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THE NITRATION OF *p*-CYMENE WITH NITROGEN DIOXIDE IN ACETIC ANHYDRIDE: THE ISOLATION AND X-RAY STRUCTURE DETERMINATION OF 6-METHYL-3-(METHYLETHYL)-*t*-5-NITRATO-1,*r*-3,*c*-4,*t*-6-TETRANITROCYCLOHEXENE

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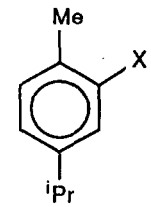
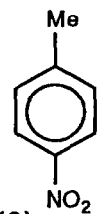
Abstract: Reaction of *p*-cymene (**1a**) with nitrogen dioxide in acetic anhydride gives 2-nitro-*p*-cymene (**1b**), *p*-nitrotoluene (**2**), and the tetranitronitratocyclohexene (**3**) as the major products; the X-ray crystal structure of (**3**) is reported.

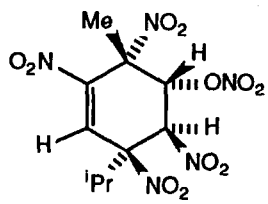
In 1933 N. Puranen reported the isolation of a crystalline material [m.p. 127-129°], assigned structure (**4**), from the reaction of *p*-cymene (**1a**) with nitrogen dioxide in acetic anhydride.[1] We now report preliminary results of a re-investigation of this reaction and the identification of the major products formed, including the crystal structure of the compound isolated by Puranen.[1]



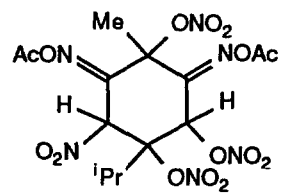
(**1a**) X = H
(**1b**) X = NO_2



(**2**)



(**3**)



(**4**)

Reaction of *p*-cymene (**1a**) with nitrogen dioxide in acetic anhydride for 24 h at 20°, followed by removal of the solvent under reduced pressure, gave a crude product from which compound (**3**) (16%) could be obtained by crystallization. The structure of this compound (**3**), m.p. 127.5-129°, was determined by X-ray structure analysis. The spectroscopic data for compound (**3**) were in accord with the determined structure.[2] A perspective drawing is given in Figure 1 and the crystal data are summarized below.[3] In the solid state the alicyclic ring of compound (**3**) exists in a flattened skew boat conformation [torsional angles: C(1)-C(2)-C(3)-C(4) 21.2(2)° ; C(2)-C(1)-C(6)-C(5) -4.1(2)°] in which the C(6)-substituents are close to being perfectly staggered with respect to the C(1)-NO_2 group; the relative orientation of the C(5)-ONO_2 and C(6)-Me groups is indicated by the torsional angle C(10)-C(6)-C(5)-O(51) 84.9(2)°. Notwithstanding the above, H(4) and H(5) remain close to *anti*-coplanar.

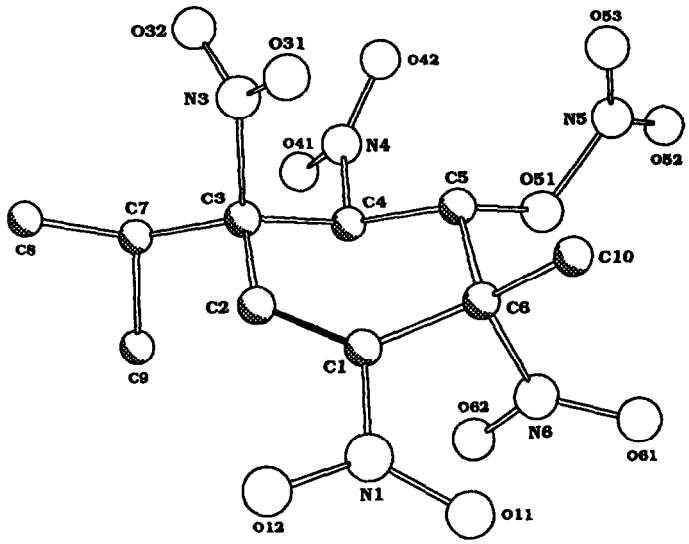


Figure 1
Double bond shown in black

Apart from the major products of reaction of *p*-cymene (**1a**) with nitrogen dioxide in acetic anhydride - 2-nitro-*p*-cymene (**1b**) (25%), *p*-nitrotoluene (**2**) (8%), and the novel tetranitro nitrate (**3**) (16%) - some nine further as yet unidentified products have been isolated [yields in the range 1-8%; total ~ 33%]. On the basis of initial spectroscopic evidence, these products appear to be structurally closely related to the tetranitro nitrate (**3**), and we believe that knowledge of these structures will be helpful in elucidating the mode of formation of compound (**3**).

References, Crystal Data and Spectroscopic Data

1. N. Puranen, *Ann. Acad. Sci. Fennicae*, 1933, **37A**, No. 10; *Chem. Abs.*, 1933, **27**, 5062.

2. ν_{max} [Nujol] 1715, 1271, 811 [ONO_2], 1588, 1557 cm^{-1} [NO_2]. ^1H n.m.r. [300MHz,$CDCl_3$] δ 1.19 [d, $J_{Me,H7}$ 6.6 Hz, Me], 1.29 [d, $J_{Me,H7}$ 7.0 Hz, Me], 2.07 [s, 6-Me], 3.18 [m, H7], 5.68 [d, $J_{H4,H5}$ 11.6 Hz, H4], 6.01[d, $J_{H5,H4}$ 11.6 Hz, H5], 7.42 [s, H2].

3. *Crystal Data:* (**3**) $C_{10}H_{13}N_5O_{11}$, M = 379.24, monoclinic, space group $P2_1/c$, a = 10.670(2), b = 11.325(2), c = 14.266(3) Å, β = 117.29(1)°, U = 1532.0 $Å^3$, T =163 K, D_m = 1.63, D_c = 1.64 g cm^{-3}, Z = 4, colourless crystal of dimensions 0.26 by 0.48 by 0.60 mm, μ = 1.41 cm^{-1}. 2844 Unique reflections [$2\theta \leq 54°$] were measured with a Nicolet R3m four-circle diffractometer using graphite monochromated Mo-Kα radiation [0.71069 Å] and ω-scans. Absorption corrections were not applied. 2306 Reflections were judged observed [$I > 2\sigma(I)$]. *R*-factor 0.036; *wR* 0.038, $w^{-1} = \sigma^2(F) + 4.1 \times 10^{-4}(F^2)$. Atomic coordinates, bond lengths and angles, torsional angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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