CCXXXI.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part V. Nitration of Benzyldiethylsulphonium Picrate.*

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THE present note, which is part of a wider, unfinished investigation, describes the nitration of a typical benzyldialkylsulphonium salt undertaken with the object of comparison with the behaviour of the benzyltrialkylammonium salts under similar conditions.

Experimentally, this section of the work was completed in 1927, and a theoretical discussion of the result, stated in general terms, was given in Part II (J., 1927, 2772); it is unnecessary to repeat the details but, of the various factors then considered to operate in making the sulphonium kation less effective than the ammonium in distributing a positive field over the nucleus, we now attribute the more important rôle to the relatively greater deformation of the ionic centres in the sulphonium than in the ammonium salts. Expressed in other words, our view is that the sulphur atom, softer than nitrogen and with a larger nuclear charge, polarises the attached anion (or anions) to the greater extent and so allows of a more complete neutralisation of its surplus positive charge, which thus develops a field of relatively weaker electric intensity at corresponding points in the surroundings, including the attached aromatic group.

This weaker field is, of course, the cause of the diminished *m*-substitution in accordance with the theory proposed by one of us (*Chem. and Ind.*, 1925, 563) and used by Ingold and other investigators who have recently been concerned with the study of the relation of polar effects and orientation.

The nitration of *benzyldiethylsulphonium picrate* by means of nitric acid (*d* 1·51) at 0° gave a mixture of the o-, m-, and p-*nitro*-derivatives. The proportion of the *m*-isomeride formed was found to be about 28% and the chief product was the *p*-isomeride; the proportion of the *o*-isomeride formed was not exactly estimated. Very remarkable are the colorations which the *o*- and *p*-nitrobenzyldiethylsulphonium salts develop when treated with alkalis under appropriate conditions, especially in view of the negative results with the corresponding quaternary ammonium salts in like circumstances. It is possible that quinonoid betaines, $-\{NO_2{:}C_6H_4{:}CH{\cdot}SR_2\}+$, are formed and are responsible for the effects observed, but this explanation cannot be regarded as wholly satisfactory and the matter is being further investigated.

EXPERIMENTAL.

Benzyldiethylsulphonium Picrate.—Benzyl bromide was mixed with an excess of diethyl sulphide and combination gradually occurred at the room temperature; the salt was washed with ether, and the *picrate* precipitated from an aqueous solution. The derivative crystallised from alcohol in bright canary-yellow needles, m. p. 115—116° (Found: C, 49·7; H, 4·6. $C_{17}H_{19}O_7N_3S$ requires C, 49·9; H, 4·6%). When it was heated with aqueous alkalis, diethyl sulphide was regenerated.

o-*Nitrobenzyldiethylsulphonium Picrate.*—Combination of *o*-nitrobenzyl bromide (or chloride) and diethyl sulphide could not be brought about, even in ethyl acetate solution, but a solution of *o*-nitrobenzyl iodide in twice its weight of diethyl sulphide and four times its weight of ethyl acetate gradually deposited crystals of *o*-nitrobenzyldiethylsulphonium iodide. The *picrate* crystallised from alcohol in deep canary-yellow needles, m. p. 118—120° (Found: C, 44·8; H, 3·9. $C_{17}H_{18}O_9N_4S$ requires C, 44·7; H, 4·0%). This salt is much more readily soluble in alcohol and acetone than are the *m*- and *p*-isomerides; it dissolves to some extent in ether.

The corresponding chloride, prepared in the usual manner, develops an intense bluish-violet coloration in acetone solution on the addition of sodium hydroxide; the colour in alcoholic solution is very feeble in comparison and is almost discharged on the addition of water.

m-*Nitrobenzyldiethylsulphonium Picrate.*—Ethyl acetate accelerated the combination of *m*-nitrobenzyl bromide and diethyl sulphide; the *picrate* crystallised from alcohol in lemon-yellow plates, m. p. 147—148° (Found: C, 44·7; H, 4·0%). This salt is very much more sparingly soluble than the *o*- and *p*-isomerides in alcohol and acetone. The related chloride exhibited no characteristic colour reaction with alkalis.

p-*Nitrobenzyldiethylsulphonium Picrate.*—*p*-Nitrobenzyl bromide was found inert towards diethyl sulphide alone, but combination occurred readily in ethyl acetate solution. The *picrate*, obtained by the action of aqueous picric acid on the bromide, crystallised from alcohol in canary-yellow plates, m. p. 112—114° (Found: C, 44·8; H, 4·0%).

The *p*-nitrobenzyldiethylsulphonium salts give a bright eosin-red coloration in aqueous-alcoholic potassium hydroxide; the colour is even more intense in acetone solution. The coloration fades, and this process is hastened by the presence of the *m*-isomeride. The colorimetric estimations were, therefore, carried out expeditiously.

Separations.—Experiments with the pure isomerides showed that a single crystallisation from acetone served to separate the *o*- and *m*-nitro-picrates completely for all practical purposes, but the *p*-isomeride, if present, occurred both in the crystals and in the mother-liquor. A complete separation of the *o*- and *p*-nitro-picrates is illustrated by the following experiment. The *o*-nitro-picrate (0·05 g.) and the *p*-nitro-picrate (0·05 g.) were together dissolved in ethyl acetate (7 c.c.), and ether (25 c.c.) was added. The crystalline precipitate (dried, 0·05 g.) was the almost pure *p*-nitro-picrate, m. p. 109—111°, the *o*-salt remaining in the solution.

The Nitration.—The product obtained under conditions similar to those described below was washed with a little alcohol and dried (Found : C, 44·6; H, 4·1%). The *o*-, *m*-, and *p*-nitrobenzyldiethylsulphonium picrates were also separated in a pure condition in the course of preliminary experiments and identified by analysis and by comparison with authentic specimens.

The picrate (18·0 g.) was carefully added to stirred nitric acid (54 c.c., *d* 1·51) at 0° during 1 hour, the stirrer was washed with nitric acid (6 c.c.), and the mixture allowed to reach the room temperature during 1 hour and then kept for 1 hour. The product was added to crushed ice (250 g.); a yellow precipitate was then thrown down. The filtrate and washings from this were concentrated under diminished pressure and diluted and the process was continued until most of the nitric acid was removed; the residue was then nearly neutralised with ammonia and mixed with the original precipitate and the whole was gently heated on the steam-bath, cooled, and filtered (solid, 18·0 g.). The liquid was exactly neutralised with ammonia, stirred with picric acid (2·0 g.), and kept at about 0° for 12 hours. The solid was collected (2·6 g.) and combined with the main fraction. The increment of 0·6 g. is evidently due to the nitrobenzylsulphonium kation, so the total yield may be estimated as 19·2 g. or 96%. In the calculations, we assume that the yield was quantitative, so the result for the proportion of *m*-isomeride formed will be a little low and other small errors should be in the same direction.

The crude product (20·6 g.) was ground with cold acetone (25 c.c.), and the residue washed with acetone (10 c.c.) and dried (I, 7·8 g.). On slow evaporation, the acetone solution first deposited large, canary-yellow, rhombic crystals (3·5 g.) of the pure *p*-isomeride

(m. p. 111—113°; mixed with a synthetic specimen, m. p. 112—114°, the m. p. was 111—113°; the synthetic specimen crystallised from acetone in the same form); the second fraction consisted of the *p*-isomeride, mixed with paler yellow needles (II, 2·98 g.). The solution was then evaporated to dryness, the residue dissolved in ethyl acetate, and ether added, giving a precipitate (IIA, 2·75 g., m. p. 91—98°). Addition of much ether then gave a further amount (IIB, 0·5 g., m. p. 87—94°), and, on evaporation, there was obtained 0·2 g., m. p. above 200° (decomp.), and some picric acid, m. p. 121°.

Fraction II was found by the ethyl acetate–ether method to contain 2·03 g. of the *p*-isomeride, the remainder consisting of the *o*-isomeride. Similarly, the fractions IIA and IIB were impure specimens of the *p*-isomeride. The main acetone mother-liquors, therefore, did not yield an appreciable amount of the *m*-isomeride.

5 Grams of fraction I were dissolved in hot acetone (50 c.c.); on cooling and keeping, lemon-yellow needles (2·35 g.) separated, m. p. 140—143°, and a second crop (0·55 g.), m. p. 141—144°; these specimens of the *m*-isomeride were almost pure. On further keeping, mixtures were obtained and these were fractionated by means of acetone and methyl alcohol, 0·3 g. of the *m*-isomeride being isolated. The remainder of the fraction was found to consist of the *p*-isomeride, which was isolated in a pure condition; the *o*-isomeride did not appear at any stage in the fractionation of I. From the amount of the *m*-isomeride separated, the yield of the *m*-isomeride in the nitration was found to be 25·7%. Confirmation of this result was obtained by the colorimetric estimation of the *p*-isomeride in the fraction I.

Solutions employed.—Potassium hydroxide (100 g.) in water (400 c.c.). The pure *p*-isomeride (50·004 mg.) was dissolved in 3% alcoholic hydrogen chloride, ether (200 c.c.) added, and the solution washed with 1% aqueous hydrochloric acid (50 c.c.) and then with further small successive quantities of 1% hydrochloric acid to make the volume of the aqueous solution up to 100 c.c. The fraction I (50·005 mg.) was treated in exactly the same way and, moreover, a special 1% hydrochloric acid solution was prepared by carrying out the above operations without any picrate and finally adding two drops of aqueous picric acid to give the same tint as in the standard solutions prepared from the picrates.

In each comparison, the sulphonium salt solution was added to 10 c.c. of the potash solution made up to 50 c.c. with ethyl alcohol.

5 C.c. of solution from I were compared with 1 c.c. of the *p*-isomeride solution mixed with 4 c.c. of prepared 1% hydrochloric acid; the colour intensities were in the ratio 14·1/20, so the *p*-isomeride in I = 28%. Other estimations gave *p*-isomeride, 33·3, 34, 30%,

and the best value appears to be 32%. This was confirmed by the fact that the colours obtained from 20 c.c. of the solution from I and from 6·6 c.c. of the *p*-isomeride solution mixed with 13·4 c.c. of prepared 1% hydrochloric acid could not be distinguished. The perfect match proved that the *o*-isomeride was not present in I. From this result, the *m*-isomeride in the nitration product is found to amount to 27·3%, in approximate agreement with the value obtained by separation alone.

Corrected for the experimentally determined solubility of the *m*-isomeride in acetone, saturated with the *p*-isomeride at 18°, the final result becomes 28·3% for the *m*-isomeride. The *p*-isomeride actually isolated amounted to 12·5 g. or about 61%, so the *o*-isomeride formed was probably less than 10%.

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