The Nitration of Bibenzyl. Part II.† Comparison of the Products from Nitrations by Nitric Acid in Acetic Anhydride and by Nitronium Salts in Organic Solvents

By **A. Gastaminza** and **J. H. Ridd,*** Chemistry Department, University College, 20 Gordon Street, London WC1 0AJ

The nitration of bibenzyl (in excess) with a solution of nitric acid in acetic anhydride gives very little dinitration, in marked contrast to the nitration of bibenzyl (in excess) with solutions of nitronium salts in organic solvents. For the reactions with preformed nitronium ions, the isomeric composition of the dinitro-fraction and the product composition in the nitration of mixtures of bibenzyl and mononitrobibenzyls support the earlier conclusion that the dinitration arises mainly from reaction during the mixing of the reactant solutions. For dinitration, there is no evidence of a significant contribution from the addition of a nitronium ion to the first nitro-group followed by an intramolecular NO_2^- transfer to the second ring.

A RECENT study [1] of the nitration of bibenzyl by nitronium fluoroborate in sulpholan has shown that dinitrobibenzyls (with one nitro-group in each ring) form the major part of the product, even when a large excess of bibenzyl is used. The result has been considered to show [1,2] that much of the reaction occurs during the mixing of the reactant solutions.

This interpretation has recently been queried [3] because of the possibility that nitration in one ring of bibenzyl may facilitate substitution in the second ring through the addition of a nitronium ion to the nitro-group followed by a presumably intramolecular transfer of the nitronium ion to the second ring. The formation of a substantial amount of dinitrobibenzyl in the reaction of nitric acid with an excess of bibenzyl has been mentioned as evidence for some facilitation of disubstitution.[3] In addition, it has been suggested that the ratio of 2- to 4-substitution in the dinitration of bibenzyl provides evidence for this addition–rearrangement mechanism of dinitration.[3]

The question of which of these interpretations is correct is an important one since the first interpretation implies that competition experiments involving the addition of solutions of nitronium salts to mixtures of benzene and toluene in sulpholan cannot provide valid measurements of the relative aromatic reactivity.[1,2] On the second interpretation, such competition experiments could still be valid. The validity (or otherwise) of these competition experiments has important implications concerning the mechanism of aromatic nitration.[2]

We have previously indicated briefly why we consider the second interpretation to be untenable [1] but the the suggestion of experimental support for this interpretation has led us to a more detailed examination of the question. It is convenient to consider first nitration by nitric acid in acetic anhydride, for the slower rate of nitration under these conditions makes the extent of reaction during the mixing of the reactant solutions far less important.

Nitration by Nitric Acid in Acetic Anhydride.—On the assumptions of independent substitution in the two aromatic rings of bibenzyl and complete mixing of the reactant solutions, the fractions of unsubstituted (x), monosubstituted (y) and disubstituted ‡ (z) products should accord with the random pairing of substituted and unsubstituted rings.[1,2] The relationship between these fractions and the ratio R of the initial number of aromatic rings to the number of substituted aromatic rings is then shown in equations (1)—(3)[2].

$$x = (1 - 1/R)^2 \qquad (1)$$

$$y = (2/R)(1 - 1/R) \qquad (2)$$

$$z = 1/R^2 \qquad (3)$$

The product composition predicted by these equations provides a standard against which to measure the possible contributions of special reaction paths favouring disubstitution.

The reaction of nitric acid with an excess of bibenzyl in acetic anhydride has been studied by the t.l.c. technique used previously. The products formed, including the amount of unchanged bibenzyl are listed in Table 1: from this product composition, the value of R is 3·34.

TABLE 1

The reaction of bibenzyl (0·04 mol) with nitric acid (0·027 mol) in acetic anhydride. Comparison of observed and calculated product compositions

	Product composition (mol %)		
	Obs.		Calc.*
Bibenzyl	45·3	45·3	49
2-Nitrobibenzyl	20·9	49·5	42
4-Nitrobibenzyl	28·6		
2,2'-Dinitrobibenzyl	1·1	5·1	9
2,4'-Dinitrobibenzyl	2·4		
4,4'-Dinitrobibenzyl	1·6		

* Calculated from equations (1)—(3).

The last two columns of the Table compare the observed percentages of unsubstituted, monosubstituted and disubstituted product with those calculated using the above value of R in equations (1)—(3).

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† The paper by P. F. Christy, J. H. Ridd, and N. D. Stears [1] is taken as Part I of this series.

‡ Disubstituted products containing two nitro-groups in one aromatic ring are not considered in this calculation; the amount of such products should be very small because of the deactivating effect of the first nitro-group.

[1] P. F. Christy, J. H. Ridd, and N. D. Stears, *J. Chem. Soc.* (*B*), 1970, 797.

[2] J. H. Ridd, *Accounts Chem. Res.*, 1971, **4**, 248.

[3] G. A. Olah, *Accounts Chem. Res.*, 1971, **4**, 244.

The amount of disubstituted product is somewhat less than that predicted by these equations but this can easily be rationalised in terms of a weak deactivation of one aromatic ring by a nitro-group in the second ring. There is no evidence here that the nitration of one ring facilitates substitution in the second ring: indeed, the opposite appears to be true.

Nitration by Nitronium Salts.—As outlined previously,[1] the addition of solutions of nitronium salts to solutions of bibenzyl gives far more disubstitution than predicted by equations (1)—(3). This can be understood easily in terms of reaction during mixing.[1] Because of the above results, the alternative interpretation in terms of a special mechanism of disubstitution requires that the mechanism should operate in sulpholan but not in acetic anhydride.

Consider first the composition of the dinitro-product. If substitution in the two rings occurs independently, the relative amounts of the isomeric dinitrobibenzyls should correspond to the random coupling of 2-substituted and 4-substituted rings. Hence the fractions of the 2,2′-isomer (*a*) and 2,4′-isomer (*b*), and 4,4′-isomer (*c*) should be related to the ratio (*P*) of 4-substituted rings to 2-substituted rings by equations (4)—(6) below.*

$$a = 1/(1 + P)^2 \qquad (4)$$

$$b = 2P/(1 + P)^2 \qquad (5)$$

$$c = P^2/(1 + P)^2 \qquad (6)$$

The results in Table 2 show that product composition accords with these equations. These results refer to the dinitro-fractions in the first three analyses listed in Table 3 of Part I. Examination of the other analyses in that paper shows some scatter about the values predicted by equations (4)—(6) but no sign of a consistent trend. Hence the composition of the dinitro-product accords with that expected for independent substitution in the aromatic rings of bibenzyl and provides no evidence for any special mechanism of disubstitution.

TABLE 2

Composition of the dinitro-product (mol %) in the nitration of bibenzyl by nitronium fluoroborate in sulpholan.[a] Comparison of observed and calculated results. Run A: bibenzyl 0·2M, NO_2BF_4 = 0·2M. Run B: bibenzyl 0·125M, NO_2BF_4 = 0·125M. Run C: bibenzyl 0·05M, NO_2BF_4 = 0·05M

	Run A		Run B		Run C	
	Obs.	Calc.[b]	Obs.	Calc.[b]	Obs.	Calc.[b]
2,2′-Isomer	19	18	19	19·5	18	18
2,4′-Isomer	47	49	49	48·5	49	49
4,4′-Isomer	34	33	32	32	33	33

[a] The full product composition (including the mononitro-products) is given in Part I, Table 3. [b] Calculated from equations (4)—(6).

It could perhaps be argued that the special mechanism of disubstitution operates with both the 2- and 4-nitrobibenzyls and by accident gives the statistical distribution of dinitro-products. If so, the introduction of the first nitro-group must activate the second aromatic ring by more than a factor of **18**. This follows because the reaction of nitronium fluoroborate (0·125M) with bibenzyl (0·625M) gives mainly disubstitution (71%, see Part I, Table 3). Thus on this interpretation at 50% reaction, the mononitrobibenzyls (<0·06M) compete successfully with the remaining bibenzyl (*ca.* 0·56M) for the majority of the remaining nitronium ions. The reactivity ratio of >9 so obtained must be doubled in assessing the relative reactivity of the aromatic rings because of the two available rings in bibenzyl molecules.

Because of this large factor, the incursion of the special mechanism of disubstitution should be easily detected by the nitration of mixtures of bibenzyl and mononitrobibenzyls. We have already pointed out[1] that the nitration of a mixture of bibenzyl (0·25M) and 4-nitrobibenzyl (0·03M) gave a product composition very close to that expected on the assumption that the unsubstituted aromatic ring in 4-nitrobibenzyl was as reactive as one of the rings in bibenzyl. However, the percentage of 4,4′-dinitrobibenzyl (21·5%) was slightly greater than that expected on this assumption (19·4%). The difference is probably within the experimental error but to remove any uncertainty on this matter, a related experiment with added 2-nitrobibenzyl has now been performed.†

In this experiment, the initial concentration of 2-nitrobibenzyl was greater than the concentration of added nitronium ions; hence, on the special mechanism of disubstitution the relative amounts of the 2,2′- and 2,4′-isomers in the dinitro-product should be greatly increased. However, since the concentration of 2-nitrobibenzyl was much less than that of bibenzyl, on the original interpretation of disubstitution, the relative amounts of these isomers in the dinitro-product should be little changed. The results in Table 3 show that the relative amount of the 2,2′-dinitro-product and the 2,4′-dinitro-product compared with the 4,4′-dinitro-product are little changed by the presence of the large amount of 2-nitrobibenzyl, (the apparent change is within experimental error) although, as a percentage of the total nitro-compounds present, all figures are of course much reduced. There appears therefore to be no evidence here for any enhanced reactivity of 2-nitrobibenzyl towards further substitution.

Conclusions.—The reaction path in which a nitro-group in a mononitrobibenzyl acts as a Lewis base towards a nitronium ion and then transfers this ion to the other ring by an intramolecular rearrangement could, in

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* The principle here is the same as that used for equations (1)—(3) but the equations look different because a different ratio of observables is used. This ratio *P* is taken as the ratio of 2-substituted to 4-substituted rings in the dinitro-product: the inclusion of the substituted rings in the mono-nitro-product would not make a significant difference to the conclusions.

† This experiment was carried out in the course of an investigation of the nitration of bibenzyl by nitronium hexafluorophosphate in nitromethane. It was therefore convenient to test the effect of added 2-nitrobibenzyl under these conditions. The change of anion and solvent should not affect the argument.

principle, lead to some increase in the rate of nitration of the unsubstituted ring. However, if this reaction path is used to explain the large percentages of dinitration in the reaction of bibenzyl with preformed nitronium salts, the increase in the reactivity of the unsubstituted ring must be by a large factor. It is difficult to estimate this factor exactly but the crude minimum figure of 18 given above would be increased greatly by a more refined calculation. Such an enhancement of the rate of substitution would be obvious from the product composition in the nitration of mixtures of bibenzyl with one of the mononitrobibenzyls, for one mononitrobibenzyl can only give rise to two of the three possible dinitrobibenzyls. However, neither the product compositions from the nitration of such mixtures nor the product composition from the nitration of bibenzyl in acetic anhydride provides evidence for such an enhanced reactivity of the mononitrobibenzyls. We conclude therefore that the dinitration in the reaction of an excess of bibenzyl with preformed nitronium salts occurs largely because of reaction during the mixing of the reactant solutions. The implications of this conclusion have been discussed elsewhere.[2]

TABLE 3

Nitration of bibenzyl (0·625M) with nitronium hexafluorophosphate (0·016M) in nitromethane (Experiment A). The same reaction in the presence of 2-nitrobibenzyl (0·125M) (Experiment B).

	Product composition (mol %)[a]	
	A	B
2-Nitrobibenzyl	20·2	88·5
4-Nitrobibenzyl	33·1	3·4
2,2′-Dinitrobibenzyl	12·9	2·0
2,4′-Dinitrobibenzyl	19·7	3·6
4,4′-Dinitrobibenzyl	13·6	2·3

[a] Including, for experiment B, the amount of unchanged 2-nitrobibenzyl.

EXPERIMENTAL

Nitration in Acetic Anhydride.—Acetic anhydride was dried over calcium chloride and distilled twice. A solution of nitric acid (2·52 g; *d* 1·42) in acetic anhydride (2 ml) was added during 45 min to a stirred solution of bibenzyl (7·29 g) in acetic anhydride (10 ml). The reaction was kept at about room temperature by a water-bath. After 2 h, the reaction mixture was quenched in ice–water and the aromatic material was extracted with ether. The ethereal layer was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure at 40° to give an orange oil (7·76 g). Part of this material (2·70 g) was separated by column chromatography on alumina using light petroleum (b.p. 60—80°)–benzene mixtures as the eluant to give bibenzyl (0·81 g), 2-nitrobibenzyl (0·57 g) and 4-nitrobibenzyl (0·70 g). The main analysis was by the t.l.c. method described previously [1] but with light petroleum (b.p. 60—80°)–chloroform (undried) (85/15 v/v) to develop the plates. The results in Table 1 are the mean of four analyses. The reproducibility of this method proved rather better than that illustrated previously (Part I, Table 5).

Nitration in Nitromethane.—Nitronium hexafluorophosphate was prepared by the method of Emeleus and Wolf.[4] Our experience with salt was less satisfactory than with the fluoroborate for there was some evidence that the product was not homogeneous and that it underwent decomposition in a dry-box in the dark. The comparison of reaction products in the nitration of bibenzyl with and without the addition of 2-nitrobenzyl was therefore carried out using the same solution of the nitronium salt. The concentration of this solution was determined in two ways (*a*) by the relative number of nitrated and unnitrated aromatic rings in the product and (*b*) from the apparent extinction coefficient of part of the product when dissolved in methanol. The two methods agreed to within 4%. The nitromethane used in these experiments was of spectroscopic quality, dried over molecular sieves and then distilled. The method of conducting the nitrations and the t.l.c. analysis was as described previously [1] (method C) except that a revised extinction coefficient for 2-nitrobibenzyl was used ($4{\cdot}94 \times 10^3$ at 258 nm) and the analysis was extended to include the unchanged bibenzyl using an extinction coefficient of $4{\cdot}32 \times 10^2$ at 260 nm. The light petroleum–chloroform eluant described above was used on the plates. The results in Table 3 are based on a total of three nitrations, each with two analyses. The reproducibility of the results was as illustrated previously.[1]

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[4] A. A. Wolf and H. J. Emeleus, *J. Chem. Soc.*, 1950, 1050.