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Preliminary communication

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ortho-MERCURATION REACTIONS OF AZOBENZENES

PAUL V. ROLING and JOSEPH L. DILL

Department of Chemistry, Central Michigan University, Mt. Pleasant, Mich. 48859 (U.S.A.)

MARVIN D. RAUSCH

Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002 (U.S.A.)

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Summary

The mercuration of azobenzene occurs exclusively in the *ortho*-position to yield 2-chloromercuriazobenzene and a mixture which on iodination produces 2,2′- and 2,6-diiodoazobenzene. 2-Methylazobenzene mercurates to form only 2-chloromercuri-6-methylazobenzene, while 2-iodoazobenzene undergoes mercuration in both 2′- and the 6-position.

Current interest in *ortho*-metalation reactions of azobenzenes [1—4] and the report [5] of a multistep procedure for the formation of a synthetically useful intermediate, 2-chloromercuriazobenzene, prompt us to communicate some of our recent studies concerning the direct *ortho*-mercuration of azobenzene and several *ortho*-substituted azobenzenes.

We have found that azobenzene and mercuric acetate react in refluxing methanol, followed by treatment with exesss lithium chloride, to yield 2-chloromercuriazobenzene (I) as the only mono-substituted product in 40% yield (m.p. 202—204°)*. Treatment of I with iodine in chloroform solution gave a 90% yield of 2-iodoazobenzene, m.p. 60—61.5°, whose mixture melting point determination with authentic 2-iodoazobenzene [6] (prepared by the condensation of nitrosobenzene and 2-iodoaniline) was undepressed. The NMR spectrum of 2-iodoazobenzene ($CDCl_3$) shows an upfield (δ 7.04) triplet-of-doublets ($J \cong 7.5$ Hz, $J \cong 2$ Hz) for the 4-proton. In addition to the monosubstituted product there was obtained an inseparable mixture of dimercurated products. Iodination of this mixture and separation of the products by column chromatography gave 2,2′-diiodoazobenzene (3% yield based on azobenzene) and 2,6-diiodoazobenzene (3% yield), suggesting that the mixture was com-

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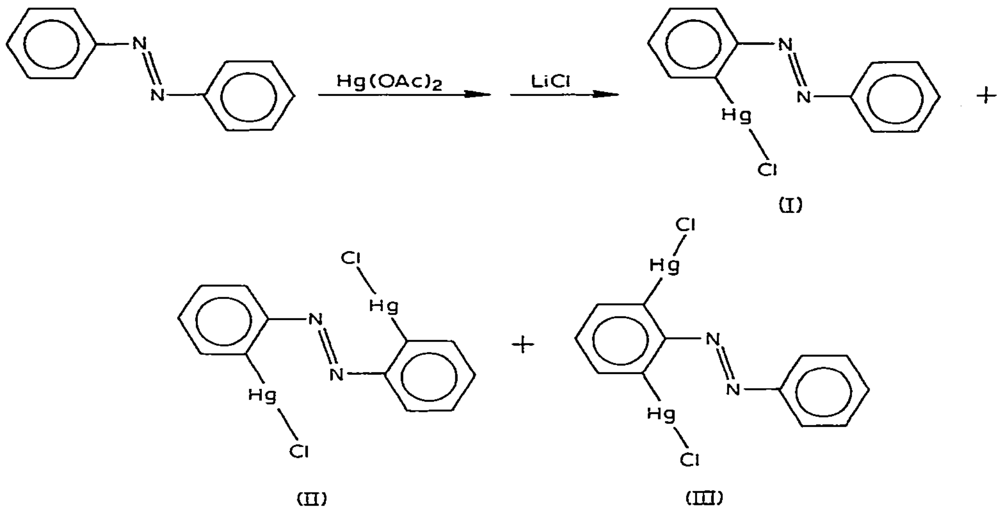
*In contrast, Cross and Tennent [5] failed to observe any reaction between azobenzene and mercuric chloride, even after prolonged reflux in ethanol.



posed of the two mercurials 2,2'-bis(chloromercuri)azobenzene (II) and 2,6-bis(chloromercuri)azobenzene (III). The melting point of 2,2'-diiodoazobenzene (m.p. 158—159°) obtained in these studies agreed with that previously reported (m.p. 158—158.5°) [7]. The NMR spectrum of this product confirms the assignment, since it exhibits a triplet-of-doublets at δ 7.09 for the 4,4'-protons as in 2-iodoazobenzene, a triplet-of-doublets at δ 7.34 for the 5,5'-protons and two doublets-of-doublets at δ 7.70 and 7.98 for the 6,6'- and 3,3'-protons. 2,6-Diiodoazobenzene (m.p. 118—119°) is assigned on the basis of a triplet ($J \cong$ 8 Hz) at δ 6.65 and a doublet at δ 7.87 ($J \cong$ 8 Hz).

Mercuration of 2-methylazobenzene yielded only one product, 2-chloromercuri-6-methylazobenzene, m.p. 209—210°, in 71% yield. Iodination of this mercurial gave 2-iodo-6-methylazobenzene which exhibited a triplet ($J \cong$ 8 Hz) at δ 6.87 for the 4-proton in its NMR spectrum. 2-Iodoazobenzene on mercuration gave two separable mercurials, 2-chloromercuri-2'-iodoazobenzene (2% yield, m.p. 196—197°) and 2-chloromercuri-6-iodoazobenzene (20% yield, m.p. 249—250°), which on iodination yielded 2,2'-diiodoazobenzene and 2,6-diiodoazobenzene, respectively.

The regiospecificity of these reactions suggests that an azo nitrogen directs, by coordination, the mercury into the *ortho* position of the benzene ring. This is in direct analogy with the proposed mechanism for *ortho*-palladation of azobenzene [1].

Acknowledgement

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