Experimental and Theoretical Investigation on the Cycloadditions of Nitrile Oxides, Nitrones, and Diazoalkanes with Acyclic Vinyl Sulphones and Thiet 1,1-Dioxide[1]

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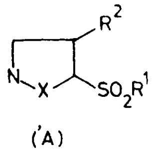
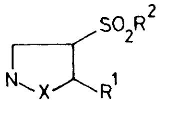
Diazoalkanes, nitrile oxides, and nitrones cycloadd thiet 1,1-dioxide showing regiochemical characteristics markedly different from those observed for acyclic vinyl sulphones. The charge-transfer stabilization energy, calculated according to the Klopman–Salem perturbational approach in the CNDO/2 approximation, is able to account for the experimental trends of the isomer ratios. An analysis of the calculations performed for *cis-syn*-vinyl sulphones explains the change of regiochemistry in the reactions of thiet 1,1-dioxide as due to its blocked *cis-syn*-structure which does not happen in the ' open ' vinyl sulphones. Unsuccessful predictions obtained with the frontier orbital approximation are discussed.

CYCLOADDITION of nitrile oxides and diazoalkanes to acyclic vinyl sulphones is, in general, highly selective; the particular regioisomer formed depends on the substituents both on the dipole and on the dipolarophile. Thus arenonitrile oxides and diazomethane react with phenyl vinyl sulphone to yield the 5-sulphonyl isomer (A) as the sole[1,2] or dominant product[3] whereas with propenyl phenyl sulphone they form the 4-sulphonylisoxazoline (B) (this work) and the 5-sulphonylpyrazoline[2] (A), respectively. On the other hand, nitrones appear to have a definite propensity to yield mixtures of the two isomers even if at least one example has been reported of a single product, the 4-sulphonyl adduct (B).[4,†]



(A)



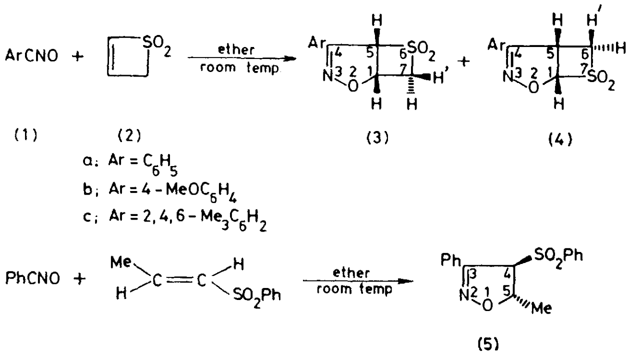
(B)

X = N or O

When the cyclic sulphone thiet 1,1-dioxide is reacted with diazomethane, the high regioselectivity of the cycloaddition of diazomethane to vinyl sulphone is lost and a mixture of the two adducts is formed.[6] Having observed this different behaviour of the cyclic sulphone with respect to the acyclic compounds we deemed it useful to examine the comparative results with nitrile oxides and nitrones. In these two cases a clear change of product ratios is evident, so that an interesting variety of results is obtained for a small set of related compounds. This appeared to constitute a good basis for a theoretical study of regioisomerism of these reactions.

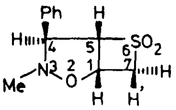
RESULTS

The reactions of thiet 1,1-dioxide and propenyl phenyl sulphone with benzonitrile oxides (1a—c) were carried out in ether at room temperature; similar conditions were used for the reactions of nitrones with thiet 1,1-dioxide whereas the reaction between propenyl phenyl sulphone and (*N*-benzylidene)methylamine *N*-oxides was conducted under reflux for 24 h in benzene. In order to minimize the influence of solvent polarity on regioisomer ratios, the reactions were carried out in low polarity media (ether or benzene). Adducts (3)—(8) were isolated by silica gel column chromatography with ethyl acetate–cyclohexane (2 : 3) as eluant. The products were stable under the work-up conditions.

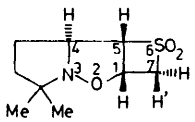


SCHEME Yields and isomer distributions for reactions of nitrile oxides with thiet 1,1-dioxide and *trans*-propenyl phenyl sulphone

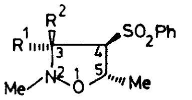
The reactions of thiet 1,1-dioxide with benzonitrile oxides (1a—c) (Scheme) yielded only (or very largely) isomers (B), *i.e.* (3a—c); at variance with vinyl phenyl sulphone,[1] *trans*-propenyl phenyl sulphone reacted with benzonitrile oxide to give the regioisomer (B), *i.e.* (5). Both thiet 1,1-dioxide and *trans*-propenyl phenyl sulphone reacted with (*N*-benzylidene)methylamine *N*-oxide to give regioisomers of type (B) [compounds (6) and (8), respectively]; the same kind of regioisomer was also obtained [compound (7)] from thiet 1,1-dioxide and 5,5-dimethyl-Δ^1-pyrroline *N*-oxide. The structures of compounds (3)—(8) were assigned



(6)



(7)



(8) a; R^1 = Ph, R^2 = H
b; R^1 = H, R^2 = Ph

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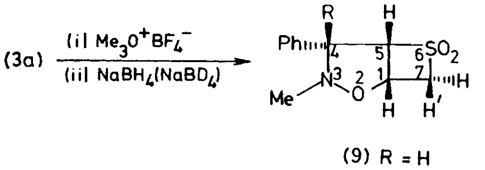
† In the reaction of *N*-benzylidineaniline *N*-oxide with phenyl styryl sulphone a single product was isolated; structure (A) was previously attributed.[5] On the basis of the ^{13}C n.m.r. spectrum, we reassigned structure (B); in fact in the ^{13}C n.m.r. spectrum the C-4 and -5 resonances are very close (δ 80.4 and 81.4 p.p.m., respectively); they are very far from the value (δ 92.7 p.p.m.) found for C-5 of 3-phenyl-5-phenylsulphonylisoxazoline.

by means of ^{1}H and ^{13}C n.m.r. analysis with the aid of the reactions in equation (1).



(1)

(9) R = H

(10) R = D

The ^{1}H and ^{13}C n.m.r. chemical shifts of compounds (3)—(10) are reported in Tables 1 and 2. At variance with compounds (3)—(5), compounds (6)—(10) were characterized by the absence of proton signals at fields δ_H 5.60; this feature allows [6,7] structures (6)—(10) to be elucidated.

The most deshielded protons [δ_H 6.58—6.91 for (3a—c) and 6.94 for (4c)] could be assigned as 5-H in compounds (3) and 1-H in compound (4c). The strong deshielding of 5-H in compounds (3) is noteworthy by comparison with compound (5) where 4-H resonates at δ_H 4.75 (see Experimental section); this effect is probably the consequence of an eclipsed relationship between 5-H and one oxygen atom of the sulphonyl group.

Table 1

^{1}H N.m.r. data for (3), (6), (7), (9), and (10) [a]

	Chemical shift δ([$^2H_6$]Me$_2$SO)					Coupling constants (Hz)					
Compound	1-H	4-H	5-H	7-H	7'-H	$J_{1,5}$	$J_{1,7}$	$J_{1,7'}$	$J_{5,7'}$	$J_{5,7}$	$J_{7,7'}$
(3a)	5.65(ddd)		6.91(ddd)	4.74(ddd)	5.05(ddd)	8.3	3.2	6.6	2.6	1.3	14.5
(3b)	5.58(ddd)		6.84(ddd)	4.66(ddd)	5.00(ddd)	9.0	3.0	6.7	2.7	1.0	15.0
(3c)	5.61(ddd)		6.58(ddd)	4.74(ddd)	4.96(ddd)	8.3	3.5	6.3	2.5	1.0	14.5
(6) [b]	4.09(dt)	4.41(d)	4.52(m)	3.63(br d)	3.39(ddd)	6.0	2.0	6.0	1.5	~1.0	14.0
(6)	5.12(dt)	4.42(d)	5.32(m)	4.18(br d)	4.48(ddd)						
(7) [c]	*d*	*e*	*d*	*e*	*e*						
(7) [f]	*g*	*g*	*g*	*g*	*h*						
(9) [i]	4.05(m)	3.05(d)	4.48(dt)	3.85(m)	3.42(ddd)	6.5	1.5	7.5	2.5		14.5
(9)	5.20(m)	3.92(d)	5.60(m)	4.40(m)							
(10)	5.20(m)		5.60(dd)	4.40(m)							
				6-H	6'-H				$J_{5,6'}$	$J_{5,6}$	$J_{6,6}$
(4c)	6.94(d)		4.83(ddd)	2.83(br d)	3.53(dd)	7.0			10.0	1.0	14.0

[a] The spectra were analysed as first-order systems. [b] In C_6D_6; $J_{4,5}$ 4.0 Hz. [c] In $CDCl_3$. [d] 4.80—5.10(m). [e] 4.00—4.60(m). [f] In C_6D_6. [g] 3.80—4.20(m). [h] 3.37(m). [i] In C_6D_6; $J_{4,5}$ 6.5 Hz.

Table 2

^{13}C N.m.r. data for (3b), (6), (9), and (10)

	Chemical shift δ ([$^2H_6$]Me$_2$SO)			
Compound	C-1	C-4	C-5	C-7
(3b)	69.7(d)	122.4(s)	93.8(d)	81.2(t)
(6)	62.8(d)	71.2(d)	92.1(d)	69.2(t)
(9)	61.9(d)	73.1(d)	90.9(d)	71.7(t)
(10) [a]	61.9(d)	73.1(t)	90.9(d)	71.7(t)

[a] $J_{C,D}$ 10 Hz.

In addition the ^{13}C n.m.r. spectra (Table 2) show the C-1 resonance at higher fields (δ_C 61.9—69.7 p.p.m.) than that observed for C-5 (δ_C 92.7 p.p.m.) in 3-phenyl-5-phenylsulphonyl-Δ^2-isoxazoline,* where the CH group is flanked by oxygen and the sulphonyl group. The assignment of resonance to C-4 in (6) and (9) was made possible by deuteriation [synthesis of (10)] while the choice between C-1 and -5 was made by considering the residual coupling constant in the off-resonance spectra.†

The stereochemistry at C-4 in isomers (6) and (9) was assigned with the aid of the aromatic solvent induced shift method (ASIS). As shown in Table 1, the 4-H resonance of (6) (where 4-H is shielded by the phenyl group) did not change on passing from [$^2H_6$]Me$_2$SO to C_6D_6, at variance with compound (9) for which the signal was strongly shifted to higher field. Moreover the attack of the borohydride ion on isoxazolinium ion was previously shown to occur from the less hindered side of the molecule.[9]

The mass spectra of these compounds were recorded but they are not decisive in attributing structures to the adducts.

DISCUSSION

The perturbational approach is a powerful tool for investigating the various aspects of 1,3-dipolar cycloaddition.[10] Even in its crudest approximation, namely the frontier orbital approximation, success has often been achieved in spite of considerable doubt as to its theoretical foundation.[11] Recently [6] the different regiochemistry of cycloaddition of diazoalkanes to thiet 1,1-dioxide compared with substituted vinyl sulphones has been justified both by the frontier orbital approximation and by calculating a significant part [HOMO(dipole) — Σ LUMO(dipolarophile)] of the charge-transfer term of the Klopman–Salem equation.[12] The new experimental results also show that nitrones and nitrile oxides cycloadd thiet 1,1-dioxide with isomer ratios reflecting an increased proportion of the 4-substituted derivative (B) compared with vinyl sulphones. In fact, on passing from the vinyl sulphone to the cyclic dipolarophile, diazoalkanes shift from 5-substituted derivatives (A) to a mixture of the two regioisomers, nitrones from a mixture to the single 4-sulphonylisoxazoline (B), and nitrile oxides invert their regiochemistry giving the 4-substituted isomer (B) instead of the 5-substituted one (A); it

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* We thank Dr. A. Coda-Corsico for supplying a sample of this compound, δ ([$^2H_6$]M$_2$SO) 4.05 (2 H, m, 4-H) and 6.20 (1 H, m, 5-H), δ_C ([$^2H_6$]Me$_2$SO) 92.7 (d, C-5) and 36.6 p.p.m. (t, C-4).

† The ^{13}C n.m.r. spectrum of (6), taken at 37 °C, is not well resolved; clear signals were obtained by recording the spectrum at 90 °C. An equilibrium between conformers or invertomers may be postulated. Invertomers were isolated in the cycloadditions of nitrone-esters with unsaturated dipolarophiles.[8]

is also interesting to observe that a *trans*-methyl group on the carbon atom of phenyl vinyl sulphone strongly favours structure (B) of cycloadducts of benzonitrile oxide and (*N*-benzylidene)methylamine *N*-oxide. This trend is clearly accounted for by the differences in the charge-transfer stabilization energies of the model transition states for the two regioisomers reported in Table 3. For the calculation of charge-transfer energies, CNDO/2 orbital energies, and coefficients of the separated molecules have been used; the combined system of the two partners, placed in parallel planes at a distance of 2.5 Å with their terminal atoms arranged so as to allow the formation of the chosen regioisomer, was considered for the mixing of filled orbitals of each molecule with empty orbitals of the other. The resonance integrals β_{ab} in the charge-transfer stabilization formula were given the following values: β_{CC} −2.63, β_{CN} −2.14, and β_{CO} −1.53.[13]

By matching the calculated and experimental results of Table 3 one finds that a difference of stabilization energy greater than *ca.* 1.25×10^3 J mol^{-1} or less than *ca.* -0.84×10^3 J mol^{-1} corresponds to full specificity (only one isomer formed in cycloaddition), whereas *ca.* $-0.84 < \Delta\Delta E <$ *ca.* 1.25 corresponds to mixtures of variable isomer ratios. A difference of $0.84—1.25 \times 10^3$ J mol^{-1} between the activation energies of the two regioisomers is not sufficient to justify regiospecificity. However, it must be stressed that the Klopman–Salem equation relates to an early point on the reaction path, so that it can account for only a fraction of the activation energy; furthermore, only the charge-transfer term has been considered here, thus assuming that repulsion energy of filled orbitals and electrostatic interaction between molecules do not affect the regiochemistry. These arguments do not allow the calculated $\Delta\Delta E$ to be anything but a regioselectivity index. Moreover, the actual values of the indices and, perhaps, even their orders of magnitude are affected by the approximations and parametrization of the MO calculations. The potential use of this index rests upon the application to series of examples showing a large variety of regiochemical results; it must be added that the regioselectivity index can reflect the difference in activation energy only if the reaction profiles for the two regioisomers are similar in shape.

Table 3 shows that $\Delta\Delta E$ values strictly parallel the trend of the available experimental results, and so a number of new results can be predicted with some reliability. However, due to the weakness of our definition of the limiting values for $\Delta\Delta E$ (they have been chosen empirically for a few examples) calculated $\Delta\Delta E$ values falling in the neighbourhood of those limits can correspond both to mixtures with a prevalent adduct and to the single regioisomer. Inspection of Table 4 reveals that the preference for adduct (B) with thiet 1,1-dioxide relative to the ' open ' vinyl sulphone can be traced to its ' blocked ' *syn*-structure and to the *cis*-substitution of the C=C bond.

Let us now compare (Table 5) some theoretical results in Table 3 with those obtained by considering only the frontier molecular orbitals. In approximation (1) a result can be predicted only if the dominant mechanism can be singled out: on the basis of calculated orbital energies, the energy gap between HO(dipole) and LU(dipolarophile) is always far lower than that between LU(dipole) and HO(dipolarophile) so that predictions are contained in the second column of approximation (1). The insufficient agreement with experiment may be due to inadequacies in these MO calculations, mostly involving the energy gap. The choice of the dominant

TABLE 3

Calculated stabilization energy differences and experimental results for 1,3-dipolar cycloaddition of αβ-unsaturated sulphones

1,3-Dipole	Dipolarophile	$10^{-3}\Delta\Delta E$[a]	Isomer	Relative percentage (B)	(A)	Reference
$CH_2=N=N$	CH_2-CHSO_2Me	+1.695	(A)			
$CH_2=N=N$	$CH_2=CHSO_2Ph$	+1.464	(A)	0	100	2
$CH_2=N=N$	*trans*-$MeCH=CHSO_2Me$	+1.800	(A)	0	100	2
$CH_2=N=N$	(2)	+0.188	(A) + (B)	40	60	6
$PhCH=N=N$	$CH_2=CHSO_2Ph$	+1.004	(A) + (B) or (A)			
$PhCH=N=N$	(2)	+0.075	(A) + (B)	70	30	6
$HC\equiv N-O$	$CH_2=CHSO_2Me$	+0.586	(A) + (B)			
$HC\equiv N-O$	$CH_2=CHSO_2Ph$	+0.385	(A) + (B)			
$HC\equiv N-O$	(2)	−1.632	(B)			
$PhC\equiv N-O$	$CH_2=CHSO_2Me$	+2.840	(A)			
$PhC\equiv N-O$	$CH_2=CHSO_2Ph$	+1.464	(A)	0	100	1
$PhC\equiv N-O$	*trans*-$MeCH=CHSO_2Ph$	−1.966	(B)	100	0	*b*
$PhC\equiv N-O$	(2)	−0.962	(B)	100	0	*b*
$CH_2=NHO$	$CH_2=CHSO_2Me$	+1.130	(A) + (B) or (A)			
$CH_2=N(Bu^t)-O$	$CH_2=CHSO_2Ph$	+0.899	(A) + (B)	30	70	4
$CH_2=NHO$	(2)	−0.753	(A) + (B) or (B)			
$PhCH=N(Me)-O$	$CH_2=CHSO_2Me$	+0.753	(A) + (B)			
$PhCH=N(Me)-O$	$CH_2=CHSO_2Ph$	+0.670	(A) + (B)	68	32	4
$PhCH=N(Me)-O$	*trans*-$MeCH=CHSO_2Ph$	−0.837	(B)	100	0	*b*
$PhCH=N(Me)-O$	(2)	−0.837	(B)	100	0	*b*

[a] $\Delta\Delta E = \Delta E\ (B) - \Delta E\ (A)$; $\Delta E = 2 \left\{ \sum_{r(K)}^{occ.} \sum_{s(L)}^{unocc.} - \sum_{s(L)}^{occ.} \sum_{r(K)}^{unocc.} \right\} \left(\sum_{ab} C_{ra}^{K} \cdot C_{sb}^{L} \cdot \beta_{ab} \right)^2 \epsilon_r - \epsilon_s)^{-1}$ where r and s denote molecular orbitals, ϵ_r and ϵ_s their energies, K and L the reacting molecules, a and b the π-atomic orbitals of atoms bonded in the chosen regioisomer; $\Delta\Delta E$ in J mol^{-1}. [b] This work.

TABLE 4

Analysis of the predicted regiochemistry differences between ' open ' and cyclic sulphones

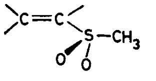
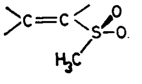
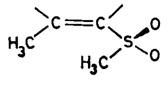
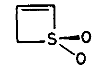
1,3-dipole				
	$10^{-3}\Delta\Delta E_{(B)-(A)}$ (isomer formed)			
$CH_2=N=N$	+1.695 (A)	+0.209 (A) + (B)	+0.711 (A) + (B)	+0.188 (A) + (B)
Ph–C≡N–O	+2.84 (A)	+0.402 (A) + (B)	−1.548 (B)	−0.963 (B)
Ph–CH=N(Me)O	+0.753 (A) + (B)	+0.460 (A) + (B)	−1.063 (B)	−0.837 (B)

TABLE 5

Comparison of different approximations to charge-transfer interaction

	Approximation (1) [a] Preferred adduct in interaction		Approximation (2) [b]	Approximation (3) [c]	Experimental percentage	
1,3-Dipole	LU–HO	HO–LU	$10^{-3}\Delta\Delta E$ (isomer formed) [d]		(A)	(B)
			Dipolarophile, thiet 1,1-dioxide			
$CH_2=N=N$	(A)	(A) + (B)	−1.360 (B)	+0.188 (A) + (B)	60	40
PhC≡N–O	(B)	(A) + (B)	−0.544 (A) + (B)	−0.962 (B)	100	0
PhCH=N(Me)O	(B)	(A) + (B)	−2.175 (B)	−0.837 (B)	100	0
			Dipolarophile, phenyl vinyl sulphone			
$CH_2=N=N$	(B)	(A)	+2.175 (A)	+1.464 (A)	0	100
Ph–C≡N–O	(A)	(B)	+0.627 (A) + (B)	+1.464 (A)	0	100
Ph–CH=N(Me)O	(A)	(B)	+2.385 (A)	+0.670 (A) + (B)	32	68

[a] The preferred regioisomeric transition state is that in which the larger terminal coefficients of the interacting π-atomic orbitals in the frontier MOs are united. [b] Frontier orbital approximation; $\Delta E = 2\,[(\sum_{ab} C^{K}_{HOa}\, C^{L}_{LUb}\, \beta_{ab})^2(\epsilon^{K}_{HO} - \epsilon^{L}_{LU})^{-1} - (\sum_{ab} C^{K}_{LUa}C^{L}_{HOb}\, \beta_{ab})^2(\epsilon^{K}_{LU} - \epsilon^{L}_{HO})^{-1}]$. [c] Complete charge-transfer term (from Table 3). [d] $\Delta\Delta E = \Delta E(B) - \Delta E(A)$.

mechanism by the use of ionization potentials and electron affinities may improve the predictions; however, this requires information on the reacting molecules outside the calculations.

Approximation (2) considers the combination of two mechanisms. The frontier interactions represent the largest contributions to the complete charge-transfer term; however it does appear that frontier interactions do not dominate the $\Delta\Delta E$ differences and therefore the prediction.

In conclusion, the participation of non-frontier orbitals improves the prediction either because it overcomes an unsuitable approximation or because it makes up for the low quality of frontier orbitals in the approximation and parametrization in the MO calculations.

CALCULATIONS

MO Calculations were performed at the Centro di Calcolo Elettronico of the University of Modena by a modified version of QCPE 141. A standard CNDO/2 parametrization was chosen; [14] standard bond lengths and bond angles have been used.[15] A significant feature of the spatial arrangement chosen for diazophenylmethane and benzylideneamine *N*-oxides is that the phenyl ring is placed with its π-system non-conjugated (perpendicular) to the C-N-X π-system of the prototype dipole; the reason for this choice rests on the argument that this π–π interaction, which is certainly present to some extent in the free molecules, disappears in the cycloaddition as a consequence of the saturation (change from sp^2 to sp^3 hybridization) of the carbon atom. Since the MO calculations are intended to be used for a description of the transition states, the spatial arrangements is nothing but a device for introducing, from the beginning, some constraints peculiar to the reaction products. In fact, as the perturbation technique relates to an early point in the reaction path, only a condition of non-conjugation in the isolated molecule can guarantee an appropriate description of the transition state.

As the change from sp to sp^2 hybridization of the carbon atom in the cycloaddition of arenonitrile oxide does not impose a similar constraint, a π-system coplanar to the phenyl π-system has been chosen for the charge-transfer interaction of benzonitrile oxide.

EXPERIMENTAL

N.m.r. spectra were recorded at 36 °C for $[^2H_6]Me_2SO$ solutions with a Varian XL-100 (100 MHz for ^1H and 25.18 MHz for ^{13}C) spectrometer (Me_4Si as internal standard). Mass spectra were recorded with a Varian MAT 112 S spectrometer at an ionizing voltage of 70 eV. Microanalyses were performed with a Carlo Erba Analyzer model 1106. Thiet 1,1-dioxide was prepared according to Dittmer *et al.*[16] Reaction mixtures were analysed by t.l.c. on silica gel GF_{254}.

Reactions of Nitrile Oxides (1a *and* b) *with Thiet* 1,1-*Dioxide* (2).—To a solution of thiet 1,1-dioxide (6.0 mmol) and arenehydroximoyl chloride (3.0 mmol) in ether (50 ml) was added a stoicheiometric amount of triethylamine in ether (20 ml) over 2 h with stirring. The mixture was left aside at room temperature for 24 h and poured into water. The organic layer was separated, dried and evaporated to give a residue which was column chromatographed with ethyl acetate–cyclohexane (2 : 3) as eluant. Adducts (3a and b) were isolated in 88 and 83% yield, respectively, *m/e* for (3a) 63 (11%), 76 (11), 77 (83), 103 (29), 117 (100), 118 (11), 127 (16), 128 (37), 129 (34), 130 (59), 144 (19), and

222 (34; $M^+ - 1$); *m/e* for (3b) 63 (44%), 64 (37), 76 (28), 77 (65), 89 (25), 90 (22), 92 (32), 115 (43), 116 (27), 132 (75), 133 (27), 146 (20), 147 (100), 159 (36), 160 (98), and 253 (42, M^+). Other data are in Table 6.

Reaction of Benzonitrile Oxide (1a) *with* trans-*Propenyl Phenyl Sulphone.*—The reaction of benzonitrile oxide (1a) with *trans*-propenyl phenyl sulphone [2] was carried out as above. The reaction was not clean but adduct (5) was isolated in 78% yield, δ($CDCl_3$) 5.40 (1 H, m, 5-H); 4.75 (1 H, d), $J_{4,5}$ 3.0 Hz, 4-H) and 1.32 (3 H, d, $J_{5\text{-Me}}$ 6.0 Hz, Me).

Reactions of Mesitonitrile Oxide (1c), (N-*Benzylidene*)-*methylamine* N-*Oxide, and* 5,5-*Dimethyl*-Δ^1-*pyrroline* N-*Oxide with Thiet* 1,1-*Dioxide* (2).—An ethereal solution of mesitonitrile oxide (3.22 g, 20 mmol) and a two-fold excess of thiet 1,1-dioxide were allowed to stand at room temperature until t.l.c. analysis indicated disappearance of the dipole. Evaporation of the solvent under reduced pressure gave a residue which was column chromatographed on silica gel with ethyl acetate–cyclohexane (2 : 3) as eluant to afford in order of elution, (3c) (4.63 g) and (4c) (0.14 g).

Similar reaction conditions were used in the cases of (*N*-benzylidene)methylamine *N*-oxide and 5,5-dimethyl-Δ^1-pyrroline *N*-oxide. Adducts (6) and (7) were obtained in 73 and 85% yield after one month and two days, respectively. Adduct (6) crystallizes from EtOH as needles, m.p. 107 °C; adduct (7) also crystallizes from EtOH as prisms, m.p. 170—171 °C; *m/e* for (3c) 77 (44%), 91 (52), 115 (38), 119 (39), 128 (29), 130 (24), 141 (30), 143 (29), 144 (76), 145 (21), 156 (55), 157 (41), 158 (100), 159 (51), 171 (20), 172 (67), 200 (19), and 256 (29, M^+); *m/e* for (4c) 77 (22%), 91 (29), 119 (33), 130 (22), 157 (34), 171 (17), 172 (100), 173 (15), and 256 (6, M^+), *m/e* for (7) 77 (36%), 91 (27), 103 (38), 115 (23), 118 (27), 129 (37), 134 (20), 160 (100), 173 (35), and 239 (36, M^+).

Reaction of (N-*Benzylidene*)*methylamine* N-*Oxide with* trans-*Propenyl Phenyl Sulphone.*—A benzene solution (50 ml) of (*N*-benzylidene)methylamine *N*-oxide (15 mmol) and *trans*-propenyl phenyl sulphone (10 mmol) was refluxed for 24 h. Evaporation of the solvent under reduced pressure gave a residue which was column chromatographed on silica gel with ethyl acetate–cyclohexane (1 : 4) as eluant to afford in order of elution, (8a) (2.65 g), needles from EtOH, m.p. 98—101 °C, and (8b) (0.17 g), needles from EtOH, m.p. 134—135.5 °C, δ($CDCl_3$) for (8a) 4.80 (1 H, m, 5-H), 4.08 (1 H, d, $J_{3,4}$ 7.0 Hz, 3-H), 3.75 (1 H, dd, $J_{4,5}$ 4.0 Hz, 4-H), 2.63 (3 H, s, NMe) and 1.34 (3 H, d, $J_{5,\text{Me}}$ 6.0 Hz, Me), δ($CDCl_3$) for (8b) 4.80 (1 H, m, 5-H), 3.80 (2 H, m, 3- and 4-H), 2.60 (3 H, s, NMe), and 1.50 (3 H, d, $J_{5,\text{Me}}$ 7.0 Hz, Me).

Synthesis of (9) *and* (10).—To a nitromethane solution of (3a) (0.5 g), a large excess of trimethyloxonium fluoroborate was added; the reaction proceeded at room temperature (24 h). The solvent was evaporated *in vacuo* and the residue dissolved in propan-2-ol (70 ml). To the resulting stirred solution an excess of sodium borohydride (or sodium borodeuteride) was added, in small portions, during 30 min, and stirring was continued for a further 30 min. The solvent was removed, the residue treated with water, and extracted with ether. After the usual work-up, compound (9) [(10)] was obtained in 85% (81%) yield. Compound (9) was crystallized from ether as prisms, m.p. 95—97 °C, and compound (10) was purified by crystallization from cyclohexane as needles, m.p. 104—105 °C, *m/e* for (9) 77 (74%), 91 (54), 105 (55), 115 (56), 118 (58), 129 (65), 134 (58), 160 (100), 173 (43), and 239 (90); *m/e* for (10) 77 (37%), 91 (21), 92 (20), 104 (34), 116 (22), 118 (38), 129 (22), 130 (46), 131 (18), 135 (63), 160 (100), 173 (31), and 240 (79). Adduct (8b) was synthesized in the same way.

TABLE 6

Analytical and physical data of compounds formed

Compound	Formula	Yield (%)	Required (%) C	Required (%) H	Required (%) N	Found (%) C	Found (%) H	Found (%) N	M.p. (°C)
(3a)	$C_{10}H_9NO_3S$	100	53.8	4.05	6.25	53.6	4.15	6.3	172—173
(3b)	$C_{11}H_{11}NO_4S$	100	52.3	4.4	5.45	52.15	4.4	5.55	183—184.5
(3c)	$C_{13}H_{15}NO_3S$	97	58.85	5.7	5.3	58.65	5.8	5.3	161—162
(4c)		3							128—130
(6)	$C_{11}H_{13}NO_3S$		55.2	5.5	5.85	55.4	5.5	5.75	
(9)									
(10)*									
(7)	$C_9H_{15}NO_3S$		49.75	6.95	6.45	49.55	7.1	6.7	
(5)	$C_{16}H_{15}NO_3S$		63.8	5.0	4.65	63.8	4.95	4.75	
(8a)	$C_{17}H_{19}NO_3S$		64.35	6.05	4.4	64.2	6.1	4.45	
(8b)						64.25	6.15	4.5	

* Deuterium behave like hydrogen.

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