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THE REACTION OF KETO-STABILIZED SULPHONIUM AND ARSONIUM YLIDES WITH α-CHLOROOXIMES

A NEW SYNTHESIS OF Δ^2-ISOXAZOLINES

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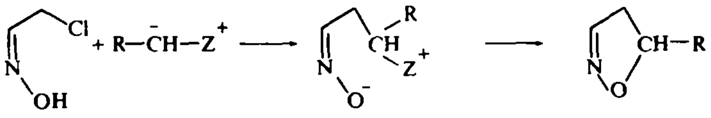
Abstract—The reaction of α-chlorooximes or the isomeric nitrosochlorides with keto-stabilized dimethylsulphonium or triphenylarsonium ylides affords *trans*-5-acyl-Δ^2-isoxazolines (VIIa–m) in good yields. The NOCl adducts of ethylpropenyl ether and ethylstyryl ether on reaction with dimethylsulphonium phenacylide lead directly to the corresponding 3-substituted-5-benzoylisoxazoles. Dimethylsulphonium carbethoxymethylide on reaction with 2-chloro-2-phenylacetone oxime affords the oxime of β-acetylcinnamic acid ethyl ester, while on reaction with 2-chlorocyclooctanone oxime leads to the thioether IXd.

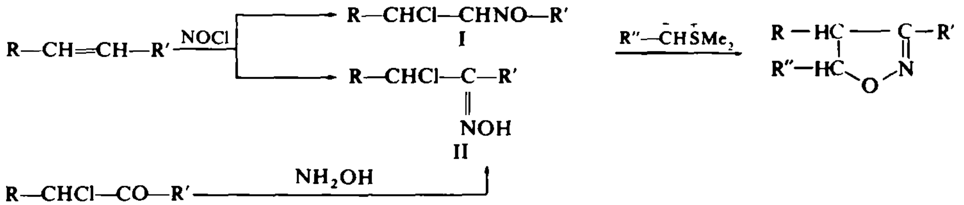
FOLLOWING OUR RESEARCH ON THE REACTION BETWEEN SULPHONIUM OR ARSONIUM ylides and α-isonitrosoketones which led to 5-hydroxyisoxazolines or to the corresponding isoxazoles[1] we have investigated the reaction of sulphonium and arsonium ylides on α-chlorooximes. These compounds, like α-isonitrosoketones, have an electrophilic centre three bonds away from the nucleophilic oximic oxygen and in principle should give Δ^2-isoxazolines when reacted with ylides according to the scheme:*



Z = SMe_2 or $AsPh_3$

We have reported that α-chlorooximes, or the isomeric nitrosochlorides, on reaction with dimethyloxosulphonium methylide (IV, R″ = H, Z = $SOMe_2$) normally give α-methylene oximes and occasionally minor amounts of Δ^2-isoxazolines[3,4]

Table 1 shows that α-chlorooximes (II) or the isomeric nitrosochlorides (I) afford Δ^2-isoxazolines in good yield without formation of α,β-unsaturated oximes when reacted with keto-stabilized sulphonium ylides (IVa and IVe). Since α-chlorooximes and nitrosochlorides are easily obtained from olefines, this reaction offers a valuable two-step synthesis of Δ^2-isoxazolines:



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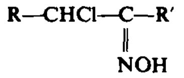
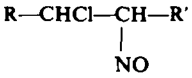
* For a general scheme for the synthesis of heterocycles by ylides see Ref 1b and 2.

TABLE 1. Δ^2-ISOXAZOLINES FROM α-CHLOROOXIMES AND NITROSOCHLOROIDES BY KETO-STABILIZED SULPHONIUM YLIDES



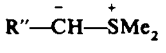
$R{-}CHCl{-}\underset{\underset{NOH}{\|}}{C}{-}R'$

II



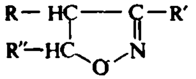
$R{-}CHCl{-}\underset{\underset{NO}{|}}{CH}{-}R'$

I



$R''{-}\overset{-}{C}H{-}\overset{+}{S}Me_2$

IV



VII

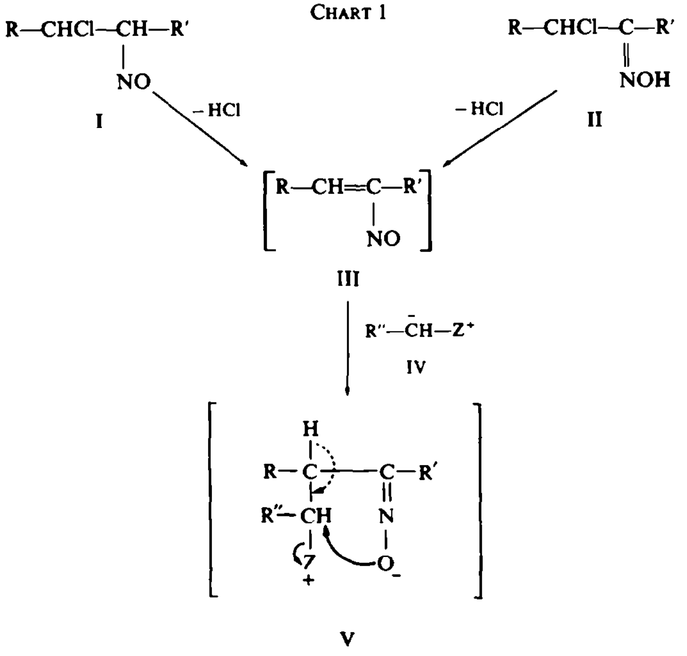
	R	R′	R″	Yields % from II	Yields % from I
a	Me	Me	PhCO	62	55
b	$-(CH_2)_4-$		PhCO		77[a]
c	$-(CH_2)_5-$		PhCO	63	98
d	$-(CH_2)_6-$		PhCO		77
e	Ph	Me	Me_3CCO	45	
f	Ph	Me	PhCO	67	71
g	$p\cdot MeOC_6H_4$	Me	PhCO	85	
h[b]	H	Ph	PhCO	69	
i	H	PhCO	PhCO		86

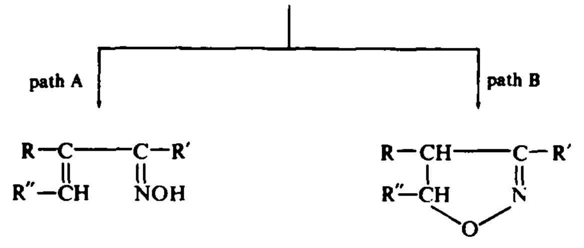
[a] In a different run, after the basic solution of the isoxazoline had been kept for a long time before extraction, the yield was much lower and benzonitrile and 3-phenylpropandione were obtained, due to the basic fission of the isoxazoline, according to the trend observed by Grünanger *et al.*[5] for 5-acylisoxazolines.

[b] IIh, Br instead of Cl.

Two different pathways are possible for the reaction of compounds of structure I or II with sulphonium ylides. A reasonable scheme is illustrated in Chart 1:

CHART 1



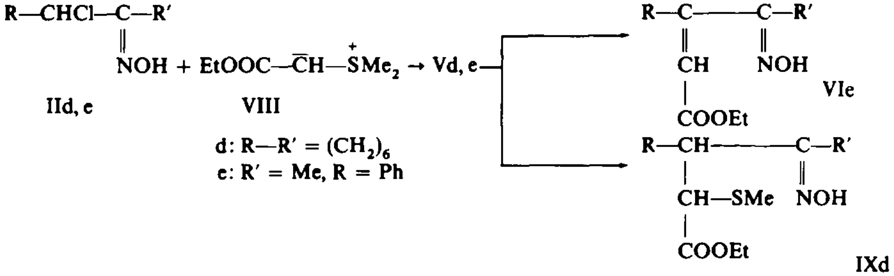


VI
when R″ = H
and Z = SOMe$_2$

VII
when R″ = aryl-CO, alkyl-CO
and Z = SMe$_2$

First the attack of the ylide (IV) on the chlorooxime (II) or nitrosochloride (I) leads to the betaine (V) probably through an intermediate nitrosoalkene (III)[6,*]. Then V can undergo either a β-elimination affording the α,β-unsaturated oxime VI (path A, when R″ = H and Z = SOMe$_2$), or the Δ^2-isoxazoline (VII) can be formed by an intramolecular nucleophilic displacement of sulphide (path B, when R″ = aryl-CO or alkyl-CO and Z = SMe$_2$).[†]

The different results obtained by dimethyloxosulphonium methylide with respect to carbonyl-stabilized ylides suggest that the basicity of the ylide is the main factor in determining the fate of the betaine (V). It is interesting that when the chlorooximes (IIe and IId) were reacted with the ylide ester (VIII) which is more basic than the keto-ylide (IVa),[8] though less basic than dimethyloxosulphonium methylide, no isoxazoline could be obtained: IIe afforded the α,β-unsaturated oxime (VIe)[‡] according to path A (chart 1) while IId afforded the thioether (IXd). This thio-ether arises from the intermediate betaine (Vd) through a demethylation of the sulphonium group by a base, a process already observed in other similar cases.[1,9]



IId, e

VIII

d: R—R′ = $(CH_2)_6$
e: R′ = Me, R = Ph

VIe

IXd

Apart from basicity, other factors, such as the configuration of the oximate anion in V and branching at the α-carbon in the chlorooxime or in the ylide should govern the fate of the betaine V. A change of the solvent does not affect greatly the course of the reaction, since dimethyloxosulphonium methylide on reaction with IIc affords the corresponding α-methylene oxime VIc [R—R′ = $(CH_2)_5$, R″ = H], either in THF

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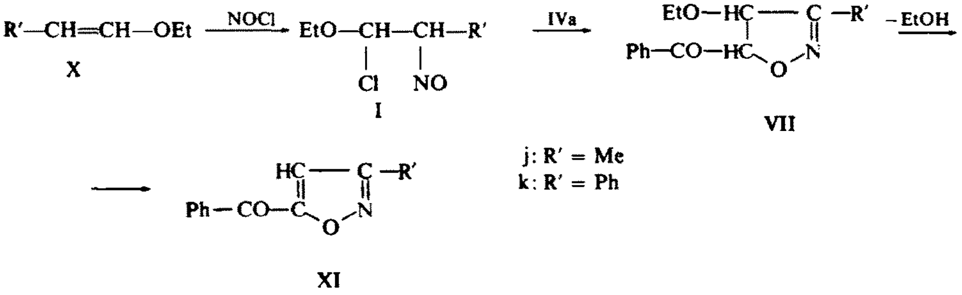
[*] Two moles of ylide are required, the first one to dehydrohalogenate I or II, the second one for the 1,4-attack on the nitrosoalkene.

[†] The formation of VII by cyclization of VI seems unlikely in view of the findings of Scott *et al.*[7]

[‡] Both *cis* and *trans* isomers.

or in the strongly polar DMSO,[3,4] while the stabilized ylide (IVa) upon reaction with IIc, affords only the isoxazoline (VIIc) in either solvent.

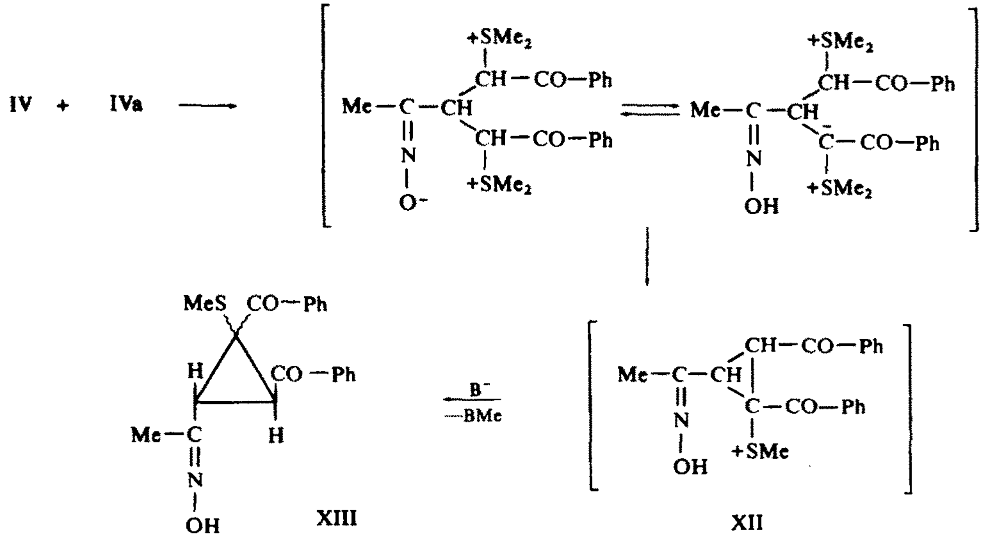
Table 1 shows that, while R″ should be an electron withdrawing group (from a stabilized ylide), R and R′ can be either hydrogen, an alkyl, an aryl or an acyl group.* Also two unstable and highly reactive α-alkoxy-α-chloronitroso compounds (Ij, k), obtained *in situ* from the enol ethers Xj, k and NOCl according to the procedure of Ogloblin,[10,11] led to the expected 4-alkoxy-Δ^2-isoxazolines (VIIj, k) which during the work up underwent loss of alcohol to give the corresponding isoxazoles (XIj, k) in an overall yield of 5% and 50% respectively;



X I VII XI

j: R′ = Me
k: R′ = Ph

An interesting product, the cyclopropane XIII has been isolated from the reaction of Ij with IVa in 20% yield. Its formation can be examined by substitution of both chlorine and ethoxyl in the nitrosochloride by two moles of IVa,† followed by cyclization and demethylation of the resulting cyclopropyl sulphonium salt (XII).



XIII XII

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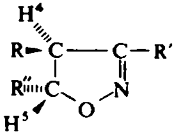
*The reaction of 2,4,4-trimethyl-2-chloro-3-nitrosopentane ($Me_2CCl{-}CHNO{-}CMe_3$) with IVa affords the corresponding α-methyleneoxime ($CH_2 = CMe{-}C(NOH){-}CMe_3$) by a β-elimination of HCl. A similar trend has been observed for nitrosochlorides (with the chlorine on a tertiary C atom) on reaction with the Corey reagent.[4]

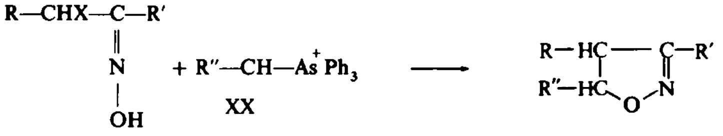
†Probably through a double elimination–addition process.

Table 2. NMR data of Δ^2-isoxazolines (δ, ppm; J, Hz; in $CDCl_3$)



Compound	H^4	H^5	R	R′	R″
VIIa	3·4–4·1 (m)	5·19 (d, $J_{H^5H^4}$ 7)	1·31 (d, Me, J_{Me,H^4} 7)	1·98 (d, Me, J_{Me,H^4} 1)	7·2–8·2 (m Ar)
VIIb	3·3–3·9 (m)	5·19 (d, J_{H^5,H^4} 8·5)	1·2–3·0 (m, —$(CH_2)_4$—)		7·2–8·2 (m, Ar)
VIIc	3·5–4·1 (m)	5·17 (d, J_{H^5,H^4} 8)	1·2–2·8 (m, —$(CH_2)_5$—)		7·1–8·1 (m, Ar)
VIId	3·5–4·1 (m)	5·27 (d, J_{H^5,H^4} 8)	1·4–2·9 (m, —$(CH_2)_6$—)		7·2–8·2 (m, Ar)
VIIe	4·59 (dd, $J_{H^4,Me}$ 1, J_{H^4,H^5} 6·5)	5·09 (d, J_{H^5,H^4} 6·5)	7·1–7·5 (m, C_6H_5)	1·82 (d, Me, J_{Me,H^4} 1)	1·21 (s, Me_3CCO)
VIIf	4·85 (dd, $J_{H^4,Me}$ 1, J_{H^4,H^5} 6)	5·58 (d, J_{H^5,H^4} 6)	7·1–8·1 (m, C_6H_5)	1·85 (d, Me, J_{Me,H^4} 1)	7·1–8·1 (m, Ar)
VIIg	4·78 (m)	5·53 (d, J_{H^5,H^4} 6)	3·78 (s, MeO); 6·8–7·3 (m, Ar)	1·84 (d, Me, J_{Me,H^4} 1)	7·3–8·3 (m, Ar)
VIIh	4·02 (ABX, J_{H^4,H^5} 7·5, $J_{H^4,R}$ 17)	5·88 (ABX, J_{H^5,H^4} 7·5, $J_{H^5,R}$ 11·5)	3·52 (ABX, H, $J_{R,H4}$ 17, J_{R,H^5} 11·5)	7·2–8·3 (m, Ar)	7·2–8·3 (m, Ar)
VIIi	3·95 (ABX, J_{H^4,H^5} 7·5, $J_{H^4,R}$ 17·5)	5·95 (ABX, $J_{H^5,H}$ 7·5, $J_{H^5,R}$ 12)	3·6 (ABX, H, J_{R,H^4} 17·5, J_{R,H^5} 12)	7·2–8·3 (m, Ar)	7·2–8·3 (m, Ar)
VIIl	3·6–4·1 (m)	5·23 (d, J_{H^5,H^4} 8·5)	1·4–2·2 (m, —$(CH_2)_6$—)		2·41 (s, Me; 7, 1–8·1, Ar)
VIIm	3·15–3·60 (m)	4·43 (d, J_{H^5,H^4} 7·5)	1·3–2·2 (m, —$(CH_2)_6$—)		2·29 (s, MeCO)

With the aim of extending our comparative studies on sulphonium and arsonium ylides,[1,12] we have reacted some ketostabilized triphenylarsonium ylides (XX, R″ = MeCO or PhCO or $p \cdot MeC_6H_4CO$) with three different halooximes (IIf, d, h). As in the case of dimethylsulphonium ylides, Δ^2-isoxazolines were obtained as the main product, though in less satisfactory yields.



IId, f, h

VII

	R	R′	R″	Yields %
f	Ph	Me	PhCO	34
h	H	Ph	PhCO	50*
l	$-(CH_2)_6-$		$p.MeC_6H_4CO$	62
m	$-(CH_2)_6-$		MeCO	20

In contrast, the reaction between IIe and triphenylphosphonium phenacylide afforded a complex mixture of compounds which was not resolved. Here again arsonium ylides behave as sulphonium rather than phosphonium ylides.[1,12,13]

Structures

The structural assignment of the Δ^2-isoxazolines has been made on the basis of their NMR spectra (Table 2). In the case of 4-substituted isoxazolines, which can exist in two configurations, only the more stable *trans* isomer was obtained, though no attempt has been made to identify any small amount of the *cis* isomer.

In Table 2, the value of $J_{4,5}$ (6–8 Hz) offer a certain degree of ambiguity (*cis* against *trans*) if compared with the data available for Δ^2-isoxazolines.[14,15] In fact for these compounds J_{trans} is usually in the range between 3 and 8 Hz, while J_{cis} is between 8 and 15 Hz. To make sure, we synthetized the *trans*-3-methyl-4-phenyl-5-benzoyl-Δ^2-isoxazoline from acetonitrile oxide and *trans* chalcone. Its identity with VIIf obtained from If (or IIf) and IVa proved the correctness of the structural assignment. By analogy we have assumed that all our isoxazolines have the *trans*† configurations.

The cinnamic ester (VIe) has been obtained in both *cis* and *trans* form‡ (VIe and VIe). The two isomers (spectroscopic data in Tables 2 and 3) show the OH signal in the NMR spectrum, taken in DMSO-d_6, at ~11·0 and 11·8 ppm, in agreement with the values given in the literature for oximic protons.[16] The vinnylic proton of both isomers falls very close to 6·3 ppm. Larger differences are found for other protons.

The crude ester IXd, as obtained by chromatography in form of a sticky material,

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* During the work up part of the isoxazoline spontaneously underwent basic fission[5] giving 3-phenylpropandione (cfr footnote a under Table 1).

† Recent NMR studies on many acyl substituted Δ^2-isoxazolines by Prof. P. Vita Finzi support our assumption. We thank Prof. P. Vita Finzi for this kind information.

‡ The possibility of a *syn–anti* isomerism due to the oximic group, though less likely, can not be completely discarded.

TABLE 3. PHYSICAL PROPERTIES OF NEW COMPOUNDS OBTAINED

Compound	Formula	M.p., solvent	IR (cm^{-1})^{a,b}	UV,^{c} λ_{max}, nm (ε)	Analyses: Calcd. Found C%	H%	N%
VIIa	$C_{12}H_{13}O_2N$	60	1695, 1450, 1380, 1285, 1240	247	70·9	6·4	6·9
		hexane	915, 855, 725, 690	(13500)	70·6	6·2	6·7
VIIb	$C_{14}H_{15}O_2N$	liquid	1700, 1450, 1270, 1230, 1005				
			935, 850, 840, 755, 695			^{d}	
VIIc	$C_{15}H_{17}O_2N$	87	1700, 1450, 1230, 1220, 940	248	74·0	7·0	5·8
		benzene–hexane	932, 900, 867, 840, 694	(13500)	73.6	6·9	5·6
VIId	$C_{16}H_{19}O_2N$	77	1695, 1470, 1445, 1370, 1240,	247	74·7	7·4	5·4
		benzene–hexane	1210, 970, 940, 875, 853, 697	(14300)	74·4	7·6	5·3
VIIe	$C_{15}H_{19}O_2N$	liquid	2920, 1710, 1490, 1430, 1375, 1360	204			5·7
			1075, 1050, 865, 755, 703	(12000)			5·4
VIIf	$C_{17}H_{15}O_2N$	41	1700, 1375, 1230, 950, 915, 892,	248	76·9	5·7	5·3
		hexane	855, 780, 750, 698	(15100)	76·3	5·5	5·2
VIIg	$C_{18}H_{17}O_3N$	80	1695, 1510, 1450, 1305, 1210, 1180,	231 247	73·2	5·8	4·7
		benzene–hexane	1075, 860, 690	(16600) (15900)	73·6	5·8	4·7
VIIh	$C_{16}H_{13}O_2N$	100	1690, 1450, 1350, 1220, 872, 847,	255	76·5	5·2	5·6
		benzene	770, 693	(24900)	76·6	5·3	5·5
VIIi	$C_{17}H_{13}O_3N$	83	1695, 1650, 1445, 1270, 1225, 1150,	254	73·1	4·7	5·0
		hexane	922, 895, 863, 705, 695	(16600)	72·9	4·6	4·9
VIIl	$C_{17}H_{21}O_2N$	53	1695, 1605, 1465, 1450, 1370, 1240.	259	75·2	7·8	5·2
		hexane	1210, 1185, 935, 875, 855	(15600)	75·6	7·9	5·0
VIIm	$C_{11}H_{17}O_2N$	liquid	1720, 1455, 1350, 1240, 1175, 940,	258			7·2
			875, 820, 795	(8,500)			7·1
VIe*	$C_{13}H_{15}O_3N$	liquid	3210, 1705, 1445, 1365, 1280, 1075	271			6·0
			772, 697	(14100)			5·8
VIe	$C_{13}H_{15}O_3N$	81	3200, 1720, 1185, 1170, 1010, 895,	259			6·0
		benzene–hexane	875, 782, 708	(12400)			5·9
IXd	$C_{13}H_{23}O_3NS$	64	3190, 1715, 1455, 1440, 1255, 1175,	203	57·1	8·5	5·1
		pentane	1110, 1100, 1025, 960, 920, 855	(6250)	57·7	8·9	4·9
XIj	$C_{11}H_9O_2N$	68	1665, 1300, 1210, 1135, 1010, 927,	265	70·6	4·8	7·4
		hexane	890, 738, 700	(16000)	70·8	4·5	7·2
XIII^{e}	$C_{20}H_{19}O_3NS$	187	3350, 1680, 1660, 1450, 1270, 1220,	250			4·0
		benzene–hexane	1010, 793, 780, 715, 705	(25200)			4·3

[a] Only prominents peaks are reported

[b] In nujol when solid, neat when liquid

[c] In 95% ethanol

[d] Mass Spectrum: 229 (M^+), 124 (M^+—PhCO), 105 ($PhCO^+$) base peak

[e] S%: Found 8·8; Calcd. 9·1.

on the basis of its NMR spectrum appeared as a mixture of two diastereoisomers (or perhaps *sin–anti* isomers). The most abundant isomer could be obtained in pure form on crystallization from pentane. Its NMR spectrum in $CDCl_3$ shows the $MeCH_2$ at 1·28 (t, *J* 7 Hz), the MeS at 2·08 (s), the CHS at 3·18 (d, *J* 11 Hz) and the CH_2Me at 4·19 ppm (q, *J* 7 Hz). The mass spectrum shows peaks at 273 (M^+), 256 (M^+—OH), 226 (M^+—SMe), 200 *m/e* (M^+—COOEt).

The structure of the cyclopropane XIII was inferred mainly on the basis of its NMR spectrum (in DMSO-d_6) which shows two Me singlets at 2·01 and 2·04 ppm. The two cyclopropane ring protons appear as two doublets at 3·20 and 3·98 ppm. The *J* value (6·5 Hz) shows a *trans* relationship between these two protons.[17] The sharpness of all signals and m.p. exclude the possibility of a mixture of diasteroisomers. The mass spectrum shows peaks at 353 (M^+), 336 (M^+—OH), 306 (M^+—MeS), 248 (M^+—PhCO), 105 *m/e*, base peak (PhCO).

EXPERIMENTAL

The chlorooximes and nitroso chlorides used, unless otherwise stated, were prepared in a pure state by known procedures.[18, 19] The sulphonium and arsonium ylides were obtained by basic treatment from the corresponding salts.[9, 20] All solvents were dried: DMSO over CaH_2, THF and ethyl ether over LAH. Physico-chemical data for new compounds are reported in Table 3 and NMR data for Δ^2-isoxazolines are reported in Table 2. M.ps are uncorrected IR spectra were measured, in nujol when solid, neat when liquid, with a Perkin–Elmer Mod. 137 Infracord spectrometer. Only prominent peaks are reported (cm^{-1}). NMR spectra were recorded on a Varian A-60 instrument; chemical shifts (δ, ppm) were measured from TMS as internal reference. Mass spectra were taken on a Hitachi–Perkin–Elmer RMU 6D (single focusing spectrometer at 70 eV. Column chromatographies were performed on silica gel 0·05–0·20 (Merck–Darmstadt).

General procedure for the reaction between chlorooximes (II) *or nitroso chlorides* (I) *and carbonyl stabilized dimethylsulphonium* (IV) *or triphenylarsonium methylides* (XX). The ylide (0·035 moles) in THF (100 ml) was added to a soln of the chlorooximes (0·015 moles) or nitrosochlorides in THF (50 ml) while stirring and cooling with an ice–water bath. The mixture was kept under N_2 at room temp overnight and, after filtration of the sulphonium or arsonium salt which separated, poured into ice–water. After neutralization with dil HCl the liquor was extracted with ether, the extracts were washed with water and dried over Na_2SO_4. The crude product obtained after evaporation of the solvent was purified by crystallization or by chromatography on silica gel using hexane–ether 90/10 as eluent.

Reaction of α-chlorocycloheptanone oxime (IIc) *with dimethylsulphonium phenacylide* (IVa) *in DMSO.* A soln of IIc (1·3 g; 0·008 moles) in DMSO (20 ml) was added under stirring and cooling to a soln of IVa (3 g; 0·016 moles) in DMSO (40 ml). After 15 min the mixture was worked up as described and the 3,4-pentamethylen-5-phenacyl-Δ^2-isoxazoline was isolated in 95% yields.

Reaction of α-chlorocylopheptanone oxime (IIc) *with dimethyloxosulphonium methylide in* THF. A soln of IIc (1·3 g; 0·008 moles) in THF (50 ml) was added to a soln of dimethyl-oxosulphonium methylide (0·02 moles) in THF (200 ml).[21] The mixture was stirred overnight at room tem and, after the usual work up, gave the α-methylencycloheptanone oxime, 0·74 g (68% yields), identified by IR and NMR comparison with an authentic sample.[4]

Reaction of α-chlorocylooctane oxime (IId) with dimethylsulphonium carbetossymethylide (VIII). A soln of IId (3·5 g; 0·02 moles) in THF (20 ml) was added to a soln of VIII[22] (6 g; 0·04 moles) in THF (40 ml). The mixture was left at room temp under N_2 for 36 hr and worked up as above. Compound IXd was isolated by silica gel chromatography (hexane–ether 85/15) as a mixture of two diasteroisomers (see general section), 3·2 g (72% yields). The isomer m.p. 64° was isolated in pure form by crystallization of the mixture from pentane in the cold.

Reaction of 1-*chloro*-1-*phenylacetone oxime* (IIe) *with dimethylsulphonium carbethoxy methylide* (VIII). A soln of IIe (2g; 0·011 moles) and VIII (6·3 g; 0·025 moles) in THF (60 ml) was stirred overnight at room temp under N_2. After the usual work up and a silica gel chromatography of the residue (hexane–ether 90/10), 0·85 g (34% yields) of VIe M.S. 233 (M^+), 216 (M^+—OH, 188 (M^+—C_2H_5O), 160 (M^+—C_2H_5OCO), 102 *m/e* (C_6H_5CCH) and 0·42 g (17% yields of VIe, liquid M.S.: 233 (M^+), 216 (M^+—OH), 188 (M^+—C_2H_5O), 160 (M^+—C_2H_5OCO), 102 *m/e* (C_6H_5CCH) were obtained.

Reaction of benzoylethylene with NOCl *and dimethylsulphonium phenacylide* (IVa). NOCl (0·46 g; 0·007 moles) was added, while stirring and cooling with an ice–water bath to a soln of benzoylethylene (0·93 g; 0·007 moles) in ether (50 ml).[23] A soln of IVa (4·3 g, 0·024 moles) was added to the suspension of the adduct. The mixture was left at room temp overnight and, after the usual work-up, gave 1·7 g (86% yields) of VIIi, m.p. 83° (benzene–hexane).

Reaction of ethyl propenyl ether (Xj) *with* NOCl *and dimethylsulphonium phenacylide* (IVa). NOCl (2·4 g; 0·04 moles) was absorbed into a soln of Xj (3·45 g; 0·04 moles) in ether (70 ml) at −75°, under stirring. A soln of IVa (11 g; (0·06 moles) in THF (50 ml) was added after 30 min. The mixture was stirred in the cold (−70, −40 °C) overnight, then poured in water, neutralized with dil HCl and extracted with ether. The extracts, after the usual work-up, gave after silica gel chromatography (hexane–ether 95/15) 200 mg (5% yields) of XIj, M.S.: 187 (M^+), 105 *m/e* (C_6H_5CO) and 0·78 g of XIII.

Reaction of β*-acetoxystyrene* (Xk) *with* NOCl *and dimethylsulphonium phenacylide* (IVa). NOCl (1·3 g; 0·02 moles) was added with stirring to a soln of Xk (3g, 0·02 moles) in ether (50 ml) at −70° under N_2. A soln of IVa (6 g; 0·05 moles) in THF (50 ml) was added to the suspension of the nitroso chloride. The mixture was left at −40° stirring for 40 min. After the usual work up 2·3 g (45% yields) of XIk were obtained, purified by silica gel chromatography (hexane–ether 95/5) and identified by IR and NMR comparison with an authentic sample.[24]

Reaction of acetonitrile oxide with trans*-chalcone:* trans*-3-methyl-4-phenyl-5-benzoyl-*Δ^2*-isoxaokline.* A soln of 1-chloroacetaldoxime (1·2 g; 0·012 moles) in ether (30 ml) and a soln of triethylamine (1·21 g; 0·012 moles in ether (20 ml) was added simultaneously to a soln of *trans*-chalcone (2·3 g; 0·011 moles) in THF (80 ml). The mixture was left a few hr at room temp and after the usual work up gave a residue from which by silica gel chromatography VIIf(0·75 g; 28 yiels) was isolated together with 0·42 of unreacted chalcone. NMR and IR spectra were identical to those of the samples obtained from the reaction of If and IIf with dimethylsulphonium phenacylide.

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