

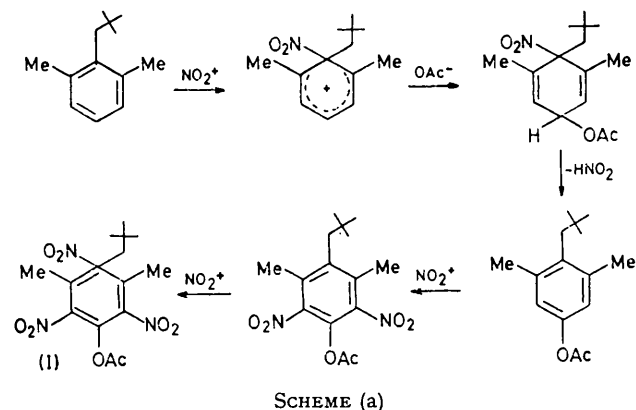
Unusual Product of Aromatic Nitration: 4-Hydroxy-3,5-dimethyl-4-neopentyl-2,6-dinitrocyclohexa-2,5-dienone

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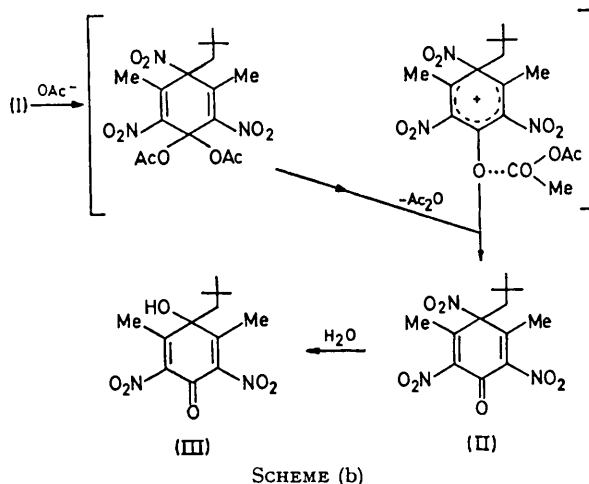
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Summary Nitration of 2,6-dimethylneopentylbenzene with nitric acid and acetic anhydride in nitromethane gives a small amount of the title compound in addition to the normal ring substitution products.

IN view of recent interest in unusual nitration products¹⁻³ we report a further example. Treatment of 2,6-dimethylneopentylbenzene in nitromethane with nitric acid (*d* 1.40) and acetic anhydride at room temperature, followed by decomposition of the mixture with ice and extraction with pentane gave light yellow needles (4%) from the pentane layer. Recrystallization from ethanol yielded a product,



m.p. 188°, with molecular formula $C_{13}H_{18}N_2O_8$ (M^+ , 298); δ [60 MHz; $(CD_3)_2SO$] 6.27 (1H, s, exchangeable with D_2O), 2.12 (6H, s), 2.05 (2H, s), and 0.90 (9H, s), p.p.m.; ν_{max}



(KBr) 1730 (C=O), and 1545 and 1375 (NO_2) cm^{-1} , which was assigned structure (III).

This product may be formed by the mechanism in the Scheme (a and b). The cyclohexadienone (II) can be formed in two ways: (i) capture of an acetate ion by the benzenonium ion (I) followed by rapid elimination of acetic anhydride as suggested by Blackstock *et al.*² for 3,4,5-trimethyl-4-nitrocyclohexa-2,5-dienone or (ii) direct attack of an acetate ion on the acetoxy-group of (I) with elimination of acetic anhydride. Hydrolysis of (II) in the moist pentane layer would then give (III). This would be the first case reported of a tertiary aliphatic nitro-compound undergoing hydrolysis under very mild conditions.

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¹ J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge University Press, 1971, p. 122.

² D. J. Blackstock, M. P. Hartshorn, A. J. Lewis, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc. (B)*, 1971, 1212.

³ H. Suzuki, M. Sawaki, and R. Sakimoto, *Chem. Comm.*, 1971, 1509; H. Suzuki and K. Nakamura, *J.C.S. Chem. Comm.*, 1972, 340.