Oxidation of Some Trinuclear Aromatic Compounds with Cerium(IV) Ammonium Nitrate

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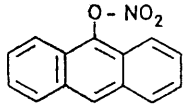
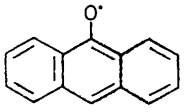
Anthrone, xanthen, and thioxanthen were oxidised with cerium(IV) ammonium nitrate (CAN) in methanol to yield anthraquinone, xanthone, and thioxanthone. In methanol, acridine gave acridone and small amounts of 3-nitro- and 3,7-dinitro-acridone; phenazine gave the mono-*N*-oxide. Oxidation of acridine or acridone in acetic acid at reflux temperature gave 1,3,7-trinitro- and 1,3,7,9-tetranitro-acridone.

CONSIDERABLE interest has been shown recently in the oxidation reactions effected by cerium(IV) salts.[1] The value of the redox couple Ce^{IV}–Ce^{III} is high; thus intermediates formed during the oxidation of organic compounds can rarely be isolated. Further complications arise when a salt such as cerium(IV) ammonium nitrate (CAN) is used. The nitrate group is sometimes found to trap reaction intermediates, giving nitrate esters which often undergo further disproportionation reactions (*e.g.* the isolation of benzyl nitrate and benzaldehyde or 9,10-dihydro-10-oxo-9-anthryl nitrate and anthraquinone in the oxidation of toluene [2] or anthracene [3] with CAN).

We have previously [3] reported the results of the oxidation of anthracene with CAN in methanol, acetonitrile, and acetic acid. It was suggested that the anthracene cation radical initially formed [4] was converted into 9-anthryl nitrate (1) by nitrate radical transfer. Homolytic cleavage of an O–N bond in the nitrate (1) could then give $\cdot NO_2$ and anthrone radical (2). Dimerisation of (2), further oxidation to the corresponding cation, or attack by a nitrate radical accounted for the observed products.



(1)

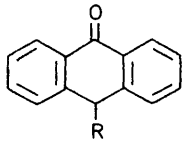


(2)

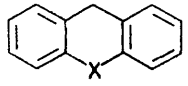
A recent paper [5] reports the oxidation of anthracene and other polynuclear aromatic systems with CAN in aqueous tetrahydrofuran. The products were the corresponding quinones (61% yield for anthraquinone; minor yields for phenanthrenequinones and naphthoquinone). These moderate to poor yields could be due to hydrolysis of some intermediates and polycondensation of the resulting phenoxyl radicals.

We now report the oxidation of some other aromatic compounds with CAN. Oxidation of anthrone (3), xanthen (4), and thioxanthen (5) with 4 mol. equiv. of CAN in methanol yielded, respectively, anthraquinone (80%), xanthone (6) (87%), and thioxanthone (7) (75%). In acetic acid solution anthrone gave anthraquinone (75%) and 10-acetoxyanthrone (8) (8%).

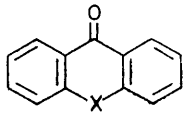
Oxidation of phenazine (9) in methanol gave the mono-*N*-oxide (10) (54%). Compound (9) did not react with CAN in acetic acid at room temperature.



(3) R = H
(8) R = OAc

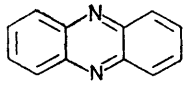


(4) X = O
(5) X = S

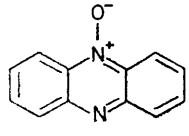


(6) X = O
(7) X = S

The oxidation of acridine (11) in methanol gave acridone (12) (66%) and small amounts (<5%) of 3-nitroacridone (13), 3,7-dinitroacridone (14), and biacridone (17). No reaction was observed at room temperature when acetic acid was the solvent. In acetic acid at reflux temperature 1,3,7-trinitroacridone (15) (16%) and 1,3,7,9-tetranitroacridone (16) (67%) were obtained. The same polynitro-derivatives were isolated in 18 and 71% yield, respectively, from oxidation of acridone (12) with 3 mol. equiv. of CAN in acetic acid at reflux temperature.



(9)

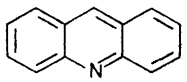


(10)

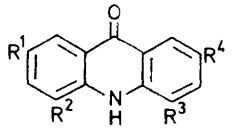
The products derived from anthrone (3), xanthen (4), and thioxanthen (5) are the same as obtained by treatment of these substrates with most other oxidants. In the oxidation with CAN, the carbonyl oxygen atom could be derived from disproportionation of a benzylic nitrate

[1] W. H. Richardson, 'Oxidations in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, vol. 5A, 1965; T. L. Ho, *Synthesis*, 1973, 347.
[2] L. A. Dust and E. W. Gill, *J. Chem. Soc.* (*C*), 1970, 1630.
[3] B. Rindone and C. Scolastico, *J. Chem. Soc.* (*B*), 1971, 2238.
[4] G. A. Russel and N. K. Norris in 'Organic Reactive Intermediates,' ed. S. P. McManus, Academic Press, New York, vol. 26, 1973
[5] T. L. Ho, *Synthesis*, 1973, 206.

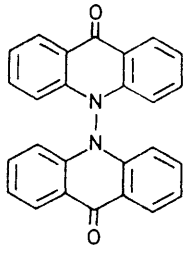
ester formed by attack of CAN on the benzylic position.[2,3] The small amount of 10-acetoxyanthrone formed in the oxidation of anthrone in acetic acid could be derived by solvolysis of the intermediate ester.[6]



(11)

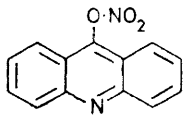


(12) $R^1=R^2=R^3=R^4=H$
(13) $R^1=NO_2, R^2=R^3=R^4=H$
(14) $R^1=R^4=NO_2, R^2=R^3=H$
(15) $R^1=R^2=R^4=NO_2, R^3=H$
(16) $R^1=R^2=R^3=R^4=NO_2$

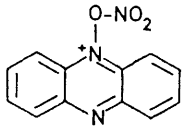


(17)

Nitration products are found in the oxidation of acridine. Here, acridone (12) could be formed *via* the intermediate nitrate ester (18), produced by reaction of acridine cation radical with CAN. Homolytic cleavage of the O–N bond in (18) would give acridone. Recombination of the two fragments from (18) could account for the formation of the small amounts of compounds (13) and (14). A variation of this mechanism could be operating in the case of phenazine. The original cation radical could give rise to the species (19) by attack of a nitrate radical. Heterolysis of this would furnish the *N*-oxide (10).



(18)



(19)

The failure of acridine and phenazine to react with CAN at room temperature in acetic acid solution could be attributed to the combined effect of low solubility of the oxidant and low reactivity of the substrate. Methanol is known to accelerate the oxidation rate of organic substrates with many metal oxidants.

The formation of the polynitro-derivatives (15) and (16) in the high temperature oxidation of both acridine and acridone with CAN could be due to either a heterolytic or a homolytic nitration reaction. A radical nitration reaction could involve thermal homolysis of the O–N bond in analogy with the nitration of anthracene by $CuNO_3$.[7] Alternatively, the nitration could occur *via* a concerted mechanism such as that observed with $Ti(NO_3)_4$[8] and other metal nitrates where the nitrate group behaves as a bidentate ligand.[9] This condition is fulfilled by CAN.[10] The similarity of the reaction yields obtained from acridine and acridone and the number of nitro-groups introduced seem however to indicate that the radical mechanism is operating. The consumption of the oxidant could be attributed to the required production of cation radicals prior to the introduction of the nitro-groups.

EXPERIMENTAL

Microanalyses were performed with a Perkin-Elmer 240 elemental analyser. I.r. spectra were measured with a Perkin-Elmer 257 spectrophotometer for Nujol mulls. M.p.s were determined with a Büchi apparatus. G.l.c. was performed with a Varian 1740 instrument (benzophenone as internal reference) under the following conditions: glass column 6 ft × 0.3 in packed with 1% NPGS on Chromosorb W, oven temp. 150 °C, injection temp. 220 °C, flame ionisation detector temp. 220 °C, carrier gas N_2 at 25 ml min^{-1}. The proportions of products were determined from g.l.c. traces by tracing the curve on paper and weighing the cut-out paper.

Oxidations in Methanol.—To a 0.025M-solution of the substrate in methanol (0.012M for acridine and 0.001M for phenazine), solid CAN (4 mol. equiv.) was added at room temperature with stirring. After consumption of the oxidant, the mixture was evaporated to dryness at reduced pressure and the residue, suspended in water, was extracted with five portions of ethyl acetate. The products from acridine required 24 h extraction in a Soxhlet apparatus. The organic extracts were dried (Na_2SO_2) and evaporated to dryness under reduced pressure. The residue from anthrone was analysed by g.l.c. Anthraquinone was obtained in 80% yield. The residue from phenazine (0.158 g) was chromatographed on silica gel G (Merck) deactivated with 15% water (11 g) [eluant benzene–methanol, 97 : 3 (10 ml fractions)]. Fractions 9—12 contained the *N*-oxide (10) (0.76 g). The residue from acridine (1.86 g) was crystallised from acetic acid to yield acridone (0.83 g). The residue from the mother liquor, dissolved in acetone (60 ml), was chromatographed on silica gel G (Merck; deactivated with 15% water; 70 g), with benzene–methanol (99 : 1) as eluant (300 ml fractions). Fraction 1 gave a mixture (0.2 g) of nitro-derivatives (13) and (14) which was separated by t.l.c. (benzene–methanol, 99 : 1). Fractions 2—13 contained a solid which, after crystallisation from acetic acid, yielded a further 0.5 g of acridone. This compound and biacridone were also present in the mother liquor.

Oxidations in Acetic Acid.—Anthrone was oxidised with CAN (4 mol. equivl) as previously described.[3] The residue from the usual work-up was analysed by g.l.c., and anthraquinone (75%) and 10-acetoxyanthrone (8%) were detected. To a suspension of acridine (2 g) in acetic acid (900 ml), solid CAN (24.5 g) was added. After 14 h at reflux temperature, cooling of the solution gave the tetranitro-derivative (16) (0.75 g). The mother liquor was evaporated to

[6] P. A. S. Smith, 'Open-chain Nitrogen Compounds,' Benjamin, New York, 1966, pp. 483 *et seq.*
[7] C. E. Braun and C. D. Cook, *Org. Synth.*, Coll. Vol. IV, 1963, p. 711.
[8] D. W. Amos, D. A. Baines, and G. W. Flewett, *Tetrahedron Letters*, 1973, 3191.
[9] C. C. Addinson, C. D. Garner, W. B. Simpson, D. Sutton, and S. C. Wallwork, *Proc. Chem. Soc.*, 1964, 367.
[10] T. A. Beineke and J. Delguadio, *Inorg. Chem.*, 1968, **7**, 215.

dryness under reduced pressure; the resulting solid was dissolved in water (400 ml) and extracted with ethyl acetate (7 × 250 ml). The solid thus obtained (3.03 g) was chromatographed on silica gel G (Merck; deactivated with 15% water; 18 g), with benzene–methanol (97 : 3) as eluant (500 ml fractions). Fractions 1—17 contained a further 2.08 g of (16) (total yield 67%); fractions 19—20 contained the trinitro-derivative (15) (0.59 g, 16%). Acridone (0.1 g) suspended in acetic acid (60 ml), was treated with solid CAN (0.84 g) and the resulting suspension was refluxed for 2 days. After work-up as described before, compounds (15) and (16) were obtained in 18 and 71% yield, respectively.

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