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ADDITION OF DINITROGEN TRIOXIDE TO Δ^1 -ARYLCYCLOHEXENES

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The addition of dinitrogen trioxide to Δ^1 -arylpropenes constitutes an important step in a method of synthesis of 3-methylisoquinolines, developed by Bruckner and co-workers.¹ With a view to adapting this method for the synthesis of 1:2:3:4-tetrahydrophenanthridines, we studied the addition of dinitrogen trioxide to Δ^1 -arylcyclohexenes. Addition of dinitrogen trioxide to Δ^1 -phenylcyclohexene yielded a mixture of products. One of these was a nitrosite of such instability that its formation could be deduced only by the isolation of its decomposition product, a nitroolefine, b.p. $88^\circ/0.01$ mm. (Found: N, 7.3, $C_{12}H_{13}O_2N$ requires N, 6.9%) This was reduced by lithium aluminium hydride to a base, whose benzoyl derivative melted at 122° (Found: C, 82.0; H, 7.8; N, 5.0. $C_{19}H_{21}ON$ requires C, 81.7; H, 7.5; N, 5.0%). This benzoyl derivative is presumably a diastereoisomer of the benzoyl derivative, m.p. 183° , of 2-phenylcyclohexylamine, prepared by a different method.²

Another product was a nitrosite, m.p. 226° , (Found: C, 61.5; H, 6.2; N, 11.7. $C_{12}H_{14}O_3N_2$ requires C, 61.5; H, 6.0; N, 12.0%), of remarkable stability. This nitrosite dissolved in an alcoholic solution of sodium hydroxide or sodium methoxide, yielding a deep red solution from which the original nitrosite could be recovered unchanged by acidification. It dissolved in acetic anhydride-sulphuric acid mixture without change; under these conditions, the nitroso group in nitrosites is invariably replaced by an acetoxy group.¹ Treatment of this nitrosite with acetic anhydride in pyridine medium yielded merely the acetate of the aci-form of the nitrosite, m.p. 103° (Found: C, 61.0; H, 5.4; N, 9.8. $C_{14}H_{16}N_2O_4$ requires C, 60.9; H, 5.8; N, 10.2%).

Evidently the nitroso group occupies the polar and the nitro group the equatorial position in the unstable nitrosite, while both the nitroso and nitro groups are equatorial in the stable nitrosite, m.p. 226° . These two nitrosites constitute a striking example of the behaviour of cyclohexane derivatives being dependent on the conformation of the substituent groups. Similarly, Δ^1 -o-tolyl, Δ^1 -p-tolyl, Δ^1 -m-anisyl, Δ^1 -p-anisyl and Δ^1 - α -naphthylcyclohexenes have each been shown to form two nitrosites differing to a marked extent in stability. A full account of this work will be published elsewhere.

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References

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- 2 Nightingale, D. & Tweedie, V., *J. Amer. chem. Soc.*, 1944, 66, 1969

