2 g.), b. p. 136—138°/766 mm., n_D^{17} 1·5032 (lit., b. p. 136°/760 mm., n_D^{15} 1·4986) (Found: C, 90·5; H, 9·2. Calc. for C_8H_{10}: C, 90·6; H, 9·4%). The infrared spectrum was identical with that of an authentic specimen.

p-*Methoxyethylbenzene from* p-*methoxyacetophenone* (3·98 g.). Distillation of the residue yielded a colourless oil (2·54 g.), b. p. 192—193°/742 mm., n_D^{19} 1·505 (lit., b. p. 195—196°/760 mm., n_D 1·509).

Diphenylmethane from benzophenone (4·26 g.). The residual oil in light petroleum was filtered through alumina. Diphenylmethane (3·44 g.) was obtained as colourless needles, m. p. and mixed m. p. 25°. The infrared spectrum was identical with that of an authentic specimen.

4-*Methoxydiphenylmethane from* α-p-*methoxyphenylbenzyl alcohol* (8·0 g.). Isolation as in the previous case and distillation yielded 4-methoxydiphenylmethane (6·7 g.), b. p. 179°/19 mm. (lit., 170°/10 mm.). Demethylation with hydriodic acid gave 4-hydroxydiphenylmethane, needles, m. p. 83—84°. Short and Stewart [9] give m. p. 84°.

4 : 4′-*Dimethoxydiphenylmethane from* 4 : 4′-*dimethoxybenzophenone* (0·54 g.). The crystalline product (0·49 g.) separated from light petroleum as plates, m. p. and mixed m. p. 50—51°.

2 : 4 : 4′-*Trimethoxydiphenylmethane from* 2 : 4 : 4′-*trimethoxybenzophenone* (2·94 g.). The residual oil (2·69 g.) in benzene (5 ml.) was put on alumina and eluted with light petroleum. Evaporation and distillation yielded 2 : 4 : 4′-*trimethoxydiphenylmethane*, b. p. 120—130°/0·07 mm. (Found: C, 74·7; H, 7·1. $C_{16}H_{18}O_3$ requires C, 74·5; H, 7·0%). The infrared spectrum of the liquid showed medium and strong bands at 720, 759, 833, 922, 934, 1034, 1116, 1153, 1172, 1206, 1242, 1290, 1333, 1418, 1439, 1460, 1508, 1595, 1618, 2841, 2941, and 3012 cm.$^{-1}$.

4 : 4′-*Bisdimethylaminodiphenylmethane from Michler's ketone* (2·0 g.). The solid crystallised from ethanol in plates (1·70 g.), m. p. 90·5° (Found: C, 80·2; H, 8·7; N, 11·3. Calc. for

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[7] Rainer, Berger, and Nystrom, Amer. Chem. Soc. (Org. Div.) Abs. Papers, Miami, Florida, 1957, p. 51-O.

[8] von Braun, *Ber.*, 1908, **41**, 2113.

[9] Short and Stewart, *J.*, 1929, 553.

$C_{17}H_{22}N_2$: C, 80·3; H, 8·7; N, 11·0%). Doebner[10] gives m. p. 90°. The compound in ethanol remained colourless on the addition of acetic acid.

Benzanthrene from benzanthrone (4·0 g.). The residual crude benzanthrene was purified on alumina and obtained as pale orange leaflets (3·1 g.), m. p. 83·5—84·5°. Bally and Scholl[11] give m. p. 84°. The picrate separated from alcohol as red needles, m. p. 109—110°. Chatterjee[12] gives m. p. 110—111°.

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[10] Doebner, *Ber.*, 1879, **12**, 810.
[11] Bally and Scholl, *Ber.*, 1911, **44**, 1667.
[12] Chatterjee, *J. Indian Chem. Soc.*, 1943, **20**, 329.