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IMMONIUM: A PARA-DIRECTING GROUP WITH A POSITIVE POLE ADJACENT TO THE RING

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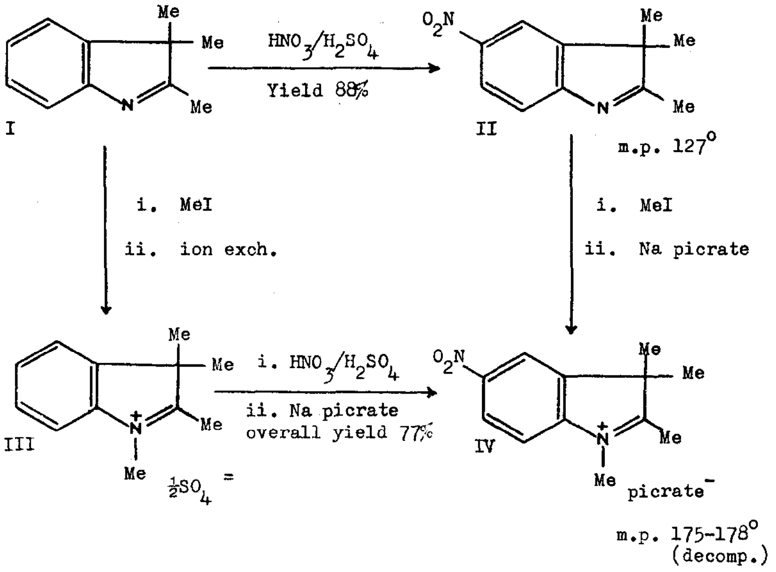
Ridd and his co-workers[1] have shown that groups NR_3^+ (R = H or Me) are not exclusively meta directing but form mixed meta and para mono-nitro derivatives including from 10% to 38% of para substitution. It seemed possible that immonium groups $-\overset{+}{N}R = CR'_2$ might be predominantly para directing, despite the positive pole adjacent to the benzene ring, and we have



now shown this is so by the reactions shown in the scheme[2]; I[3] (2,3,3-trimethyl indolenine) and II[4] were prepared by Fisher indolenine synthesis. We used the cyclic derivative (III bis-(1,2,3,3-tetramethyl indoleninium) sulphate) to prevent the ready hydrolysis to which acyclic imines are prone: ring opening had not occurred, for the ring-opened derivative should behave like $PhNMeH_2^+$. Nitrations were carried out by adding, dropwise over a period of 30 minutes, one mole of sodium nitrate dissolved in concentrated sulphuric acid to the indolenine in concentrated sulphuric acid at 0 - 10° Stirring was continued for a further 5 minutes before the reaction was quenched.

The present results strongly support the hypothesis of Noland, Smith, and Johnson[5] that the 5-nitration of indoles in sulphuric acid proceeds by initial protonation at the 3-position which yields an analogue of III.

References.

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[2] Satisfactory analyses were obtained for new compounds.

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