Formation of 5,6-Dinitrocyclohex-3-enones in the Nitration of Polyalkylbenzenes

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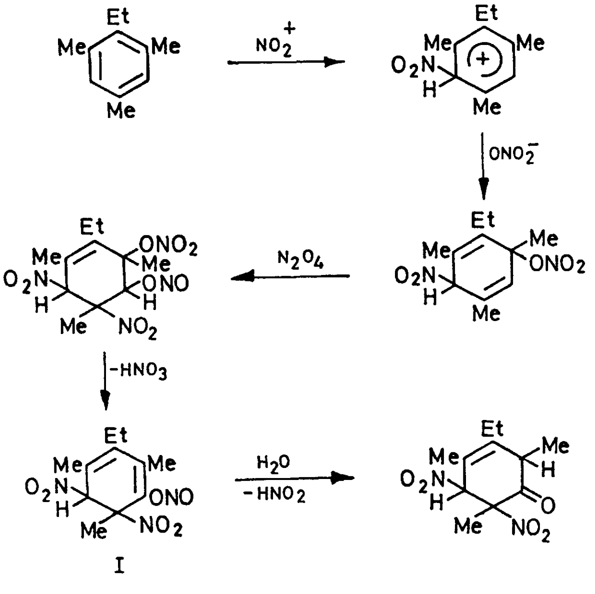
Summary Nitration of polyalkylbenzenes with fuming nitric acid gives small amounts of dinitrocyclohexenones besides ring and side-chain substitution products.

THE action of fuming nitric acid on polyalkylbenzenes and their derivatives at low temperatures often yields benzyl nitrates in addition to normal ring substitution products.[1] This unusual electrophilic reaction is characterized by the unusual orientation of the products and the high positional selectivity.[2] Various minor products including diphenylmethanes, bisbenzyl ethers, benzaldehydes, and benzyl alcohols also arise from further reaction of the benzyl nitrates.[3] We now report a further unusual nitration, which involves the formation of unsaturated cyclic dinitroketones. Our results suggest that an addition–elimination sequence may be partly involved in the nitration of polyalkylbenzenes.



I

SCHEME

Treatment of ethylmesitylene with excess of fuming nitric acid in dichloromethane at −10 to 0° followed by chromatography gave white needles, m.p. 140—141° (2—4%). The product had the formula $C_{11}H_{16}N_2O_5$ (*M*, 256); the presence of a 5,6-dinitrocyclohex-3-enone skeleton was shown by characteristic i.r., u.v., and mass spectra. Its n.m.r. spectrum (60 MHz; $CDCl_3$) showed the presence of one ethyl group, three methyl groups, and two methine protons, and so the spectral evidence is consistent with the formulation of the product as 3-ethyl-2,4,6-trimethyl-5,6-dinitrocyclohex-3-enone (I). 1,2,3,5-Tetramethylbenzene (isodurene) similarly gave 2,3,4,6-tetramethyl-5,6-dinitrocyclohex-3-enone, m.p. 137—138° (3—4%). Although these unusual products were formed from many polyalkylbenzenes, most were non-crystallizable syrups which darkened when kept.

The formation of the ketone (I) may be explained in terms of an addition-elimination mechanism, which initially involves the nitronium ion as electrophile and the nitrate ion as nucleophile. A possible sequence is shown in the Scheme. The process is supported by the recent observation[4] that the nitration of some polyalkylbenzenes in a system containing a strong nucleophile (acetic anhydride–nitric acid) leads to the extensive formation of 4-acetoxy-1-nitrocyclohexa-2,5-dienes.

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