think it likely that this effect and the effects that we have observed have a common cause.

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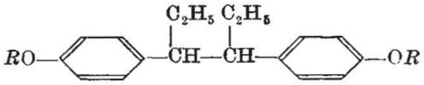
[1] Burgoyne, J. H., and Williams-Leir, G., *Proc. Roy. Soc.*, A, **193**, 525 (1948).

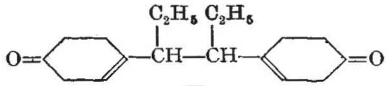
[2] Lewis, B., and Kreutz, C. D., *J. Chem. Phys.*, **1**, 89 (1933).

Reduction by Sodium – Ammonia Solutions

Reduction of methoxybenzene derivatives by the sodium–ammonia–alcohol reagent followed by acid hydrolysis leads to the formation of a number of hitherto inaccessible unsaturated ketones[1]. The process fails with some compounds because of their insolubility in liquid ammonia, a typical example being hexœstrol dimethyl ether (I, $R = CH_3$). This substance has been treated under a variety of conditions and with admixed solvents, for example, ether or ethylenediamine, but so far without success.



I



II

The observation that alcohols are often readily soluble in ammonia has now led us to replace the methyl ethers of phenols by the 2-hydroxyethyl- or glyceryl-ethers. These ethers are, in fact, more readily soluble in ammonia and are easily prepared by the action of the appropriate chloro-compound on the sodium phenoxide in hot aqueous solution. The ether side-chain is lost during acid hydrolysis, so its nature does not affect the final product. A further advantage with these ethers is that any unreduced material present in the product can be removed because of its relatively higher boiling-point.

Hexœstrol (I, R=H) gives rise to a *bis*(2-hydroxyethyl) ether (I, $R = -CH_2CH_2OH$) which crystallizes as colourless plates from benzene, m.p. 90–91° (found: C, 73·4; H, 7·9; $C_{22}H_{30}O_4$ requires C, 73·7; H, 8·4 per cent). This is readily reduced and gives after acid hydrolysis 3 : 4-di(4′-ketocyclohex-1′-enyl)hexane (II), which forms clusters of prisms from ether–light petroleum, m.p. 131–132° (shrinks 120°) (found: C, 78·6; H, 9·9; $C_{18}H_{26}O_2$ requires C, 78·5; H, 9·5 per cent) (bis-semicarbazone m.p. 242° (decomp.)). The formulation of (II) as the βγ-unsaturated ketone rests on the lack of an absorption maximum in the region 2200–2700 A. It is being tested for possible sex-hormone activity.

The reduction of other phenols, including œstrone, and the synthesis of some natural products are being carried out.

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[1] Birch, *J. Chem. Soc.*, 593 (1946).

Re-arrangement of Acyldiazoethanes

The appearance of a paper by Wilds and Meade[1] on this topic renders an account of our own experiments desirable, more especially as we have in various respects carried the matter further than the American workers.

The statement (without experimental details) by Eistert[2] that *p*-nitrobenzoyldiazoethane is convertible in hot aniline to α-(4-nitrophenyl)propionanilide has been experimentally confirmed, most satisfactorily by addition of the diazo-compound to the base at 100–105°. Similarly, anilides of *iso*butyric, α-phenyl and α-(4-methoxyphenyl)-propionic acids, and the dianilide of αα′-dimethylsuberic acid were prepared.

While these results are doubtless to be attributed to initial thermal decomposition of the diazo-compound to a ketene[3], followed by reaction with aniline, it is incorrect to assume[4] that this is also the mechanism of the Wolff re-arrangement as usually performed. This has been recognized by Eistert[5]; but we are also unable to accept his views in regard to the latter reaction; for successive additions to an ethanolic solution of benzoyl (or 4-methoxybenzoyl)-diazoethane (1 mol.) at 70° of an ethanolic solution of aniline (1 mol.) and of 10 per cent aqueous silver nitrate solution yielded β-anilinopropiophenone (or its 4-methoxy-derivative):

$$PhCOCMe = N = N \rightarrow PhCOCH_2CH_2NHPh + N_2.$$

This clearly arises from addition of aniline to benzoylethylene (I), the formation of which recalls that of olefines together with primary and secondary alcohols by decomposition of the diazonium compounds resulting from the action of nitrous acid on primary aliphatic amines[7]. We thus conclude that the course of the reaction is to be expressed as follows, the base functioning alternately as acceptor and donor of proton:

$$\begin{array}{l} PhCO.CMe{=}N{=}N \rightarrow [PhCO.CHMe.N{\equiv}N]^{\cdot} + PhNH_2 \\ \quad + PhNH_3^{\cdot} \qquad\qquad\qquad \downarrow \qquad\qquad (Ag) \\ \qquad\qquad\qquad PhCO.CH{=}CH_2 + PhNH_3^{\cdot} + N_2 \\ \qquad\qquad\qquad\qquad\quad (I) \end{array}$$

Similarly, the normal Wolff re-arrangement corresponds to the Wagner–Meerwein re-arrangement by which the formation of secondary alcohols occurs. Thus, in the case of benzoyldiazomethane and ammonia, we have

$$\begin{array}{l} PhCOCH{=}N{=}N + NH_4^{\cdot} \quad \rightarrow \quad [PhCO.CH_2.N{\equiv}N]^{\cdot} \\ \qquad\qquad\qquad\qquad\qquad\qquad + NH_3 \\ \qquad\qquad\qquad\qquad\qquad (A) \downarrow \; NH_3 \\ \qquad\qquad\qquad\quad NH_2CO.CH_2.Ph + NH_4^{\cdot} + N_2. \end{array}$$

Evidently, also, when the opportunity is available for both types of charge, the former occurs in preference to the latter.

The preparation, for the reactions just discussed, of acyldiazoalkanes from acid chloride and diazoalkane requires an excess of the latter to react with the hydrogen chloride formed[8]. Whereas, however, in the use of diazomethane any adequate excess may be employed, either this, in the case of diazoethane and, it may be presumed, its homologues, should be limited to that theoretically requisite, or, if excess be employed, the duration of the reaction should be limited; for *p*-nitrobenzoyldiazoethane, m.p. 112°, reacts with diazoethane at the ordinary temperature in ethereal solution to yield a product

$$\begin{array}{l} NO_2 . C_6H_4 . CO . CMe = N = N + MeCH = N = N \\ \rightarrow NO_2 . C_6H_4 . CO . C(Me) = N - N = CHMe \quad (II) \end{array}$$