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OXIDATION AT NITROGEN IN BENZO- BENZODI- AND BENZOTRIFUROXANS

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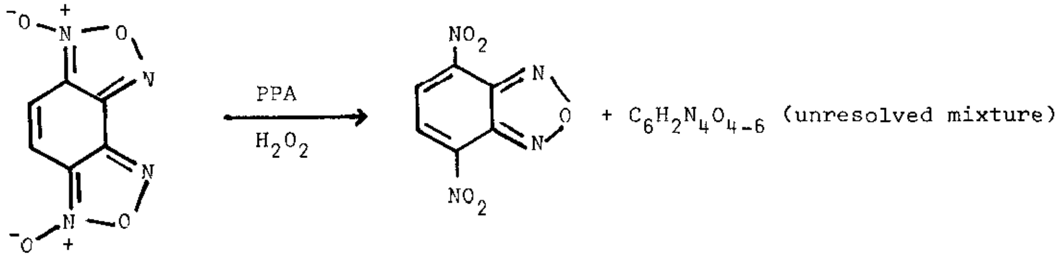
Abstract - Hydrogen peroxide in sulfuric acid oxidized 5-nitrobenzofuroxan into 1,2,4-trinitrobenzene and completed the oxidation of a mixture from benzodifuroxan and hydrogen peroxide in polyphosphoric acid into 1,2,3,4-tetranitrobenzene. The incompletely oxidized mixture also contained 4,7-dinitrobenzofurazan, a terminal oxidation product. Benzotrifuroxan was unreactive toward peroxidation.

In either sulfuric or trifluoroacetic acid hydrogen peroxide rapidly degraded benzodifuroxan 1 but in polyphosphoric acid it smoothly converted the difuroxan 1 into a mixture. Recrystallization brought about partial isolation of 4,7-dinitrobenzofurazan 2. Further treatment of the mixture by oxidation with hydrogen peroxide in sulfuric acid gave 1,2,3,4-tetranitrobenzene 3 and the furazan 2; however the latter was not a precursor to the tetranitrobenzene since it resisted all attempts to bring about oxidation at a furazan nitrogen atom.[1] Similar peroxidation of benzofuroxan into 1,2-dinitrobenzene, 4-nitrobenzofuroxan into 1,2,3-trinitrobenzene and 4,6-dinitrobenzofuroxan into 1,2,3,5-tetranitrobenzene was previously reported.[2] Benzotrifuroxan[3] was quantitatively recovered from attempts at peroxidation into hexanitrobenzene, a recently reported compound.[4]



+ $C_6H_2N_4O_{4-6}$ (unresolved mixture)

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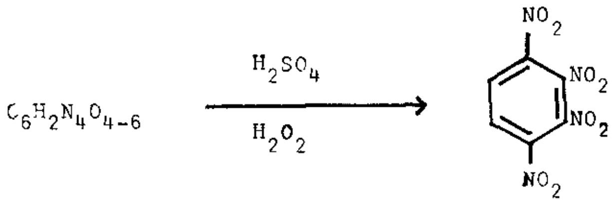

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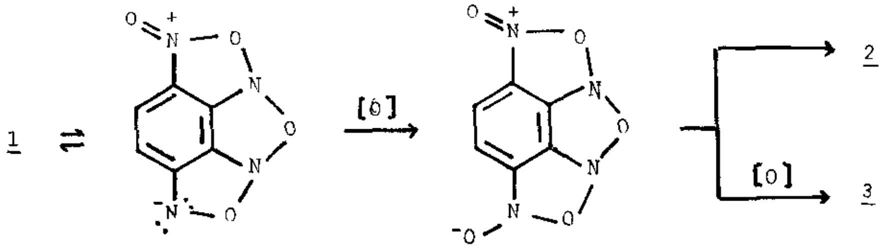
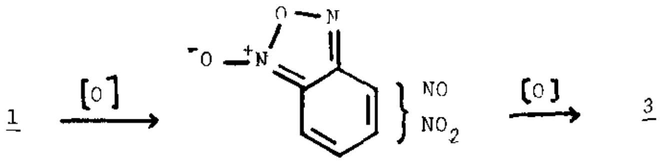
A neighboring group participation 1 → 4 between furoxan moieties and cleavage of two oxygen bridges in the intermediate 5 can account for a terminal monoxidation 1 → 2. On the other hand differentiation between intermediate 5 and an isomeric nitronitrosobenzofuroxan 6 for the oxidation 1 → 3 cannot be made at this time.





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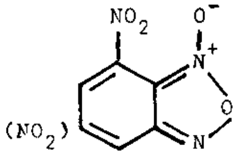
An intermediate neighboring group participation between a furoxan moiety and a 4-nitro substituent with or without the intermediacy of nitronitrosobenzenes 8, may have occurred in the oxidations of 4-nitro- and 4,6-dinitrobenzofuroxans 7 into the corresponding polynitrobenzenes 9[2,5] We now report an efficient oxidation of 5-nitrobenzofuroxan 10 by hydrogen peroxide in sulfuric acid into 1,2,4-trinitrobenzene 12. This example presumably proceeds via a dinitronitrosobenzene 11 intermediate.



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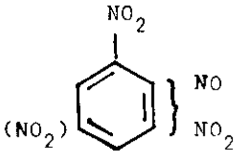

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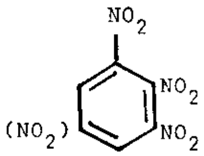

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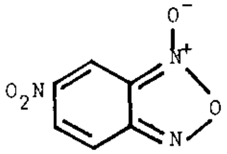

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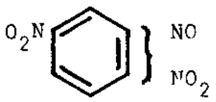

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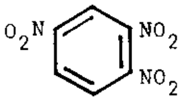

12

The identification of 4,7-dinitrobenzofurazan 2 was consistent with a single nmr ^1H signal for two equivalent hydrogen atoms, ir absorption for the nitro groups, molecular weight (ms), elemental analyses and resistance to oxidation by Caro's acid. The structure of 1,2,3,4-tetranitrobenzene 3 was supported by a single nmr ^1H signal, ir absorption for the nitro groups, molecular weight (ms), elemental analyses, a mixture melting point and the same R_f value obtained from a known sample.[4]

Acknowledgment: Financial support was received from O. N. R. Certain n.m.r. spectra were obtained from a Bruker 270MH instrument at the University of Chicago, Chicago, Illinois.

Experimental

Instruments included Perkin Elmer 237B, 283 and 521 grating i.r.; Varian A-60 and Bruker 270 n.m.r.; and an AEC Scientific limited MS 30 (70 ev, source temperature 120-150°C).

Hydrogen peroxide (90%, 4ml)[6] was added over a period of four hours to a solution of benzodifuroxan (0.22 g, 1.13 mmol) in polyphosphoric acid (10 ml).[8] After stirring at room temperature for two days,[9] ice water was added, and the products extracted into methylene chloride which was dried (magnesium sulfate), filtered and evaporated to dryness to give a mixture of yellow soilds, 0.09 g. Recrystallization from ethyl acetate gave 4,7-dinitrobenzofurazan 2, 0.03 g, mp 187-189°C; nmr(ethyl acetate); δ 8.6(s); ir(KBr); 3045,1550,1530 (NO_2),1480, 1380 and 1340 cm^{-1} (NO); m/e(70eV) (%); 210(100) M^+; calcd for $C_6H_2N_4O_5$: C, 34.28;H, 0.95; N, 26.67%; mw 210;, found: C, 34.16; H, 0.93; N, 26.42%.

The mixture of yellow solids, 0.09 g, in sulfuric acid (98%, 20 ml) was treated with hydrogen peroxide (90%, 2 ml) added slowly over a period of two hours. The reaction mixture was stirred at room temperature for three days and worked up in the manner described above. Removal of methylene chloride left a yellow solid. 1,2,3,4-Tetranitrobenzene 3 was extracted by, and then recrystallized from, carbon tetrachloride as a yellow solid, 0.03 g (12%), mp 108-109°C. Elution from silica gel by a mixture of methylene chloride and carbon tetrachloride (3:2) gave a pure sample, mp 115-116°C, mixture mp 114-116°C with an authentic sample;[4] nmr ($CDCl_3$): δ 8.50; ir (KBr): 1550 and 1350 cm^{-1} (NO_2); calcd for $C_6H_2N_4O_8$: C, 27.92; H, 0.78; N, 21.71; found: C, 28.79; O, 0.83; N, 21.50; R_f 0.3 from a tlc silica gel plate by a mixture (3:2) of methylene chloride and carbon tetrachloride.

The portion insoluble in carbon tetrachloride gave the furazan 2 0.05 g, mp 187-189°C after recrystallization from ethyl acetate (combined yield 21 %).

To a solution of 5-nitrobenzofuroxan 9[10] (0.40g, 2.2 mmol) in sulfuric acid (98%, 30ml), hydrogen peroxide (90%, 2.0 ml, 82 mmol) was added dropwise at 0°C over a period of 4 hours, stirred at 25°C for 2 days, diluted with ice-water and extracted with metheylene chloride. The extract was dried over magnesium sulfate, filtered and concentrated to give 1,2,4-trinitrobenzene 11 (0.38g, 1.8 mmol, 80% yield), m.p. 58-60°C[11] after recrystallization from chloroform; nmr ($CDCl_3$): δ 8.86 (s, 1H), 8.69-8.68(d,1H), 8.15-8.12(d,1H); ir(KBr): 1540 and 1350 cm^{-1} (NO_2).

References and footnotes.

1. Oxidation at a furazan nitrogen atom in unknown.
2. J. H. Boyer and S. E. Ellzey, *J. Org. Chem.*, 1959, **24**, 2038. Joseph H. Boyer and Chorngbao Huang, *J. Chem. Soc. Chem. Comm.*, 1981, 365.
3. A. S. Bailey, *J. Chem. Soc.*, 1960, 4710.
4. A. T. Nielsen, R. L. Atkins, W. P. Norris, C. L. Coon and M. E. Sitzmann, *J. Org. Chem.*, 1980, 45, 2341. Z. A. Akopyan, Yu. T. Struchkov and V. G. Dashevskie, *Zh. Strukt. Khim.*, 1966, **7**, 408; *Chem Abstr.*, 1966, **65**, 14551e. We thank Dr. Nielsen for a sample of 1,2,3,4-tetranitrobenzene.

5. A. J. Boulton and A. K. Katritzky, Proc. Chem. Soc., 1964, 299 assumed a similar neighboring group participation to account for the degenerate isomerization of 4-nitrobenzofuroxan.
6. Hydrogen peroxide(90 %) must be handled as a dangerous reagent. The compounds **1** - **6** are potentially explosive.
7. A. J. Boulton, A. C. Gripper Gray and A. R. Katritzky, J. Chem. Soc., 1965, 5958.
8. When polyphosphoric acid was replaced by either sulfuric or trifluoroacetic acid extensive degradation occurred with the evolution of brown fumes of nitrogen oxides.
9. The disappearance of starting material was monitored by ir.
10. R. J. Gaughran, J. P. Picard and J. V. R. Kaufman, J. Amer. Chem. Soc., 1954, **76**, 2233.
11. F. Pietra and D. Vitali, J. Chem. Soc. Perkin Trans 2, 1972, 385.

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