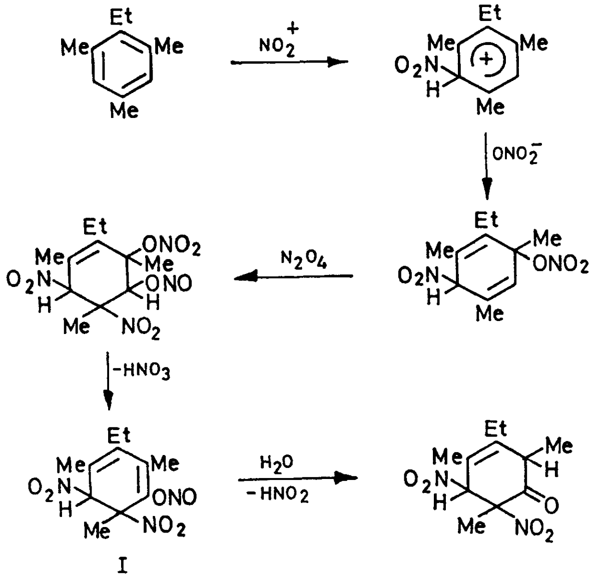
Formation of 5,6-Dinitrocyclohex-3-enones in the Nitration of Polyalkylbenzenes

By H. SUZUKI,* M. SAWAKI, and R. SAKIMOTO

(*Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto, Japan*)

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.



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.

(*Received, September 13th,* 1971; *Com.* 1589.)

---

[1] L. I. Smith and S. A. Harris, *J. Amer. Chem. Soc.*, 1935, **57**, 1289; L. I. Smith and D. Tennenbaum, *ibid.*, p. 1293; L. I. Smith F. L. Taylor, and I. M. Webster, *ibid.*, 1937, **59**, 1082; L. I. Smith and J. W. Horner, *ibid.*, 1940, **62**, 1349.

[2] H. Suzuki, *Bull. Chem. Soc. Japan*, 1970, **43**, 481; H. Suzuki and K. Nakamura, *ibid.*, 1971, **44**, 227; K. Nakamura, *ibid.*, p. 133; H. Suzuki, K. Nakamura, and M. Takeshima, *ibid.*, p. 2248.

[3] H. Suzuki and K. Nakamura, *Bull. Chem. Soc. Japan*, 1970, H. Suzuki, *ibid.*, 1970, **43**, 879.

[4] D. J. Blackstock, M. P. Hartshorn, A. J. Lewis, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc.* (*B*), 1971, 1212.