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

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Oct. 20.

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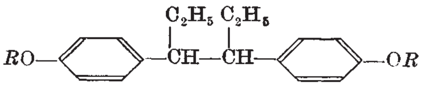
[1] Burgoyne, J. H., and Williams-Leir, G., *Proc. Roy. Soc.*, A, **193**, 525 (1948).

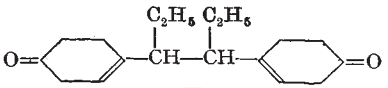
[2] Lewis, B., and Kreutz, C. D., *J. Chem. Phys.*, **1**, 89 (1933).

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:

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

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

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

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

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

characterized as the ketazine (II) by conversion into acetaldehyde, hydrazine and acetyl-*p*-nitrobenzoyl on hydrolysis with hot dilute sulphuric acid. This product is naturally also formed in the preparation of *p*-nitrobenzoyldiazoethane unless the precautions just outlined are observed. Similarly, nitrobenzoyldiazomethane and diazoethane furnish the azine $NO_2.C_6H_4COCH{=}N{-}N{=}CHMe$ (III), but the anionoid reactivity of diazomethane is inadequate to enable it to participate in this type of reaction with the cationoid nitrogen atom[8] of acyldiazoalkanes. While, however, the reactivity of this latter is doubtless enhanced by the acyl group, the formation of azine in this manner is by no means unique. The conversion of diazo-*iso*propane into $Me_2C{=}N{-}N{=}CMe$ at the ordinary temperature[9] and the numerous other examples of ketazine formation cited by Staudinger and Kupfer[10] are clearly to be regarded from this aspect, which has hitherto usually been neglected owing to the almost exclusive attention accorded to the anionoid reactivity of aliphatic diazo-compounds. But the conversion by alkali of diazoacetamide into a triazolone[11] is an example of the cationoid reactivity in question, while that of diazoacetic ester into a dihydrotetrazine dicarboxylic acid[12], as well as the classical synthesis of pyrazolines[13], also involves cationoid as well as anionoid reactivity of diazo-compounds.

The ketazine (III) does not represent the limit of the reaction between *p*-nitrobenzoyldiazomethane and diazoethane, for if excess of the latter be employed, a compound $C_{14}H_{17}O_3N_3$ (IV), m.p. 134–135°, is formed, with evolution of a corresponding volume of nitrogen. The nature of this product is not completely established; but on treatment with dilute sulphuric acid it readily yielded acetaldehyde, together with a compound, m.p. 196–197° (also obtainable by gradual addition of hydrochloric acid (2*N*) to a solution of (IV) in dioxan at the ordinary temperature), and another, m.p. 175–176° (also obtainable by gradual addition of ethanolic hydrazine hydrate to an ethanolic suspension of III at the ordinary temperature). In view of these results, ketazine (II) would also be expected to react with diazoethane, and, in fact, does so, though much more slowly than (III). It also undergoes gradual internal condensation to a compound $C_{11}H_9O_2N_3$, m.p. 158–159°, in boiling ethanolic solution.

Benzoyl- and 4-methoxybenzoyldiazoethanes react much more slowly than the 4-nitro-analogue with diazoethane; but evidence of ketazine formation in these cases also has been derived from hydrolytic experiments.

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[1] *J. Org. Chem.*, **13**, 763 (1948).

[2] *Angewandte Chemie*, **54**, 124 (1941).

[3] Compare Schroeter, *Ber.*, **42**, 2345 (1909).

[4] Compare Bachmann and Struve, "Organic Reactions", **1**, 38 (New York, 1942). Huggett, Arnold and Taylor, *J. Amer. Chem. Soc.*, **64**, 3043 (1942); also (1).

[5] *Ber.*, **68**, 208 (1935).

[6] Meyer, V., *Ber.*, **9**, 535 (1876); **10**, 130 (1877). Compare Adamson and Kenner, *J. Chem. Soc.*, 838 (1934).

[7] Staudinger, Becker and Hirzel, *Ber.*, **49**, 2522 (1916).

[8] Bradley and Robinson, *J. Chem. Soc.*, 1310 (1928).

[9] Staudinger and Gaule, *Ber.*, **49**, 1897 (1916).

[10] Staudinger and Kupfer, *Ber.*, **44**, 2197 (1911).

[11] Curtius *et al.*, *Ber.*, **39**, 4140 (1906); **43**, 2446 (1910).

[12] *Ber.*, **41**, 3161 (1908); **42**, 3284 (1909).

[13] Buchner, *Ber.*, **21**, 2638 (1888); *Annalen*, **273**, 214 (1893).

Organised Structure in Soap Solutions

MY simple picture, fully described elsewhere[1-3], of the aggregates in the clear mobile solutions of paraffin-chain salts is that they are essentially liquid in nature and spherical in form. The discovery[4], by X-ray diffraction, of a characteristic long spacing, decreasing with increase of concentration, appeared to favour a different picture—that of a lamellar micelle in which the chains lay parallel to one another and the outer faces of arrayed ionic groups were separated by a definite thickness of water. One of the protagonists of the lamellar micelle has recently[5] come to modify his picture considerably, and his collaborator[6] to consider that the X-ray data can be explained by the spherical micelle.

There are two difficulties about the lamellar micelle explanation of the X-ray spacings. One, recently raised by Bernal[7], is that in order to account for all the water, the lamellæ must be assumed to be separated laterally by a greater depth of water than that held between the ionic faces. The opposite difficulty was raised by Harkins[8]. When oil is dissolved in the soap micelles, the increase of long spacing is much *greater* than is directly accounted for by the additional volume inside the micelle.

The characteristic long spacing should be considered as a regular distance between geometrically similar groups of diffracting atoms. These need not be planes. They may be spheres regularly spaced, as in the transparent emulsion studied by Schulman and Riley[9].

There are good reasons[3] for believing the micelles to be of closely constant size in any one solution and to vary but little with the concentration. The constancy of spacing demonstrated in concentrated solutions is simply the result of a coulombic packing effect. The micelles are highly mutually repulsive and will therefore tend to array themselves so that their shortest distances of separation are as great as possible, that is, in a closely packed tetrahedron assembly. If the spheres are of radius r and together occupy a fraction φ of the total volume, then their shortest distance d of separation in this arrangement will be given by

$$d = \left(\frac{8\pi}{3\sqrt{2}}\right)^{1/3} \cdot \varphi^{-1/3} \cdot r.$$

We will apply this equation to the data of Harkins for potassium laurate and of Stauff[10] for sodium tetradecyl sulphate. To a sufficient degree of accuracy, we can take the mean density of the micelles equal to 1, and thus identify weight and volume fractions. We will calculate r from observed values of d.

Potassium laurate			Sodium tetradecyl sulphate		
Wt. %	*d* (obs.)	*r* (calc.)	Wt. %	*d* (obs.)	*r* (calc.)
9·1	57·0 A.	14·2 A.	15·1	60–65 A.	17·7–19·1 A.
12·1	56·3	15·4	40·0	55·0	22·3
16·7	51·3	15·6	60·0	48·2	22·5
25·0	47·1	16·4	80·0	42·4	21·7
33·3	44·1	17·0			
41·1	37·1	15·2			

The lengths of the fully extended chains are about 13·7 and 18·9 A. The calculated values are consistent with the sphere radius being, as expected, a little greater than this length[3].

What of the effect of dissolved oil? In a limited region in the centre of the micelle, the oil will probably be the sole component[11]. The radius of the micelle will thus be disproportionately increased, and