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Preliminary communication

ortho-MERCURATION REACTIONS OF AZOBENZENES

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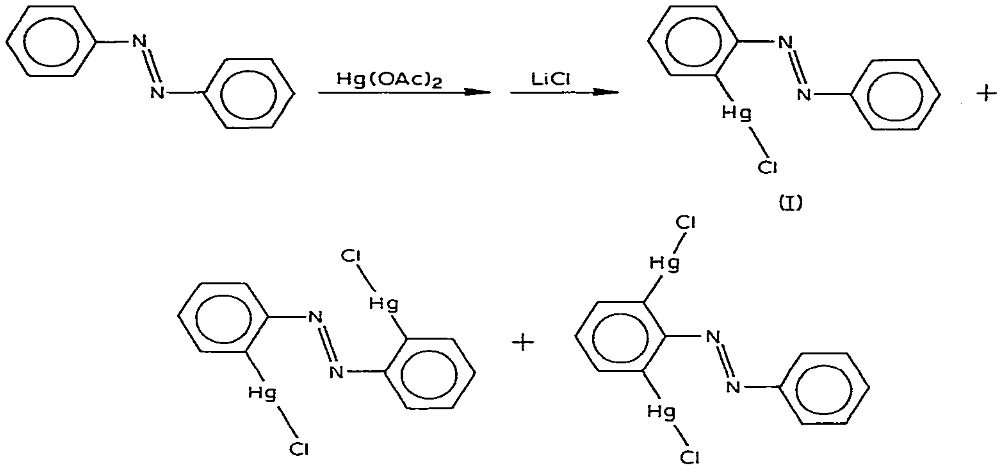
*In contrast, Cross and Tennent [5] failed to observe any reaction between azobenzene and mercuric chloride, even after prolonged reflux in ethanol.



(I) (II) (III)

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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