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REDUCTION OF BENZENE NUCLEUS WITH MAGNESIUM AND ALCOHOL IN LIQUID AMMONIA

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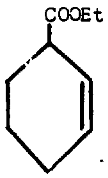
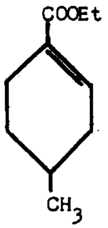
RECENTLY we found[1] that magnesium and zinc, in liquid ammonia, reduce aromatic ketones, esters and nitrocompounds, the functional group alone being affected.

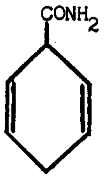
Using a combination of magnesium and alcohol in liquid ammonia, we achieved a partial reduction of a benzene nucleus, containing electron-attracting substituents. The ethyl esters and the amides of benzoic and p-toluic acids gave respectively the following reduction products:



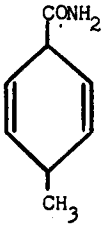
I



II



III



IV

In so far as a basis for comparison exists, our results differ from those of Kuehne and Lambert[2] obtained by the Birch reduction of the free

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[1] Chr. Ivanoff and P. Markov, *Compt. rend. Acad. Bulg. Sci.* **15**, 49 (1962).

[2] M.E. Kuehne and B.F. Lambert, *J. Amer. Chem. Soc.* **81**, 4278 (1959).

benzoic and p-toluic acids. The reduction with magnesium, in the presence of a proton source, seems to take place more specifically. With the change of the functional group there occurs a change of the number of hydrogen atoms which have joined the benzene nucleus, and the methyl radical in the nucleus of the esters conditions another position of the double bond in the reduction product. These features are probably due to the more different mechanism of the reduction with magnesium as compared with the mechanism of the Birch reduction.

We used ethyl or isopropyl alcohol as a proton source in the reduction of the esters. The yields proved to be better when operating with isopropyl alcohol. These yields are indicated here below. In the reduction of the amides ethanol alone was used as a proton source. It was established with certainty that in the absence of a reducible compound no interaction between magnesium and ethanol in liquid ammonia occurs.

In all cases the mol. ratio between magnesium and the reducible substance was 2:1, and that between the reducible substance and alcohol - 2:3. The reaction took place normally for 45-60 minutes. The experimental procedure was as follows: the ether solution of ester (75 or 90 mmols) and alcohol or the powdered amide (62 or 75 mmols) and alcohol was added at a time to magnesium dust, suspended in liquid ammonia (about 250 ml.). The yellow-brown reaction mixture was decomposed with ammonium chloride and after the evaporation of ammonia it was treated with diluted (1:1) hydrochloric acid. The reduction products of the esters were isolated by extraction with ether and careful fractionation in vacuo, and those of the amides - by repeated extraction with chloroform and recrystallization from isopropyl alcohol.

Ethyl ester of 1,2,3,4-tetrahydrobenzoic acid (I): 35% yield, b.p. 71-72° (6 mm), n_D^{20} 1.4665, d_4^{20} 0.9999. IR-spectrum ($CHCl_3$): 1735 (COOR), 1650 (C=C) cm^{-1} and absence of Ar- ring bands. The acid which was obtained by the saponification of the ester gave a bromide with m.p. 166-167.5°. The IR-spectrum of the bromide showed no carbon-carbon double bond absorption. According to Boorman and Linstead[3] the 1,2,3,4-tetrahydrobenzoic acid gives dibromide with the same melting point.

Ethyl ester of 2,3,4,5-tetrahydro-p-toluic acid (II): 39.6% yield, b.p. 72-73° (6 mm), n_D^{20} 1.4683, d_4^{20} 0.9746. IR-spectrum ($CHCl_3$): 1728 (COOR), 1620 (conjugated C=C) cm^{-1}. Calc. for $C_{10}H_{16}O_2$:C,71.44; H, 9.52; Found: C, 71.24; H, 9.14. By the saponification of the ester was obtained 2,3,4,5-tetrahydro-p-toluic acid (m.p. 135.5-136°, reported[4] m.p. 132-134°). Calc. for $C_8H_{12}O_2$: C, 68.58; H, 8.57; Found: C, 68.61; H, 8.44.

1,4-Dihydrobenzamide (III): 43.9% yield, m.p. 153-154°, showing no depression on mixed melting point with 1,4-dihydrobenzamide, obtained according to Kuehne and Lambert[2]. IR-spectrum ($CHCl_3$): 1680 (CONH), 3410,3520 (N-H) cm^{-1}, 1650 inflection (C=C) cm^{-1}.

1,4-Dihydro-p-toluamide (IV): 31.7% yield of a product with m.p. 160-166° which, after tree crystallizations, melted at 179.5-180.5°. IR-spectrum ($CHCl_3$): 1680 (CONH), 3400,3520 (N-H), 1645 inflection (C=C) cm^{-1}, but showed no CH_2-absorption. Calc. for $C_8H_{11}NO$: C, 70.09; H, 8.02; Found: C, 69.78; H, 8.10.

Work on the reduction of other aromatic compounds is in progress.

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[3] E.I. Boorman and K.P. Linstead, J. Chem. Soc. 260 (1935).

[4] A. Einhorn and R. Willstätter, Liebigs Ann. 280, 163 (1894).