An Electron Spin Resonance Study of 3-Oxypropenoyl Radicals derived from Glycidols

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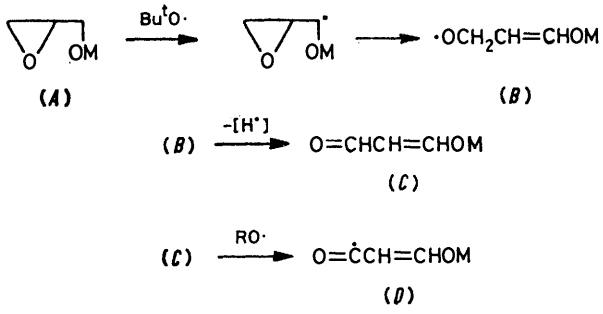
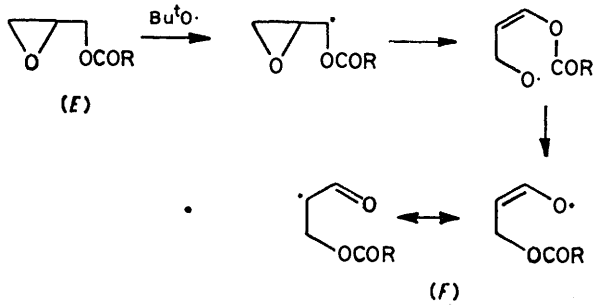
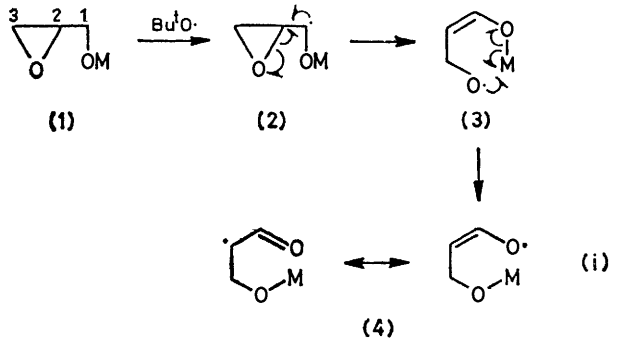
Glycidols with blocked OH groups (*A*; M = alkyl or trialkylsilyl) react with t-butoxyl radicals to show the e.s.r. spectra of the corresponding 3-oxypropenoyl radicals (*D*), and 24 examples of these acyl radicals are reported. The



reaction is thought to proceed through the formation of the allyloxyl radicals (*B*), which, in part, are converted into the aldehyde (*C*) which is very reactive towards loss of hydrogen to give the acyl radical (*D*). Glycidyl pivalate (*A*; M = $COCMe_3$) reacts cleanly in this way, but glycidyl acetate (*E*; R = Me) also undergoes intramolecular 1,5-transfer of the acyl group to show the spectrum of the enoxyl radical (*F*). Glycidyl propionate and butyrate do not undergo this acyl transfer, but show the spectra of the radicals $O{=}\dot{C}CH{=}CHOCOCH_2R'$ and $\overline{OCH_2\dot{C}HCH_2}$-$OCO\dot{C}HR'$ (R' = Me or Et).



In 1975 we showed that the photolysis of di-t-butyl peroxide in the presence of glycidol (**1**; M = H) showed the superimposed e.s.r. spectra of two radicals.[1] The one



in higher concentration was identified as the enoxyl radical (4) which is formed by the ring-opening of the initial radical (2), followed by intramolecular 1,5-hydrogen transfer within the radical (3).

The second radical showed a simple doublet spectrum. Its low *g*-value (*ca.* 2.0005) suggested that it might be an acyl radical, but the hyperfine coupling, a(1H) 19.5 G, was twice as large as any which had been reported at that time for an acyl radical.

Subsequent work however has shown that whereas simple saturated acyl radicals do show values of $a(H_\beta)$ of below 4 G, 2,3-unsaturated acyl radicals adopt an *s-trans*-conformation about the C(1)–C(2) bond, and show values of $a(1H_\beta)$ of 18—20 G.[2]

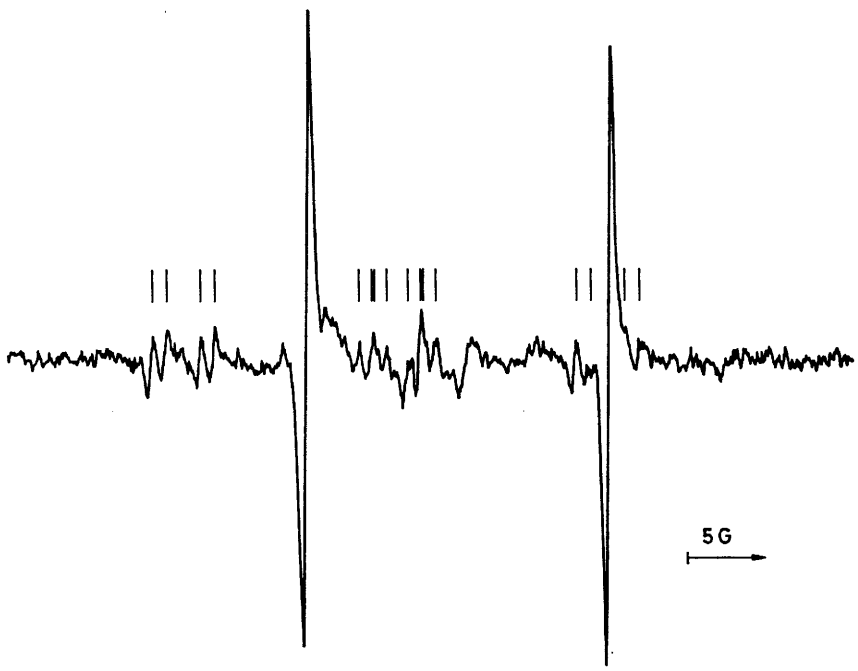
We have now returned to the question of the identity of the radical which gives rise to this doublet. It is indeed due to an unsaturated acyl radical which is formed through a ring-opening reaction. If the OH group of the glycidol is blocked by an alkyl or silyl group, acyl radicals are the principal species which are observed, and this reaction then provides a route to a variety of 3-oxypropenoyl radicals; the e.s.r. spectra of only six unsaturated acyl radicals have been reported previously,[2] none with functional substituents.

TABLE 1

E.s.r. spectra of acyl radicals derived from the reaction of t-butoxyl radicals with derivatives of glycidols and related compounds

Reactant	B.p. (°C) [p(mmHg)]	Acyl radical	$a(H_\beta)$/G [a]	g	T/°C
$\overline{OCH_2CHCH_2OH}$	161 [760]	(5) O=ĊCH=CHOH	19.5	2.0008	−29
$\overline{OCH_2CHCH_2OMe}$	35 [20]	(6) O=ĊCH=CHOMe	18.50	2.0006	−120
$\overline{OCH_2CHCH_2OEt}$	45 [17]	(7) O=ĊCH=CHOEt	18.6		−120
$\overline{OCH_2CHCH_2OCH_2CF_3}$	40—42 [17]	(8) O=ĊCH=CHOCH$_2$CF$_3$	18.65	2.0006	−100
$\overline{OCH_2CHCH_2OCH_2CMe_3}$	68 [6]	(9) O=ĊCH=CHOCH$_2$CMe$_3$	18.5	2.0006	−100
$\overline{OCH_2CHCH_2OCMe_3}$	47 [9]	(10) O=ĊCH=CHOCMe$_3$	19.79	2.0008	−100
$\overline{OCH_2CHCH_2OSiMe_3}$	80 [9]	(11) O=ĊCH=CHOSiMe$_3$	19.22	2.0008	−80
$\overline{OCH_2CHCH_2OSiEt_3}$	94 [9]	(12) O=ĊCH=CHOSiEt$_3$	19.21	2.0006	−90
$\overline{OCH_2CHCH_2OSiMe_2Bu^t}$	74 [9]	(13) O=ĊCH=CHOSiMe$_2$Bu^t	19.32	2.0005	−100
$\overline{OCH_2CHCH_2OSiMe_2CH_2Ph}$	84 [0.05]	(14) O=ĊCH=CHOSiMe$_2$CH$_2$Ph	19.6		−80
$\overline{OCH_2CHCH_2OGeMe_3}$	76 [9]	(15) O=ĊCH=CHOGeMe$_3$	19.36	2.0007	−100
$\overline{OCH_2CHCHMeOSiMe_3}$	65 [9]	(16) O=ĊCH=CMeOSiMe$_3$	18.2	2.0007	−95
$\overline{OCH_2CMeCH_2OSiMe_3}$	69 [9]	(17) O=ĊCMe=CHOSiMe$_3$	0.8 [b]	2.0007	
$\overline{OCHMeCHCH_2OSiMe_3}$	75 [9]	(18) No radical observed			
$\overline{OCH_2CHCH_2OCOMe}$	82—84 [9]	(19) O=ĊCH=CHOCOMe	19.5	2.0008	−70
$\overline{OCH_2CHCH_2OCOCH_2Me}$	80 [6]	(20) O=ĊCH=CHOCOCH$_2$Me	19.0	2.0007	−88
$\overline{OCH_2CHCH_2OCOCH_2Et}$	82—84 [6]	(21) O=ĊCH=CHOCOCH$_2$Et	19.2	2.0007	−47
$\overline{OCH_2CHCH_2OCOCMe_3}$	71 [15]	(22) O=ĊCH=CHOCOCMe$_3$	19.0		−100
cis-O=CHCH=CHOMe [c]		(23) *cis*-O=ĊCH=CHOMe	19.63	2.0008	−110
trans-O=CHCH=CHOMe [c]		(24) *trans*-O=ĊCH=CHOMe	18.21	2.0008	−120
trans-O=CHCH=CHOSiMe$_3$		(25) *trans*-O=ĊCH=CHOSiMe$_3$	18.06	2.0007	−58

[a] Values quoted to 0.1 G have been taken from the pre-calibrated chart paper. Values quoted to 0.01 G have been measured from field markers obtained using a proton magnetometer, and are uncorrected. [b] $3H_\gamma$. [c] Present as impurities in the corresponding alcohols.



E.s.r. spectrum of the radicals O=ĊCH=CHOSiMe$_2$Bu^t and (as indicated) HOĊHCH=CHOSiMe$_2$Bu^t obtained from the photolysis of di-t-butyl peroxide in the presence of $\overline{OCH_2CHCH_2OSiMe_2Bu^t}$ in cyclopropane at −100 °C

RESULTS

A number of *O*-alkyl, *O*-trialkylsilyl, *O*-trimethylgermyl, and *O*-tributylstannyl derivatives of glycidol, and the *O*-trimethylsilyl and *O*-tributylstannyl derivatives of 1-, 2-, and 3-methylglycidol were prepared, and were caused to react with photolytically generated t-butoxyl radicals, and the radicals which were formed were monitored by e.s.r. spectroscopy.

The OH and $OSnBu_3$ compounds (apart from glycidol itself as described above) showed only the spectra of the enoxyl radicals resulting from ring-opening followed by intramolecular 1,5-transfer of H or SnR_3 [*cf.* equation (1)], and this work has been published separately.[3]

Most of the other compounds showed only or principally a spectrum consisting of a doublet a(H) 18.2—19.8 G, with a low g-value (2.0005—2.0008), [Table 1, radicals (5)—(16), (19)—(22)]. Some further radicals which were observed in some of these reactions are listed in Table 2. A typical spectrum is shown in the Figure.

TABLE 2

E.s.r. spectra of other radicals derived from the reaction of t-butoxyl radicals with derivatives of glycidols

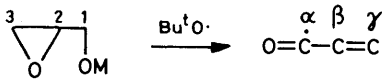
Reactant	Radical	a/G: 1 H_α	H_β	1 H_γ	Others	g	T/°C
OCH$_2$CHCH$_2$OH	(26) HOCH$_2$ĊCH=O	18.3	26.9 (2H)		1.25 (CHO)		−45
OCH$_2$CHCH$_2$OSiMe$_3$ [a]	(27) HOĊCH=CHOSiMe$_3$	13.0	3.0 (1H)	14.0	1.0 (OH)	2.0032	−100
OCH$_2$CHCH$_2$OSiEt$_3$ [a]	(28) HOĊCH=CHOSiEt$_3$	13.3	3.1 (1H)	14.1	0.9 (OH)	2.0031	−80
OCH$_2$CHCH$_2$OSiMe$_2$Bu^t [a]	(29) HOĊCH=CHOSiMe$_2$Bu^t	13.5	3.0 (1H)	14.1	0.9 (OH)	2.0033	−100
OCH$_2$CHCH$_2$OSiMe$_2$CH$_2$Ph [a]	(30) HOĊCH=CHOSiMe$_2$CH$_2$Ph	13.3	3.1 (1H)	14.1	0.9 (OH)		−80
OCH$_2$CHCH$_2$OCOMe	(31) MeCOOCH$_2$ĊCH=O	18.5	28.8 (2H)		1.4 (1H)	2.0045	−80
OCH$_2$CHCH$_2$OCOCH$_2$Me	(32) OCH$_2$ĊHCH$_2$OCOCHMe	20.3	24.6 (3H)		3.0 (2H)	2.0035	−104
OCH$_2$CHCH$_2$OCOCH$_2$CH$_2$Me	(33) OCH$_2$ĊHCH$_2$OCOĊHCH$_2$Me	20	24 (2H)		2.5 (2H)	2.0029	−99

[a] The assignment of $a(H_\alpha)$ and $a(H_\gamma)$ in the radicals (27)—(30) is arbitrary.

DISCUSSION

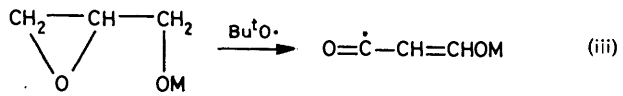
The Identification of the Acyl Radicals.—The low g-values of the radicals listed in Table 1, and the magnitudes of the hyperfine coupling constants, unambiguously identify radicals (5)—(16) and (19)—(22) as unsaturated acyl radicals containing the group =CH–Ċ=O; for comparison, the radical MeCH=CH–Ċ=O from *trans*-crotonaldehyde shows $a(H_\beta)$ 19.5 G, g 2.0005.[2,*] Similarly, the parameters for the radical (17) derived from the trimethylsilyl derivative of 2-methylglycidol are characteristic of a β-methylacyl radical containing the group =CMe–Ċ=O; for comparison, the radical EtCH=CMeĊ=O shows $a(3H_\gamma)$ 1.1 G, g 2.0005.[2] The C(2) atom of the glycidol thus provides the β-carbon atom in the acyl radical.

As methylation of the glycidol at C(1) permits an acyl radical to be formed (16), but no radical could be detected when C(3) was methylated (18), we conclude that the acyl group must originate at the C(3) centre, as in equation (ii).



(ii)

Although the variation in the values of $a(H_\beta)$ and g for the acyl radicals obtained from the various derivatives of glycidol in Table 1 is small, it is well outside the experimental error, and this was confirmed by photolysing di-t-butyl peroxide in the presence of a mixture of the methyl and t-butyl ethers of glycidol, when the superimposed spectra of the radicals (6) and (10) were observed. It appears then that these various radicals are differentiated by retention of the original OM group as shown in equation (iii).



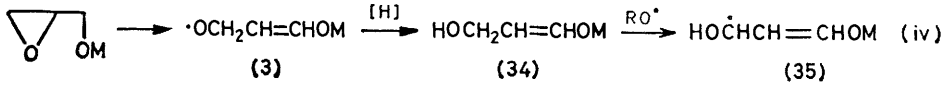
(iii)

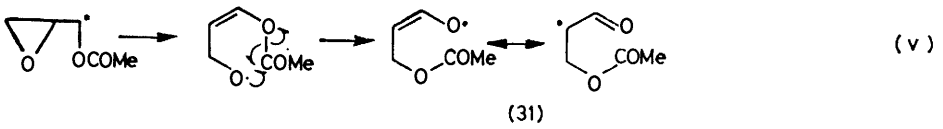
The monotrimethylsilyl ether of the *trans*-monoenol of malonic dialdehyde reacted with t-butoxyl radicals to give an acyl radical (25) with $a(H_\beta)$ 18.06 G, whereas the trimethylsilyl ether of glycidol gave an acyl radical (11) with $a(H_\beta)$ 19.22 G, which presumably therefore has the *cis*-configuration about the C=C double bond. On the other hand, the radical (6) derived from the methyl ether of glycidol gave an acyl radical with $a(H_\beta)$ close to the value for the radical (24) derived from *trans*- rather than *cis*-methoxyacrolein (see below), and therefore (6) appears to be the *trans*-isomer; the difference between the hyperfine coupling constants of the radicals (6) and (24) can probably be ascribed to the different compositions of the media.

Other Radicals observed.—The silyl ethers of glycidol showed, superimposed on the spectra of the acyl radicals, weak spectra of 1,3-dioxyallyl radicals [see Table 2, (27)—(30)]; the spectrum shown in the Figure is typical. S_H2 Reactions at silicon are almost unknown, and radical

* The oxiranylacyl radical OCH$_2$ĊH–Ċ=O is excluded because it (like the cyclopropylacyl radical CH$_2$CH$_2$ĊH–Ċ=O [4]), at −125 °C, shows the spectrum of two acyl radicals $a(H_\beta)$ 14.2 and 1.6 G, which are ascribed to the two conformations in which the plane containing the C–Ċ=O group bisects the three membered ring. At higher temperatures, rotation about the C_α–C_β bond is rapid on the e.s.r. time scale, and a time-averaged spectrum is observed, $a(H\beta)$ 12.2 G at −50 °C.[5]

(3) presumably cannot undergo 1,5-transfer of silicon. It instead decays to give at least in part the 3-oxyallyl alcohol (34), which undergoes abstraction of allylic hydrogen to give the 1,3-dioxyallyl radical (35) [equation (iv)].





The behaviour of esters of glycidol varied with the structure of the esterifying acid. The acetyl group underwent some 1,5-transfer to show the spectrum of the enoxyl radical (31) [equation (v)], as well as that of the acyl radical (19). This appears to be the first example of the homolytic intramolecular transfer of an acyl group.

The propionate and butyrate instead underwent initial attack of the t-butoxyl radical in part at hydrogen within the acyl group to show the spectra of the radicals (32) and (33) as well as the acyl radicals (20) and (21), but the pivalate gave only the acyl radical (22).

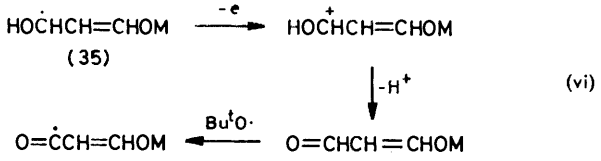
The Mechanism of the Formation of the Acyl Radicals.— The formation of acyl radicals from derivatives of glycidol by reaction (iii) involves the overall loss of three hydrogen atoms. This is an unusual requirement for a free radical reaction, and the mechanism by which it is achieved is not obvious.

The hydrogen atoms in oxiran, like those in cyclopropane, are rather unreactive to attack by t-butoxyl radicals (and oxiran, like cyclopropane, is therefore sometimes used as an ' inert ' solvent in e.s.r. studies). The initial attack of the t-butoxyl radicals would therefore appear to be at hydrogen in the CH_2OM group of the glycidol, as it is believed to be in the reactions giving rise to the enoxyl radicals [equation (i)] or allyl radicals [equation (iv)], and this is most likely followed by ring-opening to give the allyloxyl radicals (3).

It is at this stage that the nature of the group M may be relevant. If the ring-opened radical cannot undergo rapid 1,5-transfer of the group M because M is alkyl, trialkylsilyl, or trialkylgermyl, or because the radical is formed in the *trans*-configuration, the alternative route, leading to the acyl radical, can intrude.

One possible pathway by which the acyl radical might be formed appeared to be as follows. In the absence of transfer of M, the ring-opened radical will abstract hydrogen, probably from the CH_2OM group of the parent glycidol, to give the allyl alcohol (34), and thence the dioxyallyl radical (35), which is sometimes detected as a minor component (Table 2). This radical should readily lose an electron to give the allyl cation, doubly stabilised by the two oxyl substituents.[6] The second hydrogen atom might then be lost as a proton to give the unsaturated aldehyde, which would readily yield the acyl radical [equation (vi)].

The *cis*- and *trans*-isomers of 3-methoxyallyl alcohol were therefore prepared by reduction of methyl 3-methoxyacrylate with di-isobutylaluminium hydride. The alcohols appeared, by n.m.r. spectroscopy, to be free



from the corresponding aldehydes which are presumably intermediates in the reduction. Before purification by preparative g.l.c. the alcohols reacted with t-butoxyl radicals to show the spectra of the acyl radicals (23) or (24), but, after purification, they showed the formation of only the 1,3-dioxyallyl radicals (35).* This shows that it is unlikely that the alcohols (34) or the hydroxyallyl radicals (35) lie on the reaction path to the acyl radicals, and also that very small amounts of the aldehydes are enough to give rise to strong spectra of the acyl radicals.

Analysis by ^1H n.m.r. spectroscopy of the products from the photolysis of di-t-butyl peroxide in the presence of the methyl ether of glycidol showed the presence of only the *cis*- and *trans*-3-methoxyallyl alcohols (34; M = Me), and any concentration of the corresponding aldehydes was below the level of detection.

If our assumption concerning the initial stages of the reaction is correct, the route to acyl radicals must therefore diverge from reaction (iv) at the stage of the allyloxyl radicals (3).

The reaction of the radicals (3) to abstract hydrogen from the parent glycidol derivative is not sufficient to establish a long-chain isomerization to the allyl alcohol (34), and some other reaction must occur.

* The general characteristics of the spectra of the radicals $HO\dot{C}HCH{=}CHOCH_3$ [$a(H_\alpha$ and $H_\gamma)$ *ca.* 14 G, $a(H_\beta)$ *ca.* 3 G] (and of similar alkoxyallyl radicals) were apparent but the spectra could not be analysed in detail because each alcohol can give rise to two isomeric radicals, and their superimposed spectra are further complicated by hyperfine coupling [a(3H) *ca.* 1 G] through the oxygen atom to the methyl group. The spectra of the radicals $HO\dot{C}HCH{=}CHOSiR_3$ (Figure and Table 2) were free of these complications.

It seems probable that some of the allyloxyl radicals escape reduction to the allyl alcohol, and instead transfer a hydrogen atom to some suitable acceptor to leave the corresponding aldehyde [equation (vii)].

$$MOCH{=}CHCH_2O\cdot \xrightarrow{[-H\cdot]} MOCH{=}CH{-}CH{=}O \qquad (vii)$$

The allyloxyl radicals should be powerful hydrogen-transfer reagents. If approximate bond dissociation energies are taken to be $DH°_{298}$(RH) 410 and $DH°_{298}$(πC=O) 314 kJ mol^{-1}, and the resonance stabilisation in the structure C=C–C=O as 25 kJ mol^{-1},[7] the dissociation energy of the C–H bond which is being broken in reaction (vii) would be only *ca.* 71 kJ mol^{-1}, and many of its hydrogen-transfer reactions would be exothermic. Even the methoxyl radical shows $a(3H_\beta)$ 52 G,[8] implying that the canonical form (36) makes *ca.* 10% contribution to the structure of the radical.

$$H{-}CH_2{-}O\cdot \longleftrightarrow H\cdot\ CH_2{=}O$$

(36)

The aldehyde formed by reaction (vii) would then be by far the most reactive component towards t-butoxyl and allyloxyl radicals with which it rapidly reacts to show a strong spectrum of the acyl radical [equation (viii)].

$$MOCH{=}CH{-}CH{=}O \xrightarrow{RO\cdot} MOCH{=}CH{-}\dot{C}{=}O \qquad (viii)$$

The identity of the molecule which accepts the hydrogen atom in reaction (vii) is not clear but there are several reasonable candidates. One possibility is that the glycidol parent or acrolein product R'H [equation (ix)] might react at a hydrogen centre to give molecular hydrogen and to contribute to the allyl or acyl radicals which are observed. Alternatively, it is possible that di-t-butyl peroxide, despite its normal resistance to induced decomposition, might be sterically open to attack by hydrogen at peroxidic oxygen to give t-butyl alcohol and the t-butoxyl radical [equation (ix)].

$$MOCH{=}CHCH_2O\cdot \begin{cases} \xrightarrow{R'H} MOCH{=}CHCH{=}O + R'\cdot + H_2 \\ \xrightarrow{Bu^tOOBu^t} MOCH{=}CHCH{=}O + Bu^tO\cdot + Bu^tOH \end{cases} \qquad (ix)$$

EXPERIMENTAL

The preparation of the glycidols has been described previously.[3]

The glycidyl ethers were prepared from the reaction of epibromohydrin and the appropriate alcohol in the presence of boron trifluoride. A typical example is given below. The ^{1}H n.m.r. and i.r. spectra and elemental analyses were in agreement with the assigned structures. The b.p.s are given in Table 1.

(*t-Butoxymethyl*)*oxiran*.[9]—Epibromohydrin (18.53 g) was added slowly to vigorously stirred ether–boron trifluoride (0.2 cm^3) and t-butyl alcohol (10 g) at 50—55 °C. The mixture was allowed to stand overnight. A solution of sodium hydroxide (5.39 g) in water (5 cm^3) was then added with vigorous stirring. The sodium bromide which separated was filtered off and the organic layer was washed with water and dried ($MgSO_4$), and the glycidyl ether was recovered by distillation, b.p. 47 °C at 9 mmHg, τ(CCl_4) 6.64 (2 H, d, CH_2OBu^t, J 4 Hz), 6.98—7.21 (1 H, m, ring CH), and 7.29 (2 H, m, ring CH_2).

The *O*-trialkylsilyl and *O*-trialkylgermyl derivatives were prepared by silylation (or germylation) of the glycidols. The following reaction is typical. The n.m.r. and i.r. spectra of the products were in agreement with the assigned structures. B.p.s are included in Table 1.

(*Trimethylsilyloxymethyl*)*oxiran*.—Trimethylchlorosilane (1.23 g) was added slowly to a solution of glycidol (1.0 g) and pyridine (0.98 g) in dry ether (15 cm^3) under nitrogen. The mixture was stirred for 45 min, then filtered, and the silyl ether was recovered by distillation, b.p. 80 °C at 9 mmHg, τ(CCl_4) 6.28 [1 H, dd, $CH^ACH^BH^CCOSi$, J(H^AH^C) 7, J(H^BH^C) 12 Hz], 6.60 [1 H, dd, $CH^ACH^BH^CCOSi$, J(H^AH^B) 3 Hz], 6.90—7.30 (1 H, m, ring CH^A), and 7.30—7.70 (2 H, m, ring CH_2).

The following procedure is typical of the preparation of esters of glycidol. N.m.r. and i.r. spectra confirmed the assigned structures. The b.p.s are given in Table 1.

(*Acetoxymethyl*)*oxiran*.—Acetyl chloride (18.05 g) was added dropwise with vigorous stirring during 25 min to a mixture of glycidol (18.52 g) and triethylamine (27.32 g) in toluene (100 cm^3) at 0 °C. After a further 25 min, the mixture was allowed to warm to room temperature, and triethylammonium chloride was filtered off. The solution was rapidly washed three times with iced water, dried, and twice distilled, yielding glycidyl acetate (40% yield), b.p. 82—84 °C at 9 mmHg, τ(CCl_4) 5.66 [1 H, dd, $CH^ACH^BH^COAc$, J(H^AH^C) 4, J(H^BH^C) 12 Hz], 6.15 [1 H, dd, $CH^ACH^BH^COAc$, J(H^AH^B) 6 Hz], 6.70—7.08 (1 H, m, ring CH^A), 7.10—7.56 (2 H, m, ring CH_2), and 7.94 (3 H, s, CH_3).

cis- *and* trans-3-*Methoxyallyl Alcohol*.—A mixture of *trans*- and *cis*-methyl 2-methoxyacrylate was prepared by adding methanol to methyl propiolate in the presence of tributyltin methoxide.[10]

A solution of di-isobutylaluminium hydride in hexane (25 cm^3 of 2M solution) was diluted with benzene (50 cm^3) and added dropwise during 60 min to a stirred solution of the mixed methoxyacrylates (2 g) in benzene (150 cm^3) at room temperature.[11] Next day, methanol (30 cm^3) in benzene (20 cm^3) was added dropwise with vigorous stirring, then, after 60 min, water was added (10 cm^3). The solid which was precipitated was filtered off and washed with methanol, and the product was recovered by distillation at 58—60 °C at 20 mmHg, yielding *trans*-3-methoxyallyl alcohol (24%), τ(CCl_4) 6.48 (3 H, s, CH_3O), 6.08 [2 H, d, CH_2, J($HCCH_2$) 7 Hz], 5.10 [1 H, dt, H($HOCH_2$)C=, J(HC=CH) 12 Hz], and 3.54 [1 H, d, =C(OMe)H], and *cis*-3-methoxyallyl alcohol (76%), τ(CCl_4) 6.40 (3 H, s, CH_3O), 5.91 [2 H, d, CH_2, J($HCCH_2$) 7 Hz], 5.41 [1 H, dt, H($HOCH_2$)C=, J(HC=CH) 6 Hz], and 4.11 [1 H, d, =C(OMe)H].

This mixture reacted with t-butoxyl radicals to show the spectrum of the *cis*-3-methoxypropenoyl radical (23) and a weak spectrum of the *cis*- and *trans*-1-hydroxy-3-methoxyallyl radicals. The presence of the *cis*-3-methoxyacrolein was not apparent from the n.m.r. spectrum, but, after it was purified by preparative g.l.c., the mixture reacted with t-butoxyl radicals to show only the spectra of the allyl radicals.

Pure methyl *trans*-3-methoxyacrylate was prepared from the reaction of methanol (2.5 g) in ether (60 cm^3) with methyl propiolate (6.56 g) in the presence of *N*-methylmorpholine (7.70 g) in ether (60 cm^3).[12]

This was reduced as above with di-isobutylaluminium hydride yielding *trans*-3-methoxyallyl alcohol which reacted with t-butoxyl radicals to show principally the spectrum of the *trans*-3-methoxypropenoyl radical (24) together with a weak spectrum of the 1-hydroxy-3-methoxyallyl radical. Again, the presence of aldehyde was not apparent from the n.m.r. spectrum, but, after the alcohol was purified by g.l.c., it reacted with t-butoxyl radicals to show only the spectrum of the hydroxymethoxyallyl radical.

trans-3-*Trimethylsiloxyacrolein*.—The sodium salt of malonaldehyde O=CHCH=CHO$^-$Na$^+$, was prepared by the hydrolysis of malonaldehyde bis(methyl acetal) by Hüttel's method.[13] This powdered salt was suspended in dry ether and treated with an equimolar amount of trimethylchlorosilane. The sodium chloride which was precipitated was filtered off, and the ether was removed under reduced pressure yielding *trans*-3-trimethylsiloxyacrolein, $\tau(CCl_4)$ 0.55 (1 H, d, CHO, *J* 8 Hz), 2.51 [1 H, d, $Me_3Si(H)C=$, *J* 13 Hz], 4.38 [1 H, dd, =C(*H*)CHO, *J*(HC=CH) 13, *J*(HCCHO) 8 Hz], and 9.90 (9 H, s, Me_3Si); the large value of *J*(HC=CH) identifies this compound as having the *trans*-structure. The n.m.r. spectrum showed also the presence of the monoacetal and bisacetal of malonaldehyde but this did not complicate the e.s.r. experiment.

Product Analysis.—A solution of the methyl ether of glycidol (300 μl) and di-t-butyl peroxide (170 μl) in cyclopentane (150 μl) was photolysed at −76 °C for 2.5 h under the same conditions as in the e.s.r. experiments. The ^1H n.m.r. spectrum showed that most of the ether was unchanged, and the only products which could be detected were *cis*-3-methoxyallyl alcohol, and, in smaller amount, *trans*-3-methoxyallyl alcohol; if the corresponding aldehydes were present, their concentrations were too low to be detected.

E.s.r. Experiments.—Samples were photolysed in cyclopropane solution in the cavity of a Varian **E4** e.s.r. spectrometer by the technique which has been described previously.[1-3]

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