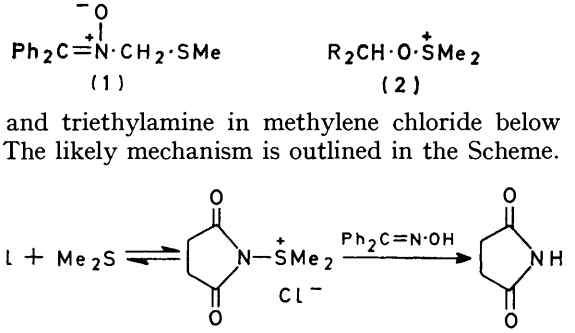
Preparation of Sulphur-containing Nitrones from Sulphides. Thermal Elimination Reactions of Nitrones

By **Wynford M. Leyshon** and **David A. Wilson,*** University College, Cathays Park, Cardiff CF1 1XL

The Corey method for oxidation of alcohols, by using *N*-chlorosuccinimide and a sulphide, has been adapted to prepare, from benzophenone oxime, nitrones bearing cyclic or acyclic alkylthioalkyl groups on nitrogen. Nitrones have been prepared from dimethyl sulphide, diethyl sulphide, ethyl methyl sulphide, benzyl methyl sulphide, thiolan, thiacyclohexane, and 1,4-oxathian. Several sulphides fail to react in this reaction, and reasons are advanced for this. When heated, those nitrones having a β-hydrogen atom on the *N*-substituent undergo a thermal elimination reaction to form oxime and olefin. Approximate rates of elimination at 111 °C for cyclopentyl, cyclohexyl, thiolan-2-yl, and thiacyclohexan-2-yl nitrones are compared. The cyclopentyl and cyclohexyl nitrones were obtained by thermal ring opening of the isomeric oxaziridines.

WE have previously used an adaptation of the Moffatt procedure for oxidation [1] of alcohols to prepare the nitrone (1) and derivatives of it from benzophenone oxime and dimethyl sulphoxide.[2] Since both the Moffatt oxidation and the recently developed oxidation method of Corey [3] are thought to proceed by way of the same, or very closely related, intermediates [*e.g.* (2)], it was expected that when the Corey method was applied to oximes rather than to alcohols, nitrones would be formed. This expectation was realised first for the nitrone (1) by using *N*-chlorosuccinimide, dimethyl sulphide, and triethylamine in methylene chloride below 0 °C. The likely mechanism is outlined in the Scheme.



SCHEME

The conversion of the intermediate (3) into the nitrone (1) has been discussed.[2]

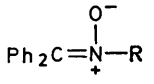
This new method has advantages over that based on the Moffatt oxidation (use of dicyclohexylcarbodi-imide and dimethyl sulphoxide). Sulphides are usually more readily available than sulphoxides, and a cleaner product is obtained with easier work-up, although careful control of reaction temperature is required to avoid the dialkyl(succinimido)sulphonium chloride reacting by alternative paths to form chloro-sulphides and *N*-alkylated succinimides.[4] This sulphide method also succeeds [5] with 4,4′-dimethoxybenzophenone oxime, whereas the sulphoxide method merely resulted in Beckmann rearrangement to 4,4′-dimethoxybenzanilide.[2]

By using this sulphide method, the parent methylthiomethyl nitrone (1) was obtained in 57% yield. When triethylamine was left out, benzanilide was formed in high yield, a result consistent with the Scheme.[2] Diethyl sulphide gave the nitrone (4a), and the cyclic sulphides thiolan, thiacyclohexane, and 1,4-oxathian gave the nitrones (4b—d), respectively. One attempted preparation of the nitrone (4b) gave instead a high yield of the corresponding *O*-substituted oxime (5); this result was attributed to acidic impurities in a reagent.[6] Ethyl methyl sulphide gave a mixture of the nitrones (4e and f) which could not be separated, but the n.m.r. spectrum clearly indicated a 1 : 5 ratio of products. Similarly, benzyl methyl sulphide gave a 2 : 1 mixture of the nitrones (4g and h) and some *N*-alkylated succinimide (6).

These successes with symmetrical sulphides indicated the generality of the reaction, and the products found from the unsymmetrical sulphides were in accord with

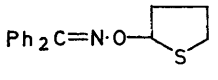
[1] J. G. Moffatt, 'Oxidation,' eds. R. L. Augustine and D. J. Trecker, Dekker, New York, 1971, vol. II, p. 1.
[2] D. A. Kerr and D. A. Wilson, *J. Chem. Soc.* (*C*), 1970, 1718.
[3] E. J. Corey and C. U. Kim, *J. Amer. Chem. Soc.*, 1972, **94**, 7586.
[4] H. Kise, G. F. Whitfield, and D. Swern, *Tetrahedron Letters*, 1971, 4839; E. Vilsmaier and W. Sprugel, *Annalen*, 1971, **747**, 151.
[5] J. R. M. Dales, unpublished results.
[6] I. W. Jones, D. A. Kerr, and D. A. Wilson, *J. Chem. Soc.* (*C*), 1971, 2591.

mechanistic considerations. It would be expected, on electronic grounds, that an intermediate (7) would preferentially lose a proton from the methyl group rather than



(4)

a; R = CHMe·SEt
b; R = CH·S·CH$_2$·CH$_2$·CH$_2$
c; R = CH·S·[CH$_2$]$_3$·CH$_2$
d; R = CH·S·CH$_2$·CH$_2$·O·CH$_2$
e; R = CHMe·SMe
f; R = CH$_2$·SEt
g; R = CHPh·SMe
h; R = CH$_2$·S·CH$_2$Ph



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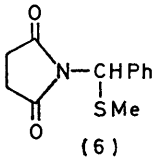
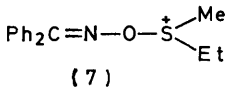


(6)

the methylene group, to form an ylide. The intermediate (8) would, on electronic grounds, be expected to lose a benzylic proton leading to the nitrone (4g) much more readily than a methyl proton, leading to the nitrone (4h). The similar yields of these two nitrones may reflect a steric effect of the phenyl group.



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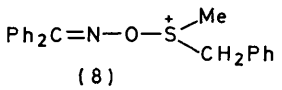
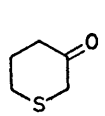
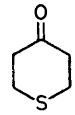


(8)

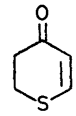
A number of sulphides, under the same reaction conditions, did not give nitrones. Both thiiran and 3,3-dimethylthietan gave complex products, but not nitrones. Thiirans are known to give ring-opened products with chlorine and with dimethylamine.[7] Thietan itself reacts with *N*-chlorosuccinimide to give *N*-(3-chloropropylthio)-succinimide.[8] Dibenzyl sulphide gave no nitrone product, suggesting that the phenyl ring may produce sufficient steric hindrance to inhibit reaction at a benzylic position, as the benzyl methyl sulphide result had indicated. Methyl phenyl sulphide also did not react, and here the reduced nucleophilicity of the sulphur atom may have been the cause. A similar explanation may account for the failure of thiacyclohexan-3-one (9) [9] to react. A transannular interaction [10] between the sulphur and the carbonyl group would make the sulphur less nucleophilic. Thiacyclohexan-4-one (10) [11] also gave no nitrone, but instead of starting material being recovered, as had been the case with the sulphides just mentioned, a product considered to be thiacyclohex-2-en-4-one (11) was obtained.* This dehydrogenation reaction occurred when the ketone (10) was treated only with *N*-chlorosuccinimide in methylene chloride at 0 °C. The effect of the carbonyl group in making the C-3 proton more acidic must account for this result.



(9)



(10)



(11)

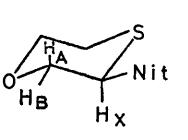
Spectroscopic characterisation of the nitrones (4a—h) was unexceptional. All showed the characteristic u.v. maxima at *ca.* 240 and 305 nm, and the characteristic low-field multiplet in the n.m.r. spectra due to the *ortho*-protons on the phenyl ring *cis* to the nitrone oxygen.[2] The oxathianyl nitrone (4d) gave n.m.r. spectra of particular interest. The aliphatic ring protons on C-2 and C-3 gave very well resolved ABX spectra in several solvents. If we regard the nitrone group (Nit) as the substituent, the heterocyclic ring would be expected to exist in two chair conformations (12a and b). The results for this ABX system are given in Table 1. Havinga *et al.* [12] have presented evidence for *trans*-2,3-dichloro-1,4-oxathian (13) having a fixed chair conformation in solution.

TABLE 1

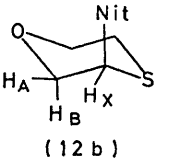
N.m.r. chemical shifts and coupling constants (Hz) for the nitrone (4d)

Solvent	τ_X	τ_B	τ_A	J_{AB}	J_{AX}(*trans*)	J_{BX}(*cis*)
C_6D_6	4.98	5.54	6.10	11.8	5.8	3.4
CCl_4	5.17	5.57	6.07	12.0	5.9	3.5
$CDCl_3$	4.96	5.61	5.89	12.1	5.4	3.4
$(CD_3)_2CO$	4.95	5.74	5.92	11.8	5.9	3.4
C_5H_5N	4.69	5.36	5.74	12.0	5.7	3.2
$(CD_3)_2SO$	5.05	5.79	5.91	11.7	6.3	3.3
CD_3OD	4.95	5.65	5.93	12.4	4.8	3.8

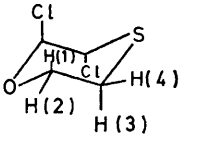
The coupling constants deduced, of relevance to the nitrone (4d), are $J_{1,2}$ 12.0, $J_{1,3}$ 12.4, $J_{1,4}$ (J_{ae} *anti* to O) 2.3, $J_{2,4}$ (J_{ee} *anti* to S and O) 2.0, and $J_{2,3}$ (J_{ae} *anti* to S) 3.4 Hz. With these constants, J_{AX} (J_{trans}) was used to calculate the conformer equilibrium. J_{AX} is more sensitive



(12a)



(12b)



(13)

to this equilibrium than is J_{BX}, and it involves no coupling paths with protons *anti* to the nitrone group, thus minimising any difference between coupling constants for compounds (12) and (13). The oxathianyl nitrone (4d) is calculated to exist with about 40% equatorial nitrone group (12a) in hexadeuteriodimethyl sulphoxide, and about 27% equatorial group in tetradeuteriomethanol. This conformer equilibrium, being the result of a balance between the preference for a polar group α to sulphur to

* Characterised by spectroscopic methods only.

[7] D. D. Reynolds and D. L. Fields, 'Heterocyclic Compounds with Three- and Four-membered Rings,' ed. A. Weissberger, Interscience–Wiley, New York, 1964, part I, p. 576.

[8] D. L. Tulleen and R. H. Bennett, *J. Heterocyclic Chem.*, 1969, **6**, 115.

[9] T. E. Young and L. H. Heitz, *J. Org. Chem.*, 1973, **38**, 1562.

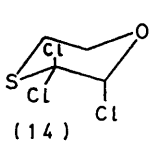
[10] S. Ikegami, T. Asai, K. Tsuneoka, S. Matsumura, and S. Akaboshi, *Tetrahedron*, 1974, **30**, 2087.

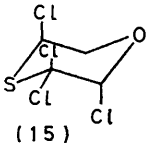
[11] P. Y. Johnson and G. A. Berchtold, *J. Org. Chem.*, 1970, **35**, 584.

[12] N. de Wolf, P. W. Henniger, and E. Havinga, *Rec. Trav. chim.*, 1967, **86**, 1227.

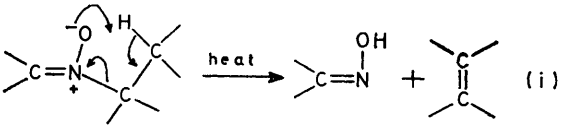
take an axial position [12,13] and the normal steric preference for an equatorial position, is thus moderately sensitive to solvent.

This analysis of conformational mobility can also be applied to the results of Havinga *et al.*[12] for 2,3,3-trichloro- and 2,3,3,5-tetrachloro-1,4-oxathian, and leads to the result that the former has about 80% of conformer (14) and the latter about 60% of conformer (15) in carbon tetrachloride solution. This seems a reasonable interpretation; Havinga *et al.* suggested fixed conformations and anomalous vicinal coupling constants and dipole moments.


(14)


(15)

We have previously discussed in detail the mass spectra of the nitrone (1) and related compounds.[14] The nitrones (4a—h) all gave mass spectra interpretable in terms of the fragmentations previously proposed, and are not recorded here.[15] An additional fragment, *m/e* 197, was


(i)

observed for the nitrones (4a—d) due to the benzophenone oxime molecular ion, formed by an elimination reaction.

Recently, several papers [16] have drawn attention to the cyclic thermal elimination reaction (i) of nitrones, analogous to the Cope elimination of amine oxides. We have previously studied the thermal reactions of the nitrone (1), where such an elimination is not possible,[17] and so it was of interest to observe the thermal behaviour of the sulphur-containing nitrones prepared in this work.

It was first demonstrated qualitatively that the nitrones (4a—d) did indeed react thermally in hexadeuteriobenzene in sealed tubes to give benzophenone oxime and the olefins ethyl vinyl sulphide, Δ^2-thiolen, thiacyclohex-2-ene, and 2,3-dihydro-1,4-oxathiin, respectively. The nitrone (4a) also gave the rearranged *O*-substituted oxime (19), and the nitrone (4d) also gave a third product, which has not yet been identified. The first three olefins were compared with authentic samples prepared by the general method (ii); [18] the dihydro-oxathiin was prepared by dehydrochlorination of 3-chloro-1,4-oxathian.[19] It became clear that quantitative information might be obtained about these elimination reactions, and for comparison the carbocyclic analogues were made.

The imines (16) [20] were oxidised with *meta*-chloroperbenzoic acid to yield the oxaziridines (17). When these were heated in deuteriobenzene in sealed n.m.r. tubes, the expected isomerisation–elimination sequence (iii) was observed. The composition of the reaction mixture at any time could be found from the n.m.r. spectrum. The amount of oxime was assumed to equal that of olefin, and the lowest-field signals of the nitrone (see above) allowed estimation of that intermediate. The unchanged oxaziridine was then determined by difference from signals in the aromatic and aliphatic regions. In hexadeuteriobenzene, benzophenone oxime and the oxaziridines all showed signals for two aryl protons at τ *ca.* 2.3, two aryl protons at τ *ca.* 2.5, and six aryl protons at τ *ca.* 2.9. Each lower-field group was attributed to *ortho*-protons on one of the non-equivalent phenyl rings. Inversion at the nitrogen of oxaziridines is slow at normal n.m.r. probe temperatures.[21]

Also, the nitrones (18) were isolated from incomplete reactions and characterised, and their rates of elimination were determined in separate experiments. This was particularly necessary for the case (17a) ⟶ (18a) ⟶ cyclopentene because that sequence represented an example, not common in organic chemistry, of two consecutive unimolecular reactions of very similar rate constants.[22] The observed rate constants are given in

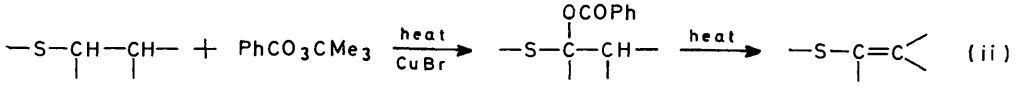
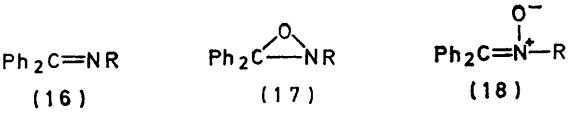
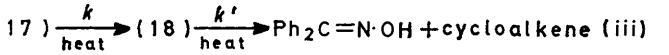

(ii)

Table 2. The accuracy of these determinations is not high because integration of multiplets was involved, and


(16) (17) (18)

a; R = cyclopentyl
b; R = cyclohexyl

in the case of nitrone (18b), some decomposition to benzophenone was observed during the weeks that were required for this measurement. The rates of isomerisation (17) ⟶ (18) are similar to those recorded in the


(iii)

literature; the rates of elimination are discussed below in comparison with the sulphur-containing nitrones.

[13] H. T. Kalff and E. Havinga, *Rec. Trav. chim.*, 1962, **81**, 282; 1966, **85**, 637.
[14] W. M. Leyshon and D. A. Wilson, *Org. Mass Spectrometry*, 1973, **7**, 251.
[15] W. M. Leyshon (Ph.D. Thesis, University of Wales, 1974) records these results.
[16] D. R. Boyd, *Tetrahedron Letters*, 1973, 3467; K. Sommermeyer, W. Seiffert, and W. Wilker, *ibid*, 1974, 1821; M. H. Goodrow, J. A. Villarreal, and E. J. Grubbs, *J. Org. Chem.*, 1974, **39**, 3447.
[17] I. W. Jones, D. A. Kerr, and D. A. Wilson, *J. Chem. Soc.* (*C*), 1971, 2595.
[18] G. Sosnovsky, *Tetrahedron*, 1962, **18**, 903.
[19] A. H. Haubein, *J. Amer. Chem. Soc.*, 1959, **81**, 144.
[20] A. Lawson and J. O. Stevens, *J. Chem. Soc.* (*C*), 1968, 1514.
[21] J. Bjørgo and D. R. Boyd, *J.C.S. Perkin II*, 1973, 1575.
[22] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 2nd edn., 1961, p. 166.

TABLE 2

Rate constants (±20%) for isomerisations (17) ⟶ (18) and eliminations (18) ⟶ cycloalkene, at 111 C°

		k/s^{-1}	
Isomerisation	(17a)	2×10^{-6}	C_6D_6
	(17b)	3.5×10^{-6}	
Elimination	(18a)	1×10^{-6}	
	(18b)	3×10^{-8}	
Isomerisation	$Ph_2C(O)NMe$	1.8×10^{-6}	in $HCl_2 \cdot CHCl_2$ [a]
	$PhCH \cdot C(O) \cdot N \cdot CMe_3$	1.7×10^{-4}	in 3,6,9-trioxaundecane [b]

[a] F. Montantiri, I. Moretti, and G. Torre, *Chem. Comm.*, 1969, 1086. [b] M. F. Hawthorne and R. D. Strahm, *J. Org. Chem.*, 1957, **22**, 1263.

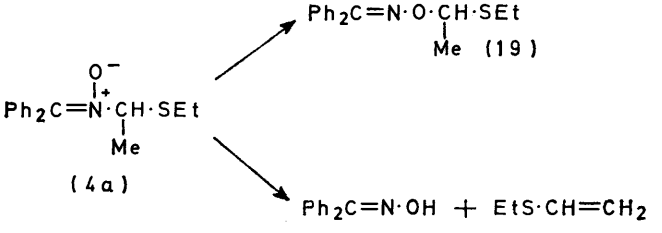
The rates of elimination of nitrones (4a—c) were then measured for solutions in hexadeuteriobenzene at 111 °C by n.m.r. and are given in Table 3. Again the accuracy

TABLE 3

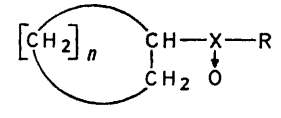
Rate contants (±20%) for elimination from nitrones (4a—c) at 111 °C in C_6D_6

	(4a)	(4b)	(4c)
k/s^{-1}	4.5×10^{-5}	4.5×10^{-4}	2.0×10^{-4}

is not high when integration methods are used. The thiolanyl and thiacyclohexyl nitrones (4b and c) underwent elimination cleanly, whereas the ethylthioethyl nitrone (4a) gave two parallel first-order reactions, elimination and isomerisation to the *O*-substituted (19) oxime.



The ratio of elimination to isomerisation was constant at 3:2 throughout the reaction. Because the elimination was slow compared with those of the cyclic compounds, the competing isomerisation was observed. It is also clear that any corresponding isomerisation of the carbocyclic nitrones (18) would be much slower, because the radical intermediates [23] from the sulphur-containing nitrones are stabilised to some extent by the presence of sulphur [see (iv)]. The oxathianyl nitrone (4d) did



(20) a; R = Me_2, X = N
b; R = Ph, X = S

undergo elimination, but the reaction was not cleanly first-order, and an unidentified third product was formed, which is being investigated.

[23] J. S. Vincent and E. J. Grubb, *J. Amer. Chem. Soc.*, 1969, **91**, 2022.

With these results available, it is instructive to compare the relative rates of *syn* β-eliminations involving five-membered cyclic transition states from five- and six-membered cyclic compounds. The results obtained in this work, together with two from the literature, are summarised in Table 4. It is generally accepted [24] that *syn*-elimination from cyclopentyl systems is faster than from cyclohexyl systems because in the former the reacting groups are nearly eclipsed in the ground state, whereas in the latter the cyclohexyl ring needs considerable distortion to achieve near coplanarity of the reacting groups. Also, ground state steric interaction between the X(O)R group and the rest of the molecule, which is

TABLE 4

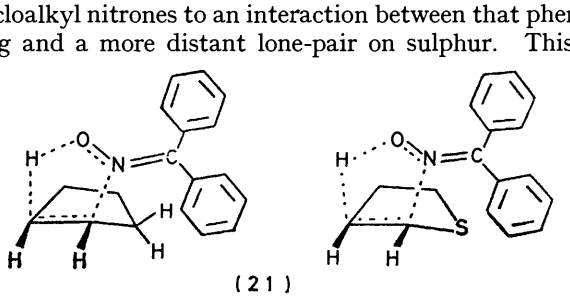
Cyclic β-eliminations from five- and six-membered cyclic compounds

Reactants	Temp. (°C)	Solvent	Ratio 5-membered ring / 6-membered ring
(20a; n = 3 and 4)	70.6	Bu^tOH	400 [a]
(20b; n = 3 and 4)	129.6	$O(CH_2 \cdot CH_2 \cdot OMe)_2$	25 [b]
(18a and b)	111	C_6D_6	*ca.* 33
(4b and c)	111	C_6D_6	*ca.* 2

[a] Ref. 24. [b] J. L. Kice and J. D. Campbell, *J. Org. Chem.*, 1967, **32**, 1631.

relieved as reaction proceeds, will be greater for the cyclopentyl than for the cyclohexyl compounds. This factor may contribute to the large rate ratio seen with cycloalkyldimethylamine oxides in t-butyl alcohol.[24]

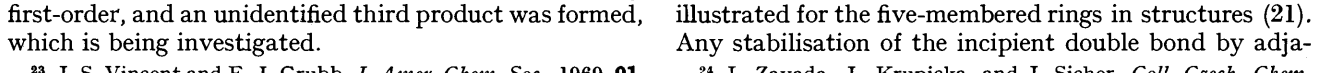
Elimination from the thiolanyl nitrone (4b) is *ca.* 450 times faster than from the cyclopentyl nitrone (18a) ($\Delta\Delta G^{\ddagger}$ 4.7 kcal mol^{-1}), and elimination from the thiacyclohexyl nitrone (4c) is *ca.* 6 700 times faster than from the cyclohexyl nitrone (18b) ($\Delta\Delta G^{\ddagger}$ 6.7 kcal mol^{-1}). This rate-enhancing effect of sulphur may be due to a composite of several factors. The introduction of the polar C–S bond would raise the ground state energies of the nitrones (4b and c), whilst the longer C–S bonds may allow easier accommodation of the developing double bond. Of greater effect than these may well be the change of steric interaction in the transition state between one phenyl ring of the nitrone group and an adjacent hydrogen of the cycloalkyl nitrones to an interaction between that phenyl ring and a more distant lone-pair on sulphur. This is



(21)

illustrated for the five-membered rings in structures (21). Any stabilisation of the incipient double bond by adja-

[24] J. Zavada, J. Krupicka, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1966, **31**, 4273.



cent sulphur is likely to be small.[25] The thiacyclohexyl case (4c) may be exceptionally fast owing also to a lower energy barrier to the conformational change necessary for reaction. It is reported[26] that thiacyclohexane itself has a barrier to ring inversion lower than cyclohexane by about 1.5 kcal mol^{-1}.

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls or liquid films, and u.v. spectra for ethanolic solutions. N.m.r. spectra were recorded at 100 MHz for solutions in deuteriochloroform, unless otherwise stated. In this solvent, all the nitrones showed signals for 8 aryl protons at τ 2.6—2.8, and 2 aryl protons as a multiplet at τ 2.0. Light petroleum had b.p. 60—80°.

General Method for Preparing Nitrones.—N-(*Diphenylmethylene*)*methylthiomethylamine* N-*Oxide* [*Nitrone* (1)].—To *N*-chlorosuccinimide (14.3 g) in dry methylene chloride (200 ml), kept below 0 °C, was added dimethyl sulphide (15 ml). The mixture was cooled to −25 °C and benzophenone oxime (19.7 g) in methylene chloride (50 ml) was added, followed at once by redistilled triethylamine (20 ml). The mixture was kept at 0 °C for 48 h, and was then poured into brine. Ether (50 ml) was added, the organic layer was separated, and the aqueous layer was extracted with ether (2 × 100 ml). The combined organic solutions were washed with water (2 × 100 ml) and dried ($MgSO_4$). Removal of the solvent and crystallisation of the residue from chloroform–light petroleum gave the nitrone (1) (13.8 g, 57%), m.p. 91—92°, identical with that prepared previously.[2]

N-(*Diphenylmethylene*)-1-*ethylthioethylamine* N-*Oxide* [*Nitrone* (4a)].—The above method, with diethyl sulphide, gave the *nitrone* (4a) (48%), m.p. 74—76° (from ether), $\lambda_{max.}$ 239 (ε 12,500) and 304 nm (13 500), $\nu_{max.}$ 1 510 and 1 160 cm^{-1}, τ 8.87 (t, *J* 8 Hz, CH_3), 8.25 (d, *J* 7 Hz, CH_3), 7.32 (q, SCH_2), and 4.63 (q, SCH), *m/e* 285 (M^+, 1%) and 89 ($C_4H_9S^+$, 100%) (Found: C, 71.5; H, 6.8; N, 4.9. $C_{17}H_{19}NOS$ requires C, 71.6: H, 6.7; N, 4.8%).

N-(*Diphenylmethylene*)*thiolan*-2-*ylamine* N-*Oxide* [*Nitrone* (4b)].—With tetrahydrothiophen the general method gave the *nitrone* (4b) (70%), m.p. 110—112° (from ether–carbon tetrachloride), $\lambda_{max.}$ 239 (ε 12 500) and 304 nm (13 500), $\nu_{max.}$ 1 510, 1 220, and 1 210 cm^{-1}, τ 8.0 (m, 4-H_2), 7.3 (m, 5-H and 3-H_2), 6.7 (m, 5-H), and 4.25 (dd, *J* 3 and 2 Hz, 2-H), *m/e* 283 (M^+, 2%) and 87 ($C_4H_7S^+$, 100%) (Found: C, 71.9; H, 6.0; N, 4.9. $C_{17}H_{17}NOS$ requires C, 72.1; H, 6.0; N, 4.7%).

Benzophenone O-Thiolan-2-*yloxime* (5).—One particular reaction, when undistilled methylene chloride and a reaction time of 3 days were used, with tetrahydrothiophen, gave the O-*substituted oxime* (5) (65%), m.p. 95—97° (from ether), $\lambda_{max.}$ 233 (ε 14 500) and 264 nm (10 500), $\nu_{max.}$ 1 230, 1 140, 1 080, 1 050, 980, and 960 cm^{-1}, τ 8.15—7.0 (m, 6 aliphatic H), 3.9 (m, thiolan 2-H), and *ca.* 2.7 (m, 10 aryl H), *m/e* 283 (M^+, 5%) and 87 ($C_4H_7S^+$, 100%) (Found: C, 72.0; H, 5.9; N, 4.9%).

N-(*Diphenylmethylene*)*thiacyclohexan*-2-*ylamine* N-*Oxide* [*Nitrone* (4c)].—Thiacyclohexane, by the general procedure, gave the *nitrone* (4c) (50%), m.p. 112—114° (from ether–carbon tetrachloride), $\lambda_{max.}$ 238 (ε 12 500) and 304 nm (13 700), $\nu_{max.}$ 1 520, 1 255, and 1 220 cm^{-1}, τ 8.25—7.35 (m, 7 aliphatic H), 6.7 (m, 6-H), and 4.87 (t, 2-H), *m/e* 297 (M^+, 2%) and 101 ($C_5H_9S^+$, 100%) (Found: C, 73.0; H, 6.3; N, 4.5. $C_{18}H_{19}NOS$ requires C, 72.7; H, 6.4; N, 4.7%).

N-(*Diphenylmethylene*)-1,4-*oxathian*-3-*ylamine* N-*Oxide* [*Nitrone* (4d)].—1,4-Oxathian by the general procedure gave the *nitrone* (4d) (35%), m.p. 118—120° (from ether–chloroform), $\lambda_{max.}$ 236 (ε 12 500) and 306 nm (13 500), $\nu_{max.}$ 1 515, 1 340, 1 280, 1 100, 1 000, and 960 cm^{-1}, τ (CCl_4) 7.45 (m, 5-H), 6.70 (m, 5-H), and 6.1 (m, 6-H_2) (see Table 1 for remaining n.m.r.), *m/e* 299 (M^+, 5%) and 103 ($C_4H_7SO^+$ 100%) (Found: C, 68.0; H, 5.8; N, 5.0. $C_{17}H_{17}NO_2S$ requires C, 68.3; H, 5.7; N, 4.7%).

Reaction of Ethyl Methyl Sulphide.—The general reaction described above, with this sulphide, afforded a gum which, after chromatography on silica gel, contained the two nitrones (4e and f) in the ratio 1 : 5. Separation was not achieved by column or high pressure liquid chromatography. *N*-(Diphenylmethylene)ethylthiomethylamine *N*-oxide (4f) had τ 8.70 (t, *J* 7 Hz, CH_3), 6.94 (q, CH_2), and 5.14 (s, CH_2); *N*-(diphenylmethylene)-1-methylthioethylamine *N*-oxide (4e) had τ 8.26 (t, *J* 7 Hz, CH_3), 7.78 (s, SCH_3), and 4.70 (q, SCH).

Reaction of Benzyl Methyl Sulphide.—The general reaction with this sulphide gave a gum that contained the isomeric nitrones (4g and h) in a 2 : 1 ratio, and an alkylated succinimide. *N*-(Diphenylmethylene)methylthiobenzylamine *N*-oxide (4g) had τ 7.84 (s, SCH_3) and 3.78 (s, CHPh), and *N*-(diphenylmethylene)benzylthiomethylamine *N*-oxide (4h) had τ 5.76 (s, CH_2Ph) and 5.30 (s, NCH_2S). Chromatography on silica gel gave a sample of the nitrone (4h) which was slowly hydrolysed to benzophenone, and a sample of N-(*methylthio*)*benzylsuccinimide* (6), m.p. 61—63° (from ether), $\lambda_{max.}$ 302 nm, $\nu_{max.}$ 1 710 and 1 170 cm^{-1}, τ 7.87 (s, SCH_3), 7.35 (s, CH_2CH_2), 3.80 (s, NCH), 2.7 (m, 3 aryl H), and 2.4 (m, 2 aryl H), *m/e* 235 (M^+, 22%) and 188 ($C_{11}H_{10}NO_2$, 100%) (Found: C, 60.9; H, 5.6; N, 5.8. $C_{12}H_{13}NO_2S$ requires C, 61.2; H, 5.5; N, 6.0%).

Reaction of Thiacyclohexan-4-*one* (10).—The general reaction procedure afforded an oil, $\lambda_{max.}$ 307 nm, that did not contain any nitrone. Chromatography afforded a sample of thiacyclohex-2-en-4-one (11), $\lambda_{max.}$ 308 nm, $\nu_{max.}$ 3 060, 3 000, 2 950, 1 685, and 1 575 cm^{-1}, τ 7.30 (m, CH_2CO), 6.75 (m, CH_2S), 3.82 (d, *J* 11 Hz, CHCO), and 2.55 (d, CHS). Thiacyclohexan-4-one (20 mg) and *N*-chlorosuccinimide (30 mg) in deuteriochloroform (0.4 ml) at 0 °C were allowed to reach room temperature; n.m.r. then showed the presence of the olefin (11).

2-*Cyclopentyl*-3,3-*diphenyloxaziridine* (17a).—*N*-(Diphenylmethylene)cyclopentylamine contaminated with benzophenone (20%) (16 g), in methylene chloride (50 ml) at 0 °C, was treated with *m*-chloroperbenzoic acid (9.5 g) in methylene chloride (200 ml). After 2 h at 0 °C the mixture was filtered, and the filtrate was washed with dilute sodium hydroxide solution and water. The residue left after evaporation was crystallised twice from light petroleum to give the *oxaziridine* (9.7 g), m.p. 97—100°, τ 8.6—8.0 (m, 8 aliphatic H), 7.44 (m, CHN), and *ca.* 2.5 (m, 10 aryl H), τ (C_6D_6) 8.9—7.8 (m, 8 aliphatic H), 7.34 (m, CHN), 2.85 (m, 6 aryl H), 2.57 (m, 2 aryl H), and 2.37 (m, 2 aryl H), *m/e* 265 (M^+, 15%) and 105 ($PhCO^+$, 100%) (Found: C, 81.4; H, 7.1; N, 5.3. $C_{18}H_{19}NO$ requires C, 81.5; H, 7.2; N, 5.3%). The oxaziridine liberated iodine from potassium iodide in ethanol–acetic acid.

2-*Cyclohexyl*-3,3-*diphenyloxaziridine* (17b).—A mixture (27 g) of *N*-(diphenylmethylene)cyclohexylamine (40%) and

[25] J. V. Davies and S. Sunner, *Acta Chem. Scand.*, 1962, **16**, 1870.

[26] R. K. Harris and R. A. Spragg, *J. Chem. Soc.* (*B*), 1968, 684.

benzophenone (60%) in methylene chloride (75 ml) was oxidised at 0 °C with *m*-chloroperbenzoic acid (9 g) in methylene chloride (250 ml) during 4 h. The resultant crude product was washed several times with light petroleum (b.p. below 40°) and was crystallised thrice from light petroleum to give the *oxaziridine*, m.p. 101—104°, τ (CCl_4) 8.9—8.1 (m, 11 aliphatic H) and *ca.* 2.6 (m, 10 aryl H), τ (C_6D_6) 9.3—7.8 (m, 11 aliphatic H), 2.9 (m, 6 aryl H), 2.54 (m, 2 aryl H), and 2.32 (m, 2 aryl H), *m/e* 279 (M^+, 9%) and 105 ($PhCO^+$, 100%) (Found: C, 81.8; H, 7.6; N, 5.2. $C_{19}H_{21}NO$ requires C, 81.8; H, 7.6; N, 5.0%). This oxaziridine liberated iodine from potassium iodide in ethanol–acetic acid.

N-(*Diphenylmethylene*)*cyclopentylamine* N-*Oxide* [*Nitrone* (18a)].—The oxaziridine (17a) (4 g) was heated in refluxing toluene for 29.5 h. The product was chromatographed on silica gel (elution with light petroleum–chloroform) and the fractions showing u.v. absorption at 300 nm were combined to afford, after several crystallisations from light petroleum, the *nitrone* (18a) (30%), m.p. 109—111°, $\lambda_{max.}$ 235 (ε 10 800) and 298 nm (11 800), $\nu_{max.}$ 1 520 and 1 245 cm^{-1}, τ 8.5—7.5 (m, 8 aliphatic H) and 5.46 (m, CHN), τ (C_6D_6) 5.55 (m, CHN), *ca.* 2.9 (m, 8 aryl H), and 1.60 (m, 2 aryl H), *m/e* 265 (M^+, 33%) and 165 ($C_{13}H_9^+$, 100%) (Found: C, 81.6; H, 7.4; N, 5.3. $C_{18}H_{19}NO$ requires C, 81.5; H, 7.3; N, 5.3%). Irradiation with u.v. light in deuteriochloroform solution gave back the oxaziridine (17a).

N-(*Diphenylmethylene*)*cyclohexylamine* N-*Oxide* [*Nitrone* (18b)].—The oxaziridine (17b) (500 mg) was heated in refluxing ethylbenzene for 46 h. The residue left on removal of solvent was twice crystallised from light petroleum to give the *nitrone* (18b) (60%), m.p. 105—106°, $\lambda_{max.}$ 235 (ε 10 500) and 298 nm (11 500), $\nu_{max.}$ 1 570, 1 255, and 1 225 cm^{-1}, τ 9.1—7.7 (m, 10 aliphatic H) and 6.04 (m, CHN), τ (C_6D_6) 6.04 (m, CHN), 2.9 (m, 8 aryl H), and 1.5 (m, 2 aryl H), *m/e* 279 (M^+, 37%) and 180 ($Ph_2C{=}N^+$, 100%) (Found: C, 81.6; H, 7.6; N, 5.0. $C_{19}H_{21}NO$ requires C, 81.8; H, 7.6; N, 5.0%). This nitrone formed the oxaziridine (17b) when irradiated with u.v. light in deuteriochloroform solution.

Thermal Elimination Reactions.—The nitrones in deuteriobenzene solution were sealed in n.m.r. tubes and suspended in the vapour of boiling toluene (111 °C). N.m.r. spectra were run at suitable times, and after complete reaction the products were identified. Benzophenone oxime was isolated; the olefinic products were identified by g.l.c. comparison with authentic samples, to confirm the n.m.r. identification already made. Chemical shifts [τ(C_6D_6)] were: Δ^2-thiolen 7.70 (2H), 7.16 (2H), 4.70 (3-H), and 4.02 (2-H); thiacyclohex-2-ene 8.30 (4H), 7.51 (2H), 4.47 (3-H), and 4.03 (2-H); 2,3-dihydro-1,4-oxathiin 7.58 (m, SCH_2), 6.14 (m, OCH_2), 5.17 (d, *J* 7 Hz, SCH), and 3.56 (d, OCH); ethyl vinyl sulphide 9.0 (t, *J* 9 Hz, CH_3), 7.67 (q, CH_2), 4.99 (d, *J* 17 Hz, methylene H), 4.95 (d, *J* 10 Hz, methylene H), and 3.78 (dd, SCH=).

The thermal reaction of the nitrone (4a) also gave *benzophenone* O-(1-*ethylthioethyl*)*oxime* (19), as an oil, $\lambda_{max.}$ 231 (ε 15 500) and 262 nm (11 400), $\nu_{max.}$ (CCl_4) 1 500, 1 450, and 1 180 cm^{-1}, τ ($CDCl_3$) 8.75 (t, *J* 8 Hz, CH_3), 8.40 (d, *J* 8 Hz, CH_3), 7.25 (dq, CH_2), 4.44 (q, OCH), and 2.60 (m, 10 aryl H), *m/e* 285 (M^+, 0.5%) and 89 ($C_4H_9S^+$, 100%) (Found: C, 72.4; H, 6.4; N, 4.7. $C_{17}H_{19}NOS$ requires C, 71.6; H, 6.7; N, 4.9%).

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