429. *A Reduction of Diaryl Ketones.*

By T. MOLE.

Formaldehyde in methanolic sodium hydroxide solution reduces diaryl ketones to the secondary alcohols. This reduction is also accomplished by using salicylaldehyde in alkaline ethylene glycol.

THE Cannizzaro disproportionation of aldehydes in alkaline solution is thought to occur by way of a hydride-anion transfer from one aldehyde molecule to another.[1] Transfer of hydride ions from aldehydes to ketones should be similarly possible. The process should occur less easily than the Cannizzaro disproportionation, because replacement of the aldehydic hydrogen atom by a second alkyl or aryl group must make the carbonyl group less susceptible to nucleophilic attack and thus a poorer hydride-ion acceptor. It is known that enolisable ketones are reduced by formaldehyde, but only after the acidic hydrogen atoms are replaced by hydroxymethyl groups.[2-5]

This paper describes the reduction of several diaryl ketones by formaldehyde in refluxing, strongly alkaline methanol. Reaction was slow at room temperature. A many-fold excess of formaldehyde was slowly added to the other reagents during several hours. The reduction of diaryl ketones by alkaline ethanol is a well-documented reaction.[6] Alkaline methanol is likewise a source of hydride ions. It was, however, established that reduction of diaryl ketones by methanolic sodium hydroxide is much slower than reduction by formaldehyde.

Salicylaldehyde was also used as the reducing agent with ethylene glycol as solvent at 150—190°. With a large excess of the reducing agent good yields of diarylmethanols were obtained after only a few minutes' reaction. Salicylaldehyde alone does not undergo a Cannizzaro reaction,[7] although it gives hydrogen and salicylic acid on fusion with alkali [8] or when heated with a concentrated solution of alkali in glycol. Such a solution acts as a source of hydride ions at high temperature,[9] just as does methanolic alkali, but it seems

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[1] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, N.Y., 1953, p. 154; Hammett, " Physical Organic Chemistry," McGraw-Hill, N.Y., 1940, p. 350.

[2] Apel and Tollens, *Ber.*, 1894, **27**, 1087.

[3] Mannich and Brose, *Ber.*, 1923, **56**, 833.

[4] Roach, Witticoff, and Miller, *J. Amer. Chem. Soc.*, 1947, **69**, 265.

[5] Witticoff, *Org. Synth.*, 1951, **31**, 101.

[6] Montagne, *Rec. Trav. chim.*, 1908, **27**, 327.

[7] Cannizzaro and Bertagini, *Annalen*, 1856, **98**, 192.

[8] Piria, *Annalen*, 1839, **30**, 165; Lock, *Ber.*, 1928, **61**, 2234.

[9] Barnes and Palmer, *Australian J. Chem.*, 1957, **10**, 334.

unlikely that the reducing action of the glycol competes effectively with reduction by salicylaldehyde.

Benzophenone, 1-naphthyl phenyl ketone, and 4-phenylbenzophenone were successfully reduced by both formaldehyde and salicylaldehyde. 4-Chlorobenzophenone was reduced by both procedures; reduction by salicylaldehyde in glycol gave a much lower yield, probably owing to partial hydrolysis of the chloro-group. 2-Phenylbenzophenone and 2-benzoylbenzoic acid were reduced by salicylaldehyde but not by formaldehyde; this suggests that the salicylaldehyde reduction is the more vigorous. Fluorenone was smoothly reduced by salicylaldehyde, but 9-hydroxymethylfluoren-9-ol was the only product isolated from the reaction of fluorenone with formaldehyde in alcoholic alkali. Reduction to fluorenol must have occurred initially, followed by condensation with formaldehyde. No attempts were made to reduce amino- and nitro-substituted benzophenones, since the reagents would be expected to react with the substituent groups.

EXPERIMENTAL

Structures of all products were checked by infrared spectroscopy. Microanalyses were carried out in the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory.

Reduction by Formaldehyde.—(a) *Of benzophenone.* Benzophenone (18·5 g.), sodium hydroxide (22 g.), and methanol (150 ml.) were refluxed on a steam-bath. Formalin (15 ml.) in methanol (20 ml.) was added dropwise during 3 hr. The mixture, which turned brown towards the end of the addition, was cooled, poured into water, and extracted with ether. An ethereal extract of the diluted reaction product yielded diphenylmethanol (80% yield), m. p. and mixed m. p. 66—67°.

(b) *Of other ketones.* Other ketones were reduced similarly. The methanols were purified by recrystallisation from benzene–light petroleum and by chromatography on alumina. 1-Naphthylphenyl- and 4-biphenylylphenyl-methanol were obtained in approx. 80% yields, and *p*-chlorodiphenylmethanol was obtained in 72% yield.

(c) *Control experiment.* Sodium hydroxide (14 g.), benzophenone (7 g.), and methanol (70 ml.) were refluxed for 2 hr. The infrared spectrum of the extracted product indicated a yield of only 20% of diphenylmethanol.

Reaction of Fluorenone with Formaldehyde.—Formalin (10 ml.) was added slowly (5½ hr.) to a refluxing solution of sodium hydroxide (20 g.), fluorenone (2·0 g.), and ethanol (50 ml.) in methanol (100 ml.). The solution was then poured into water and extracted with ether. The extract was dried (Na_2SO_4), and the ether was distilled to leave a yellow oil, which was chromatographed on alumina from a series of solvents. Elution with light petroleum (b. p. 40—60°) yielded unchanged fluorenone; ether eluted unidentified oils; finally, methanol eluted a viscous oil which gave 9-*hydroxymethylfluoren*-9-*ol* (0·25 g.) as white needles, m. p. 105—108° (Found: C, 79·1; H, 5·8. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%) after three recrystallisations from benzene. The infrared spectrum showed the presence of hydroxyl groups (3100—3300 cm.$^{-1}$ in Nujol; 3610 cm.$^{-1}$ in chloroform); there was no absorption due to carbonyl groups. Oxidation of an alcoholic solution of the compound with potassium periodate in N-sulphuric acid gave a good yield of fluorenone, m. p. 83—84°.

Reduction by Salicylaldehyde.—(a) *Of benzophenone.* Benzophenone (3·8 g.), salicylaldehyde (4·2 g.), sodium hydroxide (3·5 g.), and ethylene glycol (4 ml.) were heated to 150° for 15 min. in a test-tube. Some evolution of hydrogen occurred. A homogeneous, light brown liquid resulted. This was cooled, diluted with methanol, poured into water, and extracted with ether. The extract yielded diphenylmethanol (73% yield).

(b) *Of other ketones.* The method was similar to that of the previous experiment. Chromatography on alumina of the reaction products yielded 1-naphthylphenylmethanol (85% yield), 2-biphenylylphenylmethanol (40%), and 4-chlorodiphenylmethanol (22%) from the corresponding ketones. Fluoren-9-ol (80% yield) was obtained by recrystallisation from ethanol–light petroleum of the product obtained from fluorenone.

(c) *Of 2-benzoylbenzoic acid.* A mixture of this acid (1·1 g.), salicylaldehyde (4 g.), sodium hydroxide (5 g.), and ethylene glycol (5 ml.) was heated to 180° for 6 min., then cooled, diluted with methanol, poured into water, and acidified with hydrochloric acid. The products were warmed (to aid lactone formation), then cooled and extracted with ether. The extract was washed with sodium hydrogen carbonate solution and water. Removal of the ether left an oil which was crystallised from aqueous methanol and then ethanol to give white plates (0·6 g.; yield 59%), m. p. 115—117° (Found: C, 80·0; H, 4·9. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%). The infrared spectrum showed a peak at 1745 cm.$^{-1}$ but no hydroxyl absorption above 3000 cm.$^{-1}$. The compound must be 3-phenylphthalide (lit.,[10] m. p. 117°).

(d) *Control experiment.* Benzophenone (3 g.), sodium hydroxide (4 g.), and ethylene glycol (3 ml.) were refluxed for 40 min. Benzophenone was recovered, containing little diphenylmethanol.

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ORGANIC CHEMISTRY SECTION,
CHEMICAL RESEARCH LABORATORIES,
C.S.I.R.O., MELBOURNE, AUSTRALIA.

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[10] Tasman, *Rec. Trav. chim.*, 1927, **46**, 681.