# Deoxygenation Reactions of as-Triazine Oxides: Unusual Reactivity of Naphtho[1,2-e][1,2,4]triazin-2(3H)-one 1-Oxides and the Crystal and Molecular Structure of 3-Methylnaphtho[1,2-e][1,2,4]triazin-2(3H)-one 1-Oxide

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The ease of removal of the N-oxide oxygen from a variety of naphtho[1,2,4]triazine N-oxides has been investigated. Naphtho[1,2-e][1,2,4]triazin-2(3H)-one 1-oxide (Ia) and its 3-methyl derivative (Ib), were found to be unusually reactive, being cleanly deoxygenated by boiling 50% aqueous ethanol, and the molecular geometry of (Ib) was unequivocally defined by a crystal-structure analysis. The lability of these compounds is rationalised in terms of a combination of steric and electronic effects.

CONJUGATION between the N-oxide group and the π cloud of an aromatic ring system renders heteroaromatic N-oxides more resistant to deoxygenation than aliphatic or alicyclic N-oxides.[1,2] We have observed [3] that the heterocycle formulated [4] as naphtho[1,2-e][1,2,4]triazin-2(3H)-one 1-oxide (Ia) and its 3-methyl derivative (Ib) are smoothly reduced by boiling 50% (v/v) aqueous ethanol, the products being the triazines (IIa) and (IIb)


(I)   (II)
a; R = H   a; R = H
b; R = Me   b; R = Me
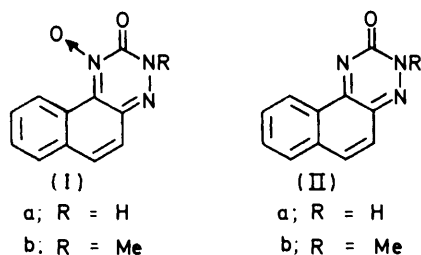
respectively, and acetaldehyde. With the exception of a series of dipolar 2-arylbenzo[1,2,3]triazin-4-one 1-oxides [5] deoxygenation under such mild conditions seems to be unique among heteroaromatic N-oxides and thus appeared to merit further study.

RESULTS AND DISCUSSION

In order to gain insight into the unusual behaviour of (Ia) and (Ib) we have investigated a variety of deoxygenation reactions in the naphtho[1,2,4]triazine oxide series. Besides aqueous ethanol, triazine oxide (Ia) is also cleanly reduced to triazine (IIa) by boiling acetic acid (reported to convert phenazine 5,10-dioxides into the mono-N-oxides [6]), by boiling NN-dimethylformamide and by triphenylphosphine in 5 : 1 (v/v) benzene–dioxan at 100 °C. (Triphenylphosphine is known to be· an efficient reagent for deoxygenation of N-oxides but six-membered aza-aromatic oxides such as pyridine and quinoline 1-oxides require temperatures in excess of 350 °C for reaction.[2]) Loss of oxide oxygen from (Ia)

does not appear to be pyrolytic since no reaction was observed when the oxide was heated to 100° in 5 : 1 benzene–dioxan in the absence of triphenylphosphine, or heated to 100 °C in vacuo in the absence of a solvent. Attempts to induce a Wallach-like reaction [7] in oxide (Ia) were unsuccessful and (Ia) was recovered unchanged after solution in cold 70% sulphuric acid or brief periods of heating under reflux in 40% sulphuric acid.

While triazine oxide (Ib) is fixed in the lactam-like structure (A) it is possible that (Ia) undergoes deoxygen-

(A)   (B)   (C)

(III)   (IV)
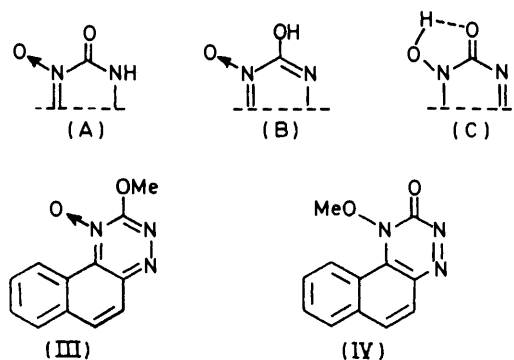
ation in aqueous ethanol via the alternative hydroxy- or hydroxamic acid tautomers (B) or (C). Attempts to prepare the 2-methoxytriazine 1-oxide (III) as a model-compound for the hydroxy-tautomer of (Ia) are summarised in Scheme 1.

The 2-methylthiotriazine 1-oxide (VII) and the 2-methoxytriazine (VIII) were identified by microanalysis and [1]H n.m.r. spectroscopy (see later, Table 2). Base-induced cyclisation of the dithioacylhydrazone (V) yielded, apart from oxide (VII), an unstable red acidic compound which was assigned structure (VI) by analogy with previous results.[4] Although the desired 2-methoxytriazine 1-oxide (III) was not obtained, some of its properties may be inferred from the behaviour of the

[1] A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic N-Oxides,' Academic Press, New York, 1971, p. 168.
[2] L. Horner and H. Hoffmann, Angew. Chem., 1956, **68**, 473; E. Howard, jun., and W. F. Olszewski, J. Amer. Chem. Soc., 1959, **81**, 1483.
[3] F. L. Scott and F. J. Lalor, Tetrahedron Letters, 1964, 641.
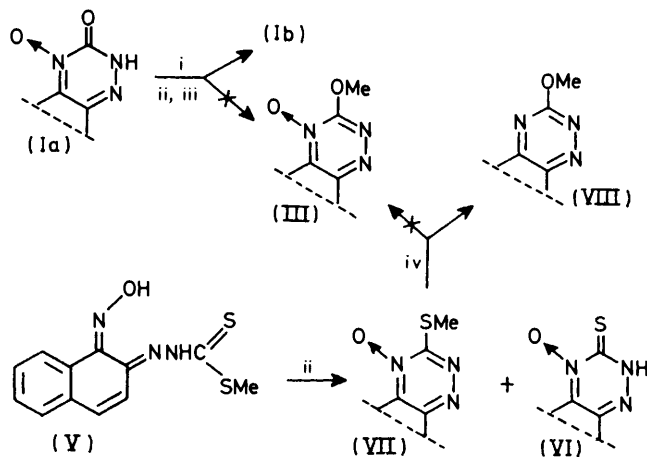[4] F. J. Lalor and F. L. Scott, J. Chem. Soc. (C), 1969, 1034.
[5] R. C. Kerber, J. Org. Chem., 1972, **37**, 1587 and references therein.
[6] D. L. Vivian, J. Org. Chem., 1956, **21**, 1034.
[7] O. Wallach and L. Belli, Ber., 1880, **13**, 525.

2-methylthio-analogue (VII) (see later). Naphthoquinone 1-methoxyimine 2-acylhydrazones, unlike the 1-oximes,[4] do not undergo ring-closure to 1-methoxy-


SCHEME 1

Reagents: i, MeI; ii, OH⁻; iii, dimethyl sulphoxide; iv, MeO⁻

triazines such as (IV) and no satisfactory model compound was found for the hydroxamic acid tautomer of (Ia).

The lability of the N-oxide group in (Ia) and (Ib) was not shared by the 2-methylthio oxide (VII), the 2-amino and 2-anilino oxides (IXa) and (IXb) or by the triazin-3-one 4-oxide (XI) [an isomer of (Ia)]. All four oxides

(IX)
a; R = H
b; R = Ph

(X)
a; R = H
b; R = Ph
c; R = PhCH₂

(XI)

(XII)
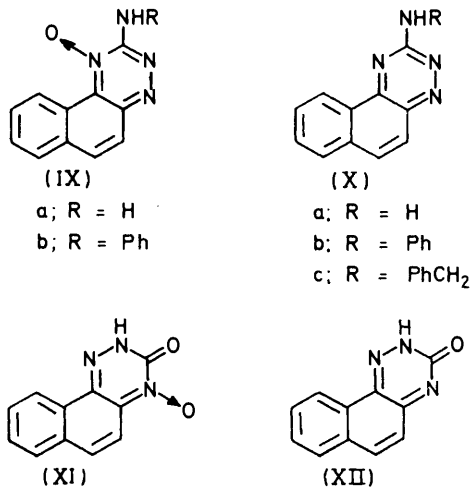
were recovered unchanged after long periods of heating under reflux in 50% aqueous ethanol. Although inert to aqueous ethanol, the oxides (IXa) and (IXb) could be deoxygenated under more forcing conditions. Thus the triazines (Xa) and (Xb) were produced when (IXa) and (IXb) were heated under reflux in aniline or morpholine. Deoxygenation of oxide (IXa) in boiling benzylamine was accompanied by transaminolysis yielding the benzyl-aminotriazine (Xc) which may also be obtained from aminotriazine (Xa) under similar conditions. As postulated previously,[4] oxides (IX) can be cleanly deoxygen-

ated to triazines (X) by hydrogen sulphide in boiling acidified ethanol. Finally, the triazine (XII) which was required for comparison with oxide (XI) was prepared from the latter by an indirect route.

The results described here raise questions as to which of the possible tautomers of (Ia) undergoes deoxygenation in aqueous ethanol and as to the origin of the unusual reactivity of the N-oxide group in (Ia) and (Ib).

Since the low solubility of (Ia) hindered the application of the usual spectroscopic techniques under conditions in which deoxygenation by ethanol takes place, the first question cannot be answered with certainty. There is, however, some indirect evidence. Hydroxy-tautomers of six-membered aza-heterocycles are destabilised by an adjacent ring-nitrogen atom [8] or N-oxide group [9] and thus are unlikely to predominate in solutions of (Ia). The failure of the related 2-methylthio oxide (VII) to

TABLE 1

Electronic absorption spectra of triazines *

	Methanol	Dioxan
(a) Triazinone oxide (Ia)		
	373i (3.56)	372i (3.89)
	387m (4.01)	389m (4.34)
	415m (4.01)	405i (4.1)
	435i (3.52)	435i (2.99)
(b) Triazinone oxide (Ib)		
	372i (4.26)	365i (4.18)
	387m (4.57)	391m (4.94)
	417m (4.47)	412m (4.94)
	437i (3.91)	437i (3.91)
(c) Triazinone (IIa)		
	411i (2.72)	415i (4.74)
	422m (3.87)	430m (3.11)
	448i (1.96)	452i (2.09)
(d) Triazinone (IIb)		
	412i (3.07)	413i (3.43)
	427m (3.54)	430m (4.14)
	446i (2.95)	450i (3.11)

* Wavelengths in millimicrons. Values in parentheses are extinction coefficients $\times 10^{-3}$; i = inflection, m = maximum.

deoxygenate in aqueous ethanol argues against the hydroxy-tautomer being the reactive, though minor, component of the tautomeric equilibrium. The i.r. spectra of (Ia) and (Ib) [ν(CO 1 740 and 1 729 cm⁻¹ respectively, KBr disc or Nujol mull] show no evidence for strong intramolecular (N–OH · · · O=C) hydrogen bonding in (Ia) as would be expected [9] for the hydroxamic acid tautomer which therefore does not predominate in the solid state. Lacking an N-oxide group the latter is unlikely to be the reactive tautomer of (Ia) in solution. Strong similarities between the electronic spectra (methanol or dioxan, Table 1) and ¹H n.m.r. spectra ([²H₆]-dimethyl sulphoxide, Table 2) of triazine oxide (Ia) and triazine (IIa) and the analogous lactams (Ib) and (IIb) favour lactam structures for the former compounds in these solvents. The observation that of the six triazine oxides studied, only (Ia) and the lactam (Ib) are deoxygenated by aqueous ethanol argues in favour of the lactam as the reactive tautomer of (Ia).

[8] A. R. Katritzky, Chem. and Ind., 1965, 331.
[9] Ref. 1, p. 407, and references therein.

The [1]H n.m.r. spectra of triazine oxides (I), (VII), (IXa), and (XI) and of triazines (II), (VIII), (Xa), and (XII) are summarised in Table 2. In all ten compounds, H-10 (see Table 2 for numbering system) resonates at much lower field than the other protons or the naphthalene nucleus,* presumably in consequence of anisotropic deshielding by the closely adjacent C–N structure of the triazine ring. The 1-oxides (I), (VII), and (IXa) show a further deshielding of H-10 (ca. 1.38—1.48 p.p.m. with respect to the triazines) arising from anisotropic deshielding by the N-oxide group. This very large anisotropic deshielding effect indicates steric crowding between the N-oxide structure and H-10 and may be compared with the deshielding of ca. 0.18—0.52 p.p.m. observed [11] in triazine oxides (XIII) in which

X-ray methods. Only crystals of (Ib) were suitable for X-ray analysis. The crystal structure of (Ib) contains discrete well separated molecules with intermolecular

(XIII)
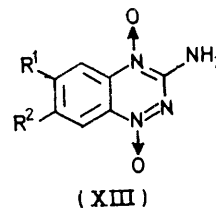
contacts (Table 3) corresponding to van der Waals distances. An ORTEP [12] view of the molecule and the numbering scheme are shown in the Figure along with
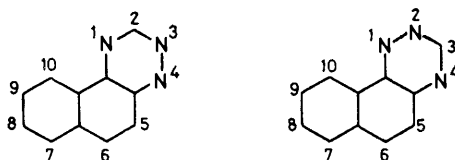
TABLE 2

[1]H Nuclear magnetic resonance spectra [a]

	H-5	H-6	H-7, H-8, H-9	H-10
(Ia)	2.63, d (9.68)	2.33, d (9.68)	2.15, m	−0.16, d (7.5)
(Ib) [b]	2.58, d (9.45)	2.24, d (9.45)	2.06, m	−0.15, d (7.5)
(IIa)	2.57, d (9.35)	2.35, d (9.35)	2.16, m	1.22, d (8.18)
(IIb) [c]	2.66, d (10.2)	2.32, d (10.2)	1.15, m	1.23, d (7.35)
(VII) [d]	←————————2.40—1.80, m————————→			−0.32, m
(VIII) [e]	←————————2.35—1.70, m————————→			1.00, m
(IXa)	←————————2.30—1.60, m————————→			−0.43, m
(Xa)	2.20, d (8.27)	1.93, d (8.27)	2.30, m	1.05, m
(XI)	←————————2.30—1.90, m————————→			1.38, m
(XII)	2.80, d (9.56)	1.84, d (9.56)	2.16, m	1.48, m

[a] Numbering system:

Spectra were determined in [[2]H$_6$]dimethyl sulphoxide and recorded on Varian HA 100 [compounds (1), (II), (IXa), (Xa), (XI), and (XII), 1 000 Hz sideband of [[2]H$_5$]dimethyl sulphoxide reference] or Perkin-Elmer–Hitachi R 20A spectrometers [(VII) and (VIII), internal tetramethylsilane reference]. Resonance positions are τ given in p.p.m. s = singlet, d = doublet, m = multiplet. Values in parentheses are coupling constants. Normally the resonance positions quoted are the centres of gravity of the doublets or multiplets concerned but in the case of very complex multiplets the two limits of the multiplet are given. All spectra gave the correct integration values for the assigned structures. [b] N–CH$_3$ at τ 5.97 (s). [c] N–CH$_3$ at τ 6.05 (s). [d] S–CH$_3$ at τ 7.17 (s). [e] O–CH$_3$ at τ 5.72 (s).

(because of the differing geometry of the ring system) the oxide oxygens and adjacent protons do not approach each other as closely as in the naphthotriazine 1-oxides.

To establish the nature of the steric crowding in (Ia) and (Ib) we examined crystals of these compounds by

* A prominent AB pair of doublets is visible in the spectra of triazines (I), (II), and (Xa). This is assigned to the H-5 and H-6 protons. The lower-field doublet of the AB pair in triazine (IIa) shows some second-order splitting which disappears when the sample is irradiated at the frequency of H-10. By analogy with the quinoline nucleus (in which similar long-range coupling effects have been observed [10]) the low-field doublet is assigned to H-6 and that at higher field to H-5. Triazine oxide (XI) and triazine (XII) are isomers of compounds (Ia) and (Ib) respectively, differing only in the manner in which the 1,2,4-triazine ring is fused to the naphthalene nucleus. A similar but more widely spaced AB pair of doublets may be recognised in the spectrum of the triazine (XII). Introduction of the N-oxide group in (XI) causes the up-field doublet of the pair to move ca. 0.5 p.p.m. to lower field and coalesce with the complex multiplet due to H-7 to H-9. This would be expected on the basis of anisotropic deshielding by the N-oxide group and supports the assignment of this resonance to H-5. A simultaneous but smaller up-field shift of the H-6 resonance is observed.

torsion angle data; other details of molecular geometry are in Table 3.

In the triazine ring the bond-length distribution, which is very similar to that found in 3-methoxy-1-methyl-6-pyridazone,[13] is consistent with a major contribution from canonical form (Ib). The N→O bond length (1.274 Å) is within the usual range for unconjugated nitroxide radicals in, for example, 2,2,6,6-tetramethyl-4-piperidon-1-oxyl nitroxide [1.276(3) Å],[14] di-t-butyl nitroxide 1.28(2) Å,[15] and caryophyllene iodonitrosite 1.31(2) Å.[16] The central carbon ring of the molecule is

[10] F. A. L. Anet, J. Chem. Phys., 1960, 32, 1274.
[11] J. C. Mason and G. Tennant, J. Chem. Soc. (B), 1970, 911.
[12] C. K. Johnson, ORTEP, Technical Report ORNL 3794, 1965, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
[13] T. Ottersen, Acta Chem. Scand., 1974, A28, 666.
[14] D. Bordeaux and J. Lajzerowicz, Acta Cryst., 1974, B30, 790.
[15] B. Andersen and P. Andersen, Acta Chem. Scand., 1966, 20, 2278.
[16] D. M. Hawley, G. Ferguson, and J. M. Robertson, J. Chem. Soc. (B), 1968, 1225.

TABLE 3

Interatomic distances (Å) and valency angles (°) for (Ib), with standard deviations in parentheses

(a) Bond lengths

	Uncorr.	Corr.[a]		Uncorr.	Corr.[a]
N(1)–O(1)	1.267(3)	1.274	C(7)–H(7)	0.94(3)	
N(1)–C(2)	1.448(4)	1.450	C(7)–C(8)	1.380(5)	1.385
N(1)–C(12)	1.354(4)	1.357	C(8)–C(9)	1.381(5)	1.386
C(2)–O(2)	1.206(4)	1.212	C(8)–H(8)	0.95(3)	
C(2)–N(3)	1.361(4)	1.367	C(9)–C(10)	1.371(5)	1.373
N(3)–N(4)	1.338(3)	1.344	C(9)–H(9)	0.95(3)	
N(3)–C(15)	1.470(5)	1.470	C(10)–C(11)	1.412(4)	1.417
N(4)–C(13)	1.320(4)	1.323	C(10)–H(10)	0.95(3)	
C(5)–C(13)	1.439(5)	1.441	C(11)–C(14)	1.421(4)	1.427
C(5)–C(6)	1.328(5)	1.330	C(11)–C(12)	1.452(4)	1.454
C(5)–H(5)	0.99(3)		C(12)–C(13)	1.427(4)	1.432
C(6)–C(14)	1.444(5)	1.445	C(15)–H(15)	0.95(4)	
C(6)–H(6)	0.99(4)		C(15)–H(152)	0.97(5)	
C(7)–C(14)	1.394(5)	1.396	C(15)–H(153)	0.90(5)	

(b) Valency angles

	Uncorr.	Corr.
C(1)–N(1)–C(2)	113.6(2)	113.5
O(1)–N(1)–C(12)	124.7(3)	124.9
C(2)–N(1)–C(12)	121.7(2)	121.6
N(1)–C(2)–N(3)	114.3(3)	114.3
N(1)–C(2)–O(2)	121.2(3)	121.1
N(3)–C(2)–O(2)	124.5(3)	124.6
C(2)–N(3)–N(4)	126.6(3)	126.7
C(2)–N(3)–C(15)	118.3(3)	118.3
N(4)–N(3)–C(15)	115.0(3)	114.9
N(3)–N(4)–C(13)	116.8(2)	116.7
C(6)–C(5)–C(13)	120.6(3)	120.6
C(6)–C(5)–H(5)	127(2)	
C(13)–C(5)–H(5)	113(2)	
C(5)–C(6)–C(14)	121.7(3)	121.7
C(5)–C(6)–H(6)	121(2)	
C(14)–C(6)–H(6)	117(2)	
C(8)–C(7)–C(14)	121.1(3)	121.1
C(8)–C(7)–H(7)	120(2)	
C(14)–C(7)–H(7)	119(2)	
C(7)–C(8)–C(9)	119.9(4)	120.1
C(7)–C(8)–H(8)	118(2)	
C(9)–C(8)–H(8)	122(2)	
C(8)–C(9)–C(10)	120.5(3)	120.4
C(8)–C(9)–H(9)	120(2)	
C(10)–C(9)–H(9)	120(2)	
C(9)–C(10)–C(11)	121.2(3)	121.1
C(9)–C(10)–H(10)	122(2)	
C(11)–C(10)–H(10)	117(2)	
C(10)–C(11)–C(12)	125.1(3)	125.0
C(10)–C(11)–C(14)	118.0(3)	118.1
C(12)–C(11)–C(14)	117.0(2)	116.9
C(11)–C(12)–C(13)	120.4(2)	120.3
C(11)–C(12)–N(1)	123.4(2)	123.3
C(13)–C(12)–N(1)	116.3(3)	116.4
C(12)–C(13)–N(4)	124.1(2)	124.1
C(12)–C(13)–C(5)	119.6(3)	119.6
C(5)–C(13)–N(4)	116.4(3)	116.3
C(6)–C(14)–C(7)	119.9(3)	119.9
C(6)–C(14)–C(11)	120.8(3)	120.9
C(7)–C(14)–C(11)	119.3(3)	119.2
N(3)–C(15)–H(151)	109(3)	
N(3)–C(15)–H(152)	110(2)	
N(3)–C(15)–H(153)	108(3)	
H(151)–C(15)–H(152)	114(4)	
H(151)–C(15)–H(153)	112(4)	
H(152)–C(15)–H(153)	104(4)	

(c) Intermolecular contacts[b] < 3.4 Å

N(1) · · · O(2^I)	3.130(4)		N(4) · · · C(9^{III})	3.351(5)
C(10) · · · O(1^{II})	3.164(4)		C(9) · · · O(1^{II})	3.375(4)
C(12) · · · O(2^I)	3.245(4)		O(1) · · · N(3^I)	3.381(4)
C(2) · · · N(1^I)	3.303(5)		N(4) · · · C(12^{IV})	3.383(4)

[a] Corrected for libration.[22] [b] Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $1 - x$, $-y$, $-z$ III $1 + x$, y, z
II $-x$, $-y$, $-z$ IV $1 - x$, $-y$, $1 - z$

also not delocalised. Thus, the C(5)–C(6) distance (1.330 Å) is clearly that of an isolated double bond and the remaining C–C distances are in the usual range found for single bonds between sp^2 hybridized carbon atoms. The geometry of the remaining carbocyclic ring is that of a normal aromatic system.

The torsion angles (Figure) show that whereas the two carbocyclic rings are effectively planar, the triazine ring is very slightly puckered at the carbonyl region; the N-oxide oxygen is 0.065 below and the carbonyl oxygen 0.099 Å above the ring plane. Steric crowding of the N-oxide bond by the hydrogen at C(10) is mainly relieved by in-plane bond-angle bending; angles C(10)–C(11)–C(12), C(11)–C(12)–N(1), and C(12)–N(1)–O(1) are increased to 125.1, 123.4, and 124.7°, respectively, and there is a concomitant decrease of angle O(1)–N(1)–C(2) to 113.6°. That there is little out-of-plane bending

View normal to the molecular plane of (Ib) showing the crystallographic atom numbering scheme. The numbers beside the bonds should be divided by ten to yield torsion angles (°)

here is shown by the torsion angles C(10)–C(11)–C(12)–N(1) 0.1 and C(11)–C(12)–N(1)–O(1) −1.2°.

Thus, our X-ray study establishes the nature of the steric crowding of the N-oxide (Ib) and the molecular dimensions indicate that delocalisation of N-oxide electrons into the lactam-like heterocyclic ring (and hence conjugative stabilisation of the N-oxide group) is weak or entirely absent.

Two factors may be identified as being responsible for the lability of the N-oxide group in (Ia) and (Ib): steric crowding and lack of resonance stabilisation. That neither steric nor electronic effects alone would be sufficient to produce the observed reactivity is suggested by two observations.

(1) The 2-methylthiotriazine oxide (VII) and the 2-aminotriazine oxides (IX) are all unreactive to boiling 50% aqueous ethanol although this reagent smoothly deoxygenates oxides (Ia) and (Ib). The degree to which H-10 experiences the anisotropic deshielding effect of the N-oxide group in (VII) and (IXa) (Table 2) suggests that steric crowding in (VII), (IXa), and (IXb) must if anything be more severe than in the lactams (I) because of

relayed steric effects arising from the bulkier substituents on C(2). However, in the amino[17] and methylthio N-oxides labilisation due to steric crowding can be offset by the conjugative stabilisation due to the presence of a closed aromatic 1,2,4-triazine system. Hence steric crowding alone cannot account for the reactivity of oxides.

(2) Triazine 4-oxide (XI), isomeric with 1-oxide (Ia), is likely to exist also in a lactam configuration. Hence the two N-oxides will lack conjugative stabilisation of the N-oxide to a similar degree. However, owing to the different geometries of (XI) and (Ia) steric compression of the oxide group will be much less severe in the former and the N-oxide group will therefore be labilised to a lesser extent. Significantly, the 4-oxide (XI) is not deoxygenated by boiling aqueous ethanol. Hence the lack of conjugative stabilisation, in the absence of steric crowding, does not provide sufficient driving force to initiate deoxygenation under the mild conditions described here.

EXPERIMENTAL

Previously known triazines and triazine oxides were prepared as described elsewhere.[4] M.p.s were determined on an Electrothermal apparatus. I.r. spectra were determined on a Perkin-Elmer Infracord spectrophotometer and electronic spectra on a Unicam SP 800 instrument. The 100 MHz n.m.r. spectra were determined by the late R. J. Spratt of the Department of Chemistry, Queen's University, Belfast.

Deoxygenation of Triazinone Oxide (Ia).—(a) *Aqueous ethanol.* The oxide (Ia) (0.6 g) was dissolved in the least volume of 50% aqueous ethanol and the stirred solution gently heated under reflux while being swept with a slow stream of nitrogen which was then bubbled through a solution of 2,4-dinitrophenylhydrazine in aqueous hydrochloric acid. After *ca.* 1 h the yellow solution had developed the deep red-brown colour and green fluorescence characteristic of triazinone (IIa). After 3 h the solution was concentrated *in vacuo* to give triazinone (IIa), orange-brown needles (from aqueous ethanol), m.p. 272—273 °C (80—90%). It was characterised by comparison of m.p., mixed m.p., and i.r. and n.m.r. spectra with those of authentic material.[4] Filtration of the 2,4-dinitrophenylhydrazine solution yielded acetaldehyde 2,4-dinitrophenylhydrazone (0.42 g) 72%, identified by comparison with authentic material.

(b) *Triphenylphosphine.* Triazine oxide (Ia) (0.3 g) and triphenylphosphine (0.3 g) were dissolved in benzene (100 ml) and dioxan (20 ml) and the solution heated under reflux for 12 h. Triazinone (IIa) (0.14 g) separated on cooling. A second crop of slightly less-pure material (0.08 g) was obtained on concentrating the solution *in vacuo*, to give crude (IIa) (85%). In the absence of triphenylphosphine the triazine oxide was recovered quantitatively.

(c) *Other reagents.* When triazinone oxide (Ia) was heated under reflux in glacial acetic acid (40 min) or purified dimethyl formamide (90 min), triazinone (IIa) was isolated in 80 and 85% yields.

Deoxygenation of Triazinone Oxide (Ib) *with Aqueous Ethanol.*—The triazinone oxide (Ib) (2.27 g) was dissolved in the least volume of aqueous ethanol and the solution heated under reflux for 3 h during which acetaldehyde was slowly evolved. Concentration of the deep brown reaction mixture gave 3-*methylnaphtho*[1,2-e][1,2,4]*triazin*-2(3H)-*one* (IIb)

(1.02 g), m.p. 180 °C (91%). After recrystallisation from aqueous ethanol or toluene (activated charcoal) an analytical sample, m.p. 189—190 °C, was obtained (Found: C, 68.0; H, 4.3; N, 19.9. $C_{12}H_9N_3O$ requires C, 68.24; H, 4.29; N, 19.89%).

2-*Methylthionaphtho*[1,2-e][1,2,4]*triazine* 1-*Oxide* (VII).— 1,2-Naphthoquinone 1-oxime (7.9 g) in ethanol was treated with an ethanolic solution of S-methyl dithiocarbazate[18] and concentrated hydrochloric acid (4.0 ml). After *ca.* 4 h the red precipitate of *hydrazone* (V) (6.5 g) was collected by filtration, washed with ether, and dried *in vacuo* (P_2O_5). Attempts to recrystallise (V) resulted in decomposition with evolution of MeSH. The crude solid was dissolved in 20% aqueous potassium carbonate (500 ml) and the red solution heated under reflux for 10 min. The 2-*methylthiotriazine oxide* (VII) precipitated from solution and was recrystallised from toluene (animal charcoal) as yellow needles (2.62 g, 23.6%), m.p. 187—188 °C (Found: C, 59.7; H, 4.25; N, 17.7. $C_{12}H_9N_3OS$ requires C, 59.24; H, 3.73; N, 17.27%).

Acidification of the original reaction mixture yielded an orange-red solid (1.2 g). The n.m.r. spectrum of the crude solid was compatible with that expected for the triazinthione 1-oxide (VI). On attempted purification the presumed (VI) was transformed into a totally insoluble brown substance and further investigation was abandoned.

Reaction of Triazine 1-*Oxide* (VII) *with Methoxide Ion.*— 2-Methylthiotriazine oxide (VII) was suspended in 300 ml anhydrous methanol containing 1 equivalent of potassium and the mixture heated under reflux under nitrogen for 5 h during which time MeSH was evolved. After allowing the solution to cool the volume was reduced *in vacuo* and dilution with water precipitated 2-*methoxytriazine* (VIII) as a yellow solid (0.77 g), m.p. 130—131 °C (Found: C, 67.9; H, 4.25; N, 20.2. $C_{12}H_9N_3O$ requires C, 68.24; H, 4.29; N, 19.89%).

Reaction of Aminotriazines and Aminotriazine Oxides with Amines.—An example of the reaction procedure is described and the results of analogous experiments summarised in Table 4.

TABLE 4

Cpd.	Amine	Reaction time/h	Product	Yield (%)
(IXa)	Morpholine	16	(Xa) [a]	81
(IXa)	Aniline [b]	16	(Xa) [a]	79
(IXb)	Morpholine	16	(Xb) [a]	97
(Xa)	Benzylamine	16	(Xc)	81

[a] Ref. 4. [b] Solvent removed *in vacuo* and residue recrystallised from aqueous ethanol.

Benzylaminolysis of 2-*Aminonaphtho*[1,2-e][1,2,4]-*triazine* 1-*oxide* (IXa). Triazine oxide (IXa) was heated under reflux for 4 h in freshly distilled benzylamine under nitrogen. The cooled solution was diluted with a large volume of water containing a little acetic acid and set aside overnight. The pale yellow solid which separated was washed with water and dried *in vacuo* (H_2SO_4). Analytically pure 2-*benzylaminonaphtho*[1,2-e][1,2,4]*triazine* (Xc) (89%) was obtained as fine golden needles, m.p. 160 °C from aqueous ethanol (activated charcoal) (Found: C, 75.4; H, 5.0; N, 19.5. $C_{18}H_{14}N_4$ requires C, 75.59; H, 4.93; N, 19.56%).

[17] Ref. 1, p. 420, and references therein.
[18] J. Korosi, G. P. 1,934, 809, Jan. 19 (1970); *Chem. Abs.*, 1970, **72**, 100,334.

Naphtho[2,1-e][1,2,4]*triazine*-3(2H)-*one* (XII).—Naphtho-[2,1-*e*][1,2,4]triazine-3(2*H*)-one 4-oxide (XI)[4] (0.23 g) suspended in water (*ca.* 25 ml) was stirred under nitrogen with sodium dithionite (*ca.* 6 equivalents) for 1 h. A voluminous white solid replaced the yellow triazinone oxide and was collected by filtration under nitrogen and rapidly dissolved in hot 95% ethanol. An excess of 5% aqueous iron(II) chloride was then added, the solution poured into a large volume of water, and the collected brown solid re-crystallised from aqueous ethanol (activated charcoal) to yield 0.13 g (70%) of *triazinone* (XII), m.p. 255—256 °C (Found: C, 66.75; H, 3.45; N, 21.5. $C_{11}H_7N_3O$ requires C, 67.00; H, 3.58; N, 21.31%).

Crystal Structure Analysis of (Ib).—Crystals of (Ib) are yellow plates elongated along *c* with {110} well developed. Accurate cell parameters were obtained by a least-squares procedure applied to 12 general reflections measured on a Hilger and Watts diffractometer.

Crystal data. $C_{12}H_9N_3O_2$, $M = 227.2$. Monoclinic, $a = 7.649(1)$, $b = 17.382(3)$, $c = 7.874(1)$ Å, $\beta = 105.29(1)°$, $U = 1\ 009.8$ Å^3, $Z = 4$, $D_c = 1.494$ g cm^{-3}, $F(000) = 472$. Mo-K_α radiation, $\lambda = 0.710\ 69$ Å; μ(Mo-K_α) $= 1.14$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences: $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$.

The intensities of all reflections with 2θ(Mo-K_α) $<50°$ were measured on a PDPS I controlled Hilger and Watts Y 290 four-circle diffractometer fitted with a graphite monochromator in a manner similar to that described previously.[19] Lorentz and polarization factors were applied to the intensity data and the structure amplitudes derived. Of the 1 857 unique data, 990 reflections had $I > 3\sigma(I)$, the remaining 867 data being taken as unobserved and given zero weight in refinement calculations.

The structure was solved in a straightforward manner using the multiple-solution program MULTAN.[20] The *E* map corresponding to the 'best' solution revealed all the non-hydrogen atom positions in the molecule. Refinement proceeded smoothly. Isotropic followed by anisotropic least-squares refinement gave *R* 0.073. At this stage a difference synthesis clearly revealed the positions of all nine hydrogen atoms and no other significant features. Inclusion of the hydrogen atoms in the refinement with isotropic temperature factors gave a final *R* of 0.033 for the 990 observed reflections and 0.063 for all 1 857 reflections. The final weighted R' {$R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$} was

* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1977, Index issue.

[19] See *e.g.* G. Ferguson, *J.C.S. Perkin I*, 1975, 496.

0.041 while the error in an observation of unit weight was 1.22 electrons. The final weighting scheme was that of Hughes [21] with $w = 1.0$ for $F_o < 13.0$ and $w = (13.0/F_o)^2$ for $F_o > 13.0$. The relative validity of the weighting scheme, as judged by the variation of $w(|F_o| - |F_c|)^2$ over ranges of $|F_o|$ and sin θ/λ, was satisfactory. Details of bond lengths and angles, corrected for libration [22] are in Table 3. Atomic co-ordinates are in Table 5. Anisotropic thermal

TABLE 5

Final fractional co-ordinates (C, N, O $\times$ 10^4; H $\times$ 10^3) for (Ib), with estimated standard deviations in parentheses

Atom	x	y	z
O(1)	2 299(3)	$-247(1)$	952(3)
O(2)	5 105(3)	$-1\ 054(1)$	845(3)
N(1)	3 813(4)	$-18(1)$	1 908(3)
C(2)	5 319(5)	$-507(2)$	1 820(4)
N(3)	6 938(4)	$-293(1)$	2 915(3)
N(4)	7 260(3)	333(1)	3 941(3)
C(5)	6 239(5)	1 470(2)	4 965(5)
C(6)	4 922(5)	1 964(2)	4 991(5)
C(7)	1 726(5)	2 357(2)	4 078(5)
C(8)	$-52(5)$	2 244(2)	3 140(5)
C(9)	$-517(5)$	1 603(2)	2 080(5)
C(10)	773(4)	1 071(2)	1 970(4)
C(11)	2 603(4)	1 165(2)	2 920(4)
C(12)	4 060(4)	635(2)	2 881(4)
C(13)	5 865(4)	785(2)	3 904(4)
C(14)	3 075(4)	1 832(2)	3 987(4)
C(15)	8 546(6)	$-759(2)$	2 930(6)
H(5)	753(5)	151(2)	563(5)
H(6)	516(5)	243(2)	571(5)
H(7)	204(5)	281(2)	474(5)
H(8)	$-91(5)$	262(2)	323(5)
H(9)	$-173(5)$	153(2)	141(4)
H(10)	50(4)	63(2)	123(4)
H(151)	949(7)	$-63(3)$	394(6)
H(152)	887(5)	$-70(2)$	182(5)
H(153)	823(6)	$-126(3)$	295(6)

parameters, analysis of thermal vibration, and final values of measured and calculated structure factors have been deposited as Supplementary Publication No. SUP 22231 (16 pp., 1 microfiche).*

[20] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.
[21] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.
[22] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 747; 1961, **14**, 896.