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MECHANISM OF THE BENZIDINE REARRANGEMENT

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HAMMOND and SHINE [1] showed some years ago that the benzidine rearrangement is of second order with respect to the acid catalyst; they therefore suggested that it is the diacid salt of hydrazobenzene which rearranges. Carlin and Odioso[2] found that the order with respect to acid of the rearrangement of o-hydrazotoluene is 1.6; this they ascribed to the greater basicity of o-hydrazotoluene which leads to extensive formation of the monoacid salt under the conditions used.

However, Carlin and his collaborators[3] have also found that the rearrangements of m- and p-hydrazotoluene are of second order with respect to acid, although the basic dissociation constants of the three toluidines (K_B of o, 9.48; m, 9.26; p, 8.70) suggest that both m- and p-hydrazotoluenes should be stronger bases than the o-isomer and should therefore be converted to an even larger extent to their salts - and so show a lower

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[1] G. S. Hammond and H. J. Shine, J. Amer. Chem. Soc. **72**, 220 (1950).

[2] R. B. Carlin, and R. C. Odioso, J. Amer. Chem. Soc. **76**, 100 (1954).

[3a] R. B. Carlin and G. S. Wich, J. Amer. Chem. Soc. **80**, 4023 (1958);
[b] R. B. Carlin and R. C. Odioso, Ibid. **76**, 2345 (1954).

acid dependence.

One of us[4] has suggested an alternative interpretation of the variable acid dependency based on a mechanism involving the reversible formation of a π-complex intermediate from the monoacid salt of the hydrazobenzene, which undergoes reaction with a second proton to give the products. If this mechanism is correct, steric effects should appear in the case of hydrazobenzene derivative carrying two bulky para groups.

We have examined the rearrangements of 4-methyl and 4-t-butyl-4'-chlorohydrazobenzene in 75 per cent alcohol, catalysed by hydrochloric acid at a constant ionic strength of 0.1. The orders of the reactions with respect to acid were:

4-methyl-4'-chlorohydrazobenzene, 1.58
4-t-butyl-4'-chlorohydrazobenzene, 1.51.

Since both these compounds must be less basic than p-hydrazotoluene, and since the t-butyl isomer should be not more basic than the methyl one, we consider these results to indicate the type of steric effect required by the π-complex mechanism. Preliminary experiments on 4:4'-bis-t-butylhydrazobenzene would also seem to indicate a steric effect.

Full details of this work and our interpretation of it will be published shortly.

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[4] M. J. S. Dewar, Bull. Soc. Chim. C67 (1951); also Kekule Symposium, London (1958).