

Intramolecular Participation in Ester Hydrolysis by the Diazonium Group

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ESTERS of *o*-aminophenol are generally unstable¹⁻⁴ because of the facile *O* → *N* rearrangements that occur. It appeared probable, however, that with a sufficiently hindered ester function rearrangement would not occur. Catalytic reduction of the 2,6-dimethylbenzoate of *o*-nitrophenol gave material (I), C₁₅H₁₅NO₂,⁵ with m.p. 109–112°, ν_{\max} 3472, 3401 (NH), and 1748 cm.⁻¹ (ester carbonyl). Compound (I) was soluble in dilute

acid, insoluble in 10% sodium hydroxide and its infrared spectrum showed no evidence of amide structure. Acetylation of (I) gave an acetyl derivative, C₁₇H₁₇NO₃, m.p. 135°, ν_{\max} 3436 (NH), 1748 (ester carbonyl) and 1689 cm.⁻¹ (amide carbonyl). Catalytic reduction of the 2,6-dimethylbenzoate of *p*-nitrophenol gave (II), C₁₅H₁₅NO₂, m.p. 144–148°, ν_{\max} 3475, 3400 (NH), and 1739 cm.⁻¹ (ester carbonyl).

¹ M. Bergmann, R. Ulpts, and F. Camacho, *Ber.*, 1922, **55**, 2796.

² L. C. Raiford and W. G. Huey, *J. Org. Chem.*, 1941, **6**, 858.

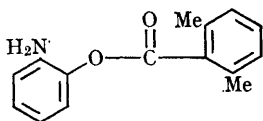
³ N. E. Crouse and L. C. Raiford, *J. Org. Chem.*, 1945, **10**, 419.

⁴ W. J. Hickingbottom in "Chemistry of Carbon Compounds", ed. E. H. Rodd, Vol. IIIA, 450, Elsevier, 1954.

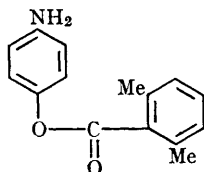
⁵ Satisfactory elemental analyses were obtained for all new compounds.

When (I) was diazotized in aqueous hydrochloric acid at 0°, an immediate and quantitative

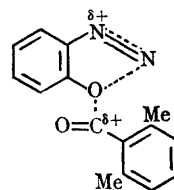
solution which was stable at 0°. In alkaline solution quantitative coupling with β -naphthol



(I)



(II)



(III)

precipitation of 2,6-dimethylbenzoic acid occurred. The aqueous solution yielded a tan solid (decomp.

90—110°), ν_{\max} 2247 cm^{-1} ($-\text{N}\equiv\text{N}^+$),^{6,7} which was identified as *o*-hydroxybenzenediazonium chloride. Diazotization of (I) in ethanolic solution (with sulphuric acid and isopentyl nitrite) gave a precipitate of *o*-hydroxybenzenediazonium bisulphate, m.p. and mixed m.p. 148—150°. The ethanolic solution yielded the ethyl and isopentyl esters of 2,6-dimethylbenzoic acid and a trace of 2,6-dimethylbenzoic acid. Diazotization of (II) in aqueous solution proceeded normally to give a clear

occurred to give an azo-derivative, $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_3$, m.p. 171—173°.

Since (II) behaved normally on diazotization, it seems probable that the extremely rapid hydrolysis of the ester function in (I) following diazotization may best be represented as an intramolecular process. A possible mechanism is shown in (III) where the 2,6-dimethylbenzoyl group is departing as the cation: this is supported by the nature of the products formed when diazotization is carried out in ethanolic solution.

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⁶ K. B. Whetsel, G. F. Hawkins, and F. E. Johnson, *J. Amer. Chem. Soc.*, 1956, **78**, 3360.

⁷ L. A. Kazitsyna, B. S. Kikot, and A. O. Reutov, *Bull. Acad. Sci. U.S.S.R.*, 1964, 894.