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THE BENZIDINE REARRANGEMENT. VI.[1]

4,4'-DI-t-BUTYLHYDRAZOBENZENE

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THREE cases of rearrangement of hydrazobenzenes have been reported in recent years in which the order with respect to acid was between first and second. These are o-hydrazotoluene[2] (1.6), 4-methyl- and 4-t-butyl-4'-chlorohydrazobenzene[3] (1.58 and 1.51). The last two results were attributed to the part played by the bulky para substituents, as proposed earlier in the π-complex theory of the benzidine rearrangement by Dewar.[4]

A new interpretation of variable acid dependence was given recently by Banthorpe, Hughes and Ingold.[5] It is still not known, however, why some compounds should rearrange by a process that is first order in acid, and others by one that is

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[1] Part V, H. J. Shine and J. T. Chamness, J. Org. Chem. in press.

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

[3] M. J. S. Dewar and H. McNicholl, Tetrahedron Letters No. 5, 22 (1959).

[4] M. J. S. Dewar, Kekule Symposium, IUPAC, London (1958).

[5] D. V. Banthorpe, E. D. Hughes and C. K. Ingold, J.Chem. Soc. 2386-2444 (1962).

second order. It is particularly interesting that the rearrangement of p-hydrazotoluene is second order in acid,[6] an occurrence, which, in comparison with the case of 4-methyl-4'-chlorohydrazobenzene, would seem not to support Dewar's[3] interpretation.

We have been investigating 4,4'-disubstituted hydrazobenzenes. We have shown[1] that the rearrangement of 4,4'-divinylhydrazobenzene is first order in acid. We now wish to report that the rearrangement of 4,4'-di-t-butylhydrazobenzene in 95% ethyl alcohol is second order in acid.

The 4,4'-di-t-butylhydrazobenzene, m.p. 127-129°, was prepared by the zinc/ammonium chloride reduction[1] of the azo compound, m.p. 185-186° (lit.[7] 183°). The o-semidine, m.p. 104-105° (lit.[7] 101°) and p-t-butylaniline[7] were prepared for use as standards in analysing products by ultraviolet spectroscopy.

The rearrangements were carried out at 0°. The hydrazo concentration was .0025 M and the acid (hydrochloric) concentration ranged from .01 to .05 M. The ionic strength was kept constant at .05 by addition of lithium chloride. The Bindschedler's Green method[1] of following the disappearance of the hydrazo compounds was used. Rate constants for duplicate runs at five acid concentrations are plotted against acid concentrations in Fig. 1. The slope of the plot, calculated by the method of least mean squares, was 1.96.

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[6] R. B. Carlin and G. S. Wich, J. Amer. Chem. Soc. **80** 4023 (1958).

[7] D. F. du Toit Malherbe, Ber. **52**, 319 (1919).

Product analysis, carried out on eight of the runs carried to complete disappearance of the hydrazo compound, showed that 45-54% of the hydrazo-t-butylbenzene rearranged and 48-50% of it underwent disproportionation. Thus, the hydrazo-t-butylbenzene conversion is analogous in kinetic and product character to that of p-hydrazotoluene.[6]

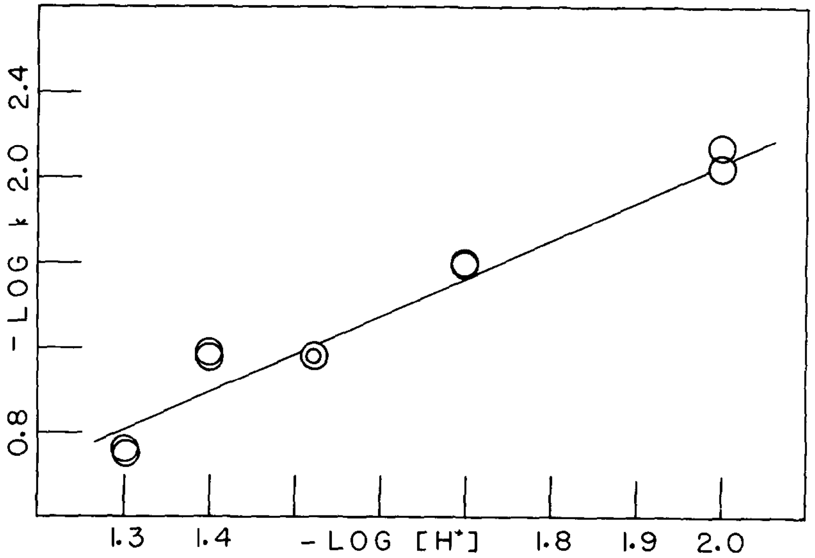

Fig. 1. Plot of log k versus log $[H^+]$ for the disappearance of 4,4'-di-t-butylhydrazobenzene.

Dewar and McNicholl[3] report briefly that preliminary experiments on the rearrangement of this hydrazo-t-butylbenzene seemed to indicate a steric effect. Since no experimental data were given we are unable to try to accomodate this statement with our own experiments. It is our opinion that our present results and those from the divinyl[1] and diméthyl[6] cases show that it is not a steric effect in 4,4'-disubstituted hydrazobenzenes that leads to variable acid dependence.

Complete data on the di-t-butyl- and some other 4,4'-disubstituted hydrazobenzenes are being prepared for publication.

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