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SYNTHESIS AND THERMAL DECOMPOSITION OF A TERTIARY β-NITROALKYL PEROXYNITRATE

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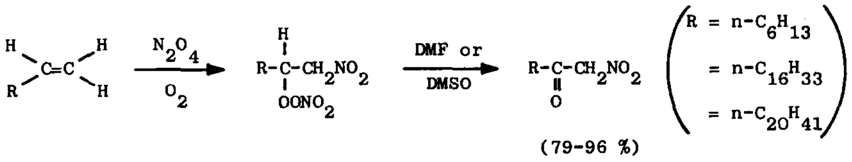
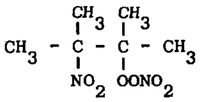
The formation of β-nitroalkyl peroxynitrates by the reaction of straight chain α-olefines with a mixture of dinitrogen tetroxide and oxygen (nitroxidation) has recently been described[1]. Above 0° these peroxynitrates readily decompose to a mixture of products one of which is the corresponding α-nitro ketone. In most solvents the yield of this last product is low but when the decomposition is carried out in DMF or DMSO much higher yields of α-nitro ketone are obtained.



We wish to report briefly on the synthesis and thermal decomposition of a β-nitroalkyl peroxynitrate ① for which elimination of HNO_3 is precluded because the peroxynitrate group is attached to a tertiary carbon atom.

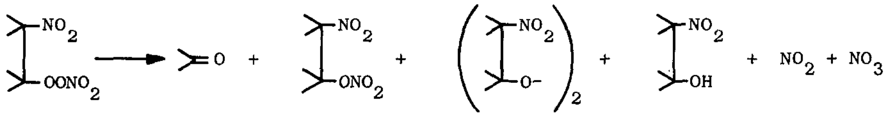


$$CH_3-\underset{NO_2}{\overset{CH_3}{C}}-\underset{OONO_2}{\overset{CH_3}{C}}-CH_3$$ ①

Compound ① was prepared by conducting a N_2O_4 and NO_2 containing stream of O_2 through a 0.5 M solution of tetramethylethylene (TME) in CCl_4 at -20° (TME : N_2O_4 : O_2 = 1 : 1 : 18).

Evaporation of solvent at -20° yielded a white solid which, according to NMR analysis (see table), consisted of 87 mole% of ① , 7 mole% of the corresponding nitrate ② and 6 % of a mixture of unknown compounds. The IR spectrum of the white solid showed strong bands at 5.85 μ , 7.75 μ and 12.7 μ indicative for the peroxynitrate group and two nitro bands (6.4 μ and 7.4 μ). Decompositions were performed with this product; no further purification was attempted.

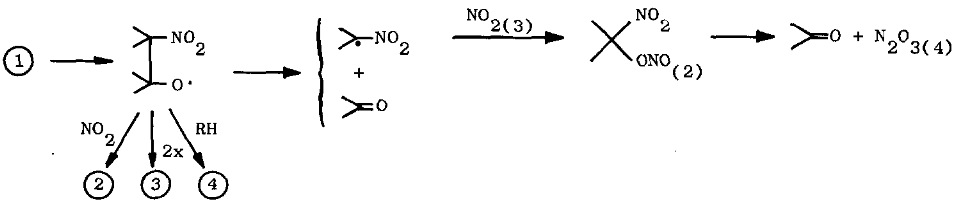
The decomposition was carried out in a flask which was connected to the aspirator via a CCl_4 containing cold trap at -190° and a $CaCl_2$ drying tube. When the white solid was warmed up to room temperature it gradually liquified; after 30 hours at room temperature and 13 mm Hg the content of the flask had resolidified while in the cold trap a white and some blue solid had formed (at -190°). After complete decomposition the products in the cold trap were allowed to melt and to dissolve in the CCl_4. During the experiment air and moisture were excluded by the use of dry N_2. The white solid residue in the flask and the slightly brown CCl_4 solution from the cold trap were then analysed. The results are represented in table I. Taking into account the products already present before the decomposition one can calculate the amounts of the products formed from the thermal decomposition of ①:



① ② ③ ④

mmoles: 100 96 30 5 9 68 20

The formation of acetone, β-nitronitrate ②, β,β'-dinitroperoxy compound ③ and β-nitroalcohol ④ is in agreement with the following scheme in which β-nitroalkoxy radical is the key intermediate:



About half of the β-nitroalkoxy radicals react with NO_2, dimerise or react with a hydrogen donor giving ②, ③ or ④ respectively. The other half gives β-fission producing acetone and

Table I

Analysis of nitroxidation product of TME before and after decomposition
at room temp, 13 mm Hg, 30 hours, under N_2

compound	60 MHz NMR (CCl_4, TMS) δ ppm	meth. of analysis	before	after	
				residue	cold trap
			mmoles		
①	1.71 1.45	a	16.3	0	0
②	1.71 1.74	a	1.3	6.2	0
③	1.62 1.33	a	0	0.8	0
④	1.62 1.27	a	0	1.4	0
unknown	6 small peaks between 2.3-1.9	a	~1.1	~1.7	0
acetone	2.17	a, b	0	0	15.6
N_2O_4		c	-	-	5.02
$NO_2^{\ominus}$		d e	-	-	3.80 3.96
total acid		f g	-	-	15.5 13.2
total N		h	-	-	14.4

a) From NMR peak integrals and the weights of the starting material and the residue; cpds ② and ③ were isolated from the decomposition product of ① by prep. TLC; IR, MS and elemental analyses were in good agreement with the proposed structures. Attempts to isolate ④ from the residue were not successful. Addition of pure ④ to the residue caused an increase of the peaks at 1.62 and 1.27 ppm.

b) GLC of tetra solution from cold trap after washing with saturated bicarbonate solution.

c) By spectrophotometry in tetra solution from cold trap (λmax 343 nm, ε = 233)[2].

d) By spectrophotometry[3] in the 1 N NaOH extract from tetra solution in cold trap.

e) Oxidimetrically (Ce^{IV})[4] in the 1 N NaOH extract from tetra solution in cold trap.

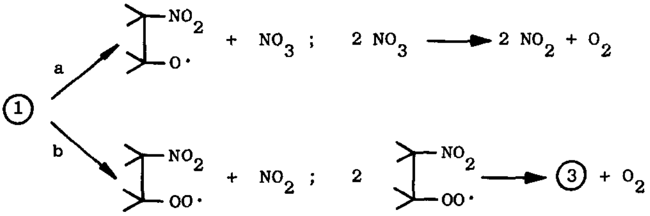
f) From $OH^{\ominus}$ consumption after shaking tetra solution from cold trap with 1 N NaOH.

g) Potentiometric titration of solution obtained by pouring tetra solution from cold trap in moist acetone.

h) In 1 N NaOH extract from tetra solution in cold trap after reduction with Devarda alloy and determination of the NH_3[5].

α-nitroisopropyl radical. The assumption that this last radical also produces acetone via the steps indicated in the scheme is based on the observation that from 51 mmoles of ① not producing ②, ③ or ④ 96 mmoles of acetone are formed.

The most likely route for the formation of β-nitroalkoxy radical from ① is O-O bond breaking (route a) indicated by the formation of NO_3[6] (or N_2O_5) besides NO_2 (or N_2O_4). The possibility of O-N bond breaking followed by interaction of two peroxy radicals (route b) cannot be ruled out however. That this route is, at least partly, followed seems probable from the formation of ③ indicating formation of two oxy radicals within the same solvent cage[7]:



Studies on the formation and decomposition of other β-nitroperoxynitrates are in progress.

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