Tetrahedron Letters No.49, pp. 6093-6095, 1966. Pergamon Press Ltd.
Printed in Great Britain.

NITRATION OF BIPHENYL BY NITRONIUM BOROFLUORIDE

by R. Taylor

(The Chemical Laboratory, University of Sussex,
Brighton, Sussex, England)

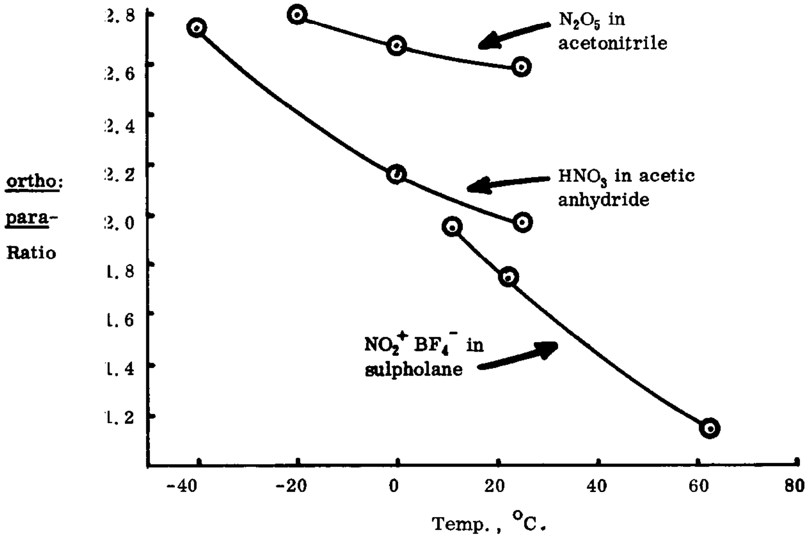
(Received 30 September 1966)

The recent examination (1) of the nitration of biphenyl by a variety of nitrating reagents has led to the conclusion that the high ortho:para-ratio which occurs with some of the reagents e.g. dinitrogen pentoxide in acetonitrile, and protonated acetyl nitrate, arises from an additional mode of ortho-nitration whereby the π-electrons of the subsequently unsubstituted phenyl ring carry out nucleophilic displacement of X or X^- from the species NO_2^+X (or NO_2X) present in these reagents, to give a π-complex involving the nitronium ion. Subsequent rearrangement gives, by virtue of the non-coplanarity of the phenyl rings, predominant ortho-substitution which is superimposed upon the normal substitution pattern produced by nitronium ions present in the reagent media.

The marked temperature dependence of the ortho:para-ratio with these reagents was attributed to the mode of direct nitration by NO_2X having a lower activation energy than that involving pre-formation of nitronium ions followed by nitration.

Kovacic and Hiller have recently reported (2) that nitration of anisole by nitronium borofluoride gives an enhanced ortho:para-ratio as has been found for nitration with acyl nitrates or nitric acid in acetic anhydride (3). It is now reported that nitration of biphenyl by nitronium borofluoride also gives rise to an enhanced *ortho*:*para*-ratio which exhibits the same pattern of temperature dependence as the other previously reported reagents (see Figure). It seems likely therefore that the mechanism of reaction is similar for each reagent, and indeed Olah *et al*. have suggested that nitronium salts react via nucleophilic displacement of the ion pair or solvated ion pair by the aromatic (4).

Figure



The decrease, at any given temperature, in the *ortho*:*para*-ratio along the series N_2O_5, NO_2^+AcOH, $NO_2^+BF_4^-$ appears to reflect the increasing ease with which the group X may be displaced and this seems reasonable bearing in mind that $NO_2^+BF_4^-$ is an ion pair.

Kovacic and Hiller have explained the enhanced ratios observed for nitration of anisole by some reagents in terms of linear coordination between the nitronium ion and the substituent. This mechanism cannot account for the specificity of the nitrating reagents and is thus less satisfactory than the mechanism proposed by Norman and Radda (5) (which related to dinitrogen pentoxide as nitrating species but which can be satisfactorily extended to reagents of the general type NO_2X since the nature of the displaced group is inconsequential, qualitatively, to the *ortho*-stereospecificity of the reagent).

The nitrations of biphenyl and aromatic ethers by species of the type NO_2X can thus be considered as closely similar; for the former, nucleophilic displacement of X is carried out by the π-electrons of the ring, whereas for the latter, the lone pair of electrons on oxygen perform this function.

Reactions were carried out by adding 10 ml. of a sulpholane solution, 0.4M in nitronium borofluoride (Alpha Inorganics Ltd.) to 10 ml. of stirred thermostatted sulpholane solution 0.9M in biphenyl. All solutions were prepared in a dry box and the nitrations were performed in a closed system after mixing. Reaction was stopped by adding water after 5-25 min., depending on the temperature (see Figure) and analyses were performed as previously described (1). Slight dinitration occurred and was estimated as $<5\%$ of the overall nitro products. Sulpholane (B. D. H.) was purified by the method stressed by Olah and Overchuk (6).

REFERENCES

1. R. Taylor, *J. Chem. Soc.*, (B) 727 (1966).
2. P. Kovacic and J. J. Hiller, *J. Org. Chem.*, *30*, 2871 (1965).
3. K. Halvarson and L. Melander, *Arkiv Kemi*, *11*, 77 (1957).
4. G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Amer. Chem. Soc.*, *84*, 3687 (1962).
5. R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3030 (1961).
6. G. A. Olah and N. A. Overchuk, *Canad. J. Chem.*, *43*, 3279 (1965).