Rearrangement of Peroxynitrite Esters

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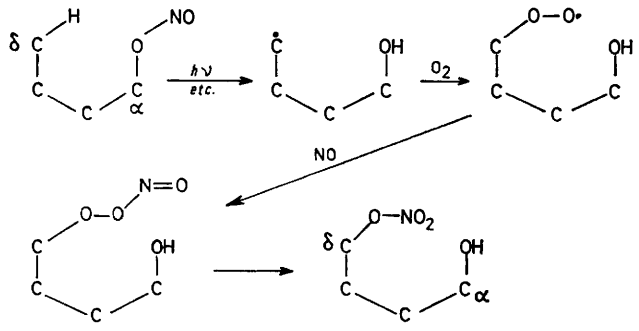
Summary Treatment of tertiary hydroperoxides with nitrosyl chloride–pyridine affords in good yield the corresponding nitrates, formed by spontaneous rearrangement of the initially produced peroxynitrites.

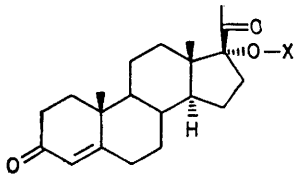
THE photolysis of nitrite esters in the presence of oxygen affords δ-nitrato-alcohols in a synthetically useful reaction.[1,2] We have postulated[1] that the nitrates are formed by rearrangement of peroxynitrite esters (Scheme).



SCHEME

We have not found any reference in the literature to a stable peroxynitrite ester.[3] In agreement with the Scheme, a peroxynitrite ester immediately rearranges in good yield to the corresponding nitrate at 0 °C.

17α-Hydroperoxyprogesterone[4] (**1**) in dry pyridine at 0 °C was treated with nitrosyl chloride until there was a permanent brown colour. Addition of ice–water and work up gave the known[5] 17α-nitratoprogesterone (**2**) (71%, after recrystallisation). Similarly, t-butyl hydroperoxide afforded t-butyl nitrate[6] (73%, after redistillation). Monitoring the reaction did not indicate the presence of any intermediate peroxynitrite ester.



(1) X = OH
(2) X = NO_2

This rearrangement of peroxynitrites provides a convenient synthesis of tertiary nitrates. In addition, the ready rearrangement of peroxynitrites is surely relevant to problems of air pollution.[7]

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[1] J. Allen, R. B. Boar, J. F. McGhie, and D. H. R. Barton, *J.C.S. Perkin I*, 1973, 2402.
[2] D. H. R. Barton, M. J. Day, R. H. Hesse, and M. M. Pechet, *J.C.S. Perkin I*, 1975, 2252; see also K. S. Pillay and Y. L. Chow, *J. C. S. Perkin II*, 1977, 93.
[3] *Cf.* J. R. Shelton and R. F. Kopczewski, *J. Org. Chem.*, 1967, **32**, 2908; E. G. Janzen, J. L. Meyer, and C. L. Ayers, *J. Phys. Chem.*, 1967, **71**, 3108; Y. Rees and G. H. Williams, *Adv. Free Radical Chem.*, 1969, **3**, 199.
[4] E. J. Bailey, D. H. R. Barton, J. Elks, and J. F. Templeton, *J. Chem. Soc.*, 1962, 1578.
[5] G. Snatzke, H. Laurent, and R. Wiechert, *Tetrahedron*, 1969, **25**, 261.
[6] A. Michael and G. H. Carlson, *J. Amer. Chem. Soc.*, 1935, **57**, 1268; *cf.* J. Blum, *Compt. rend.*, 1959, **248**, 2679.
[7] H. Levy in 'Advances in Photochemistry,' eds. J. N. Pitts, G. S. Hammond, and K. Gollnick, Vol. 9, Interscience, New York, 1974.