

90. Electron Spin Resonance of Oxiranyl Radicals in Solution: Configurational Stabilities and Rearrangement Reactions

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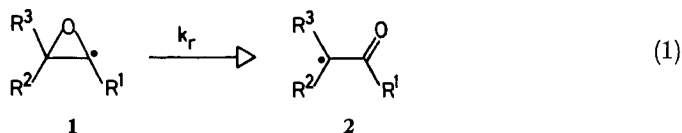
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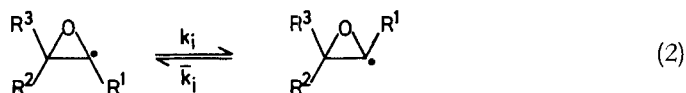
Summary. Several alkyl substituted oxiranyl radicals derived by hydrogen abstraction from oxiranes are observed in solution by ESR.-spectroscopy. The ESR.-spectra demonstrate that oxiranyl radicals have pyramidal configurations at the radical carbon atom and undergo inversion. Alkyl substituted oxiranyls rearrange by ring opening to α -keto alkyl radicals. The rates of inversion decrease and the rates of rearrangement increase with alkyl substitution. The activation parameters of these processes are given for several cases and are related to radical structure. Line broadening effects caused by inversion allow the determination of relative signs of γ -CH₃-coupling constants.

1. Introduction. – Since the discovery of the neophyl rearrangement by *Urry & Kharash* in 1944 [1] the study of free radical rearrangement reactions has received considerable interest. As evident from an excellent survey [2] most of the known rearrangements were formulated to account for product distributions observed after radical reactions in the gaseous or liquid phases. More recently it has been shown [3–6] that electron spin resonance (ESR.) may serve as a powerful tool: The rearranging and the rearranged radicals may be observed directly, and from the radical concentrations rate constants for the rearrangement may be obtained.

In this paper we apply ESR. to study a series of methylsubstituted oxiranyl radicals **1** and their ring opening rearrangement to α -keto alkyl radicals **2**. We will show that the radicals **1** have nonplanar radical carbon centers and undergo, besides



(1), an activated inversion (2). For several cases the rates of inversion and the barriers are estimated from ESR. linewidth effects. Approximate rate constants for the ring



opening (1) are determined for several radicals **1**, and for one particular case ($\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{R}^3 = \text{H}$) precise rate data are presented.

There are few previous chemical and spectroscopic studies related to oxiranyl radicals and reactions (1) and (2). *Walling & Fredricks* [7] found no rearrangement products during reactions of the unsubstituted oxiranyl ($R^1 = R^2 = R^3 = H$) at 0° or 70° but indicated that 2-methyloxiran-2-yl ($R^1 = CH_3$, $R^2 = R^3 = H$) may open under these conditions to some extent. For this latter radical *Gritter & Wallace* [8] presented clear evidence of rearrangement (1) at elevated temperatures, and they also demonstrated ring opening for radicals **1** derived from 1,2-epoxioctane, 1,2-epoxibutane and styrene oxide ($125^\circ \leq T \leq 200^\circ$). *Reusch et al.* [9] investigated the rearrangement for a radical derived from a substituted cyclohexenone oxide, and *Padwa & Das* [10] demonstrated the ring opening of 2,3-diphenyloxiran-2-yl radicals at 90° and 135° . It seems now clear that reaction (1) is activated [2] [8] [10].

By chemical means *Altman & Baldwin* [11] proved the non-planarity of the radical carbon of 2,3-dimethyloxiran-2-yl radicals ($R^1 = CH_3$, $R^2 = CH_3$, $R^3 = H$). The rate of the configurational equilibration of the two isomers (2) was estimated as $1.1 \cdot 10^7 \text{ s}^{-1}$ at 30° . These authors also calculated the barrier to inversion of the unsubstituted oxiranyl as 5.4 kcal/mol by CNDO/2 techniques but did not give the equilibrium geometry [12].

By ESR. the ethyleneoxide radical **1** ($R^1 = R^2 = R^3 = H$) was observed in solution by *Norman et al.* at 2° [13] ($g = 2.0032$, $|a_{H^1}| = 2.34 \text{ mT}$, $|a_{H^2}| = |a_{H^3}| = 0.61 \text{ mT}$), by *Beckwith et al.* at room temperature [14] ($g = 2.0031$, $|a_{H^1}| = 2.34 \text{ mT}$, $|a_{H^2}| = |a_{H^3}| = 0.61 \text{ mT}$) and by *Behrens & Schulte-Frohlinde* [15] at -30° , -60° and -70° ($g = 2.00230$, $|a_{H^1}| = 2.45 \text{ mT}$, $|a_{H^2}| = |a_{H^3}| = 0.49 \text{ mT}$ at -30°). The large absolute value of a_{H^1} and the small values of a_{H^2} and a_{H^3} were taken as evidence for non-planarity of the radical carbon and the equivalency of H^2 and H^3 was ascribed to a rapid inversion (2) in the fast exchange limit. In fact, the non-planarity was confirmed by an INDO calculation [13] which indicated an energy minimum for an angle $\varnothing = 40^\circ$ between the $\dot{C}-H^1$ -bond and its projection onto the $\dot{C}-O-C$ -plane, and which lead to an inversion barrier of 7.5 kcal/mol and to the coupling constants $a_{H^1} = +1.83 \text{ mT}$, $a_{H^2} = +0.84 \text{ mT}$, and $a_{H^3} = +0.45 \text{ mT}$. Though the magnitudes of the calculated coupling constants agree well with the observed values it should be noticed that the INDO results seem not compatible with inversion in the fast exchange limit. For an activation energy of $\simeq 7.5 \text{ kcal/mol}$, a normal frequency factor ($A = kTe/h$) and the difference $a_{H^2} - a_{H^3} = 0.39 \text{ mT}$ the theory of line widths of exchanging radicals [16] predicts an excess line width of the center line of the CH_2 -proton triplet of 0.25 mT at 0° which has not been observed. Even for $E_a = 5.4 \text{ kcal/mol}$ [12] an excess line width of 0.23 mT at $T = -70^\circ$ is expected but not reported [15]. Though tunneling may play a role, we believe that the theoretical calculations may have exaggerated the inversion barrier and/or the difference of a_{H^2} and a_{H^3} in the equilibrium configuration. These arguments are not changed if zero-point vibrations are taken into account since they will cause differences between inversion barriers and activation energies of less than 1 kcal/mol (Section 2.8.).

During reaction of *t*-butoxy radicals with methyl-oxirane *Behrens & Schulte-Frohlinde* [15] observed ESR.-spectra of the 2-methyloxiran-2-yl ($R^1 = CH_3$, $R^2 = R^3 = H$) and of the 3-methyloxiran-2-yl ($R^1 = H$, $R^2 = CH_3$, $R^3 = H$) radicals. The former radical ($|a_{CH_3}| = 1.48 \text{ mT}$, $|a_{H^2}| = |a_{H^3}| = 0.47 \text{ mT}$, $g = 2.00302$) has equiva-

lent CH_2 -protons as expected for rapid inversion. The spectrum of the latter radical was interpreted as arising from two geometrical isomers with equal g -factors (2.00316) and equal H^1 -coupling constants (2.31 mT) but unequal H^3 -coupling constants (0.495 mT and 0.375 mT). A γ - CH_3 -proton splitting was not reported, and line width effects were not mentioned. The two isomers were assigned the structures **1'** and **1''**, and their observation was taken as direct evidence for non-planarity at the radical carbon atom. If this interpretation were correct **1'** and **1''** would not invert rapidly at the temperature of observation (-40°) which contrasts with the rapid inversion of



oxiranyl and 2-methyl-oxiran-2-yl under the same conditions. As we will show later on, the spectrum of 3-methyl-oxiran-2-yl does show severe line broadening effects which indicate rapid exchange between **1'** and **1''**. Further, a γ - CH_3 -proton coupling is present, and the combined effects of CH_3 -coupling and line broadening lead to an unusual appearance of the ESR.-spectrum. Though the interpretation given by *Behrens & Schulte-Frohlinde* is not tenable, their main conclusion of a pyramidal configuration of oxiranyls remains valid. These authors [15] were also the first to detect reaction (1) by ESR, since they found acetonyl radicals **2** ($\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{R}^3 = \text{H}$) during the reaction of methyloxirane for $T \geq -10^\circ$.

From the previous studies it seems established that oxiranyl radical carbon atoms attain pyramidal configurations [11] [13–15]. They may undergo inversion (2) and ring opening rearrangement (1), and the rates of these processes may depend on the substituents [8] [10] [15]. There are no detailed experimental data on the inversion barriers or on the rearrangement kinetics and on substitution effects, and the following study concentrates on these topics.

If not mentioned otherwise the oxiranyl radicals were produced by photolysis of di-*t*-butylperoxide (DTBP, 10 Vol %) in the corresponding oxiranes. The ESR.-spectra were taken during continuous photolysis and were analyzed and simulated by conventional procedures (see Exper. Part). As in the previous literature we assign the radical carbon atom of oxiranyl radicals to position 2 of the oxiranyl ring, therefore, the labelling of the substituents in the parent compounds does not always follow the recommended nomenclature.

2. ESR.-Spectra; Structure, Inversion and Rearrangement of Oxiranyl Radicals. – 2.1. *Trimethyloxirane*. During photolysis of DTBP in trimethyloxirane at $T \leq -79^\circ$ the ESR.-spectrum of fig. 1b is observed. It is immediately analysed in terms of a radical containing three inequivalent CH_3 -groups with coupling constants $|a_1| = 1.550$ mT, $|a_2| = 0.162$ mT and $|a_3| = 0.040$ mT. A simulation is given in fig. 1a. Obviously the radical is 2,3,3-trimethyloxiran-2-yl, formed by abstraction of the CH-hydrogen. The observation of three inequivalent CH_3 -groups is direct evidence for a pyramidal configuration at the radical carbon. For $T \leq -79^\circ$ inversion must be slow since a rapid inversion would render two CH_3 -groups (R^2 and R^3 in 1) equivalent. We attribute $|a_1|$ to the CH_3 -group in position 2 and $|a_2|$ and $|a_3|$

to the two CH₃-groups in position 3. It will be noted that $|a_2|$ and $|a_3|$ are of the order of magnitude expected for γ -protons [17] while $|a_1|$ is exceptionally low for a CH₃-group bonded to a radical carbon atom (*cf.* CH₃ \dot{C} H₂: 2.687 mT [17], CH₃ \dot{C} HOH: 2.22 mT [13]). $|a_1|$ is, however, compatible with a non-planar radical site since other non- π -radicals also exhibit low CH₃-coupling constants (*cf.*: α -methylvinyl: 1.948 mT [17]; CH₃ \dot{C} F₂: 1.399 mT [18]; 2-methyl-1,3-dioxolan-2-yl: 1.28 mT [19]; (CH₃O)₂ \dot{C} CH₃: 1.48 mT [13]; acetyl: 0.40 mT [20] [21]). A close comparison of figs. 1a und 1b reveals a slight broadening of the inner line groups of the a_1 -quartet. This is ascribed to a restricted rotation of the 2-CH₃-group at T = -79°, as common for CH₃-groups on pyramidal radical carbon atoms [17] [18].

With increasing temperature the ESR.-spectra change drastically (figs. 1b–e). Firstly, the signal of 2,3,3-trimethyloxiran-2-yl becomes weaker while lines of a second radical appear. For T \geq -40° the second radical is the dominant species. Secondly, the spectrum of the oxiranyl radicals shows a strong temperature dependence.

The first observation is easily explained in terms of the rearrangement reaction (1). The new radical exhibits two more line groups outside the range of fig. 1, and its full spectrum is identical with that of the α -keto radical (R¹ = R² = R³ = CH₃) expected from reaction (1) [21]. A simulation of the inner line groups with the parameters given in table 1 is shown in fig. 1f. For T \simeq -45° oxiranyl and α -keto radicals are present in roughly equal concentrations. Thus, at this temperature the rate of ring opening is about equal to the rates of the radical termination reactions. Since, under our experimental conditions these are of the order of 10³ s⁻¹ [22] [23] we estimate $k_T = 10^3$ s⁻¹ at -45°.

The strong temperature dependence of the spectrum of 2,3,3-trimethyloxiranyl is due to two effects:

a) For T > -79° the broadening of the inner lines of the a_1 -quartet disappears as expected since the CH₃-group rotation becomes faster at higher temperatures;

b) Selective line broadening appears within the quartets which arise from the hyperfine coupling with the γ -CH₃-protons (a_2 and a_3). Two of the lines with relative intensities nine remain sharp with increasing temperature while other lines broaden drastically. The two sharp lines are (0.120 \pm 0.030) mT apart.

The line broadening effects are explained in terms of the inversion (2) at the radical carbon which exchanges the coupling constants a_2 and a_3 of the CH₃-group protons, and in particular the following considerations apply: One individual line of the quartets of quartets has the relative resonance position.

$$H_{\mathbf{r}} = -a_2M_2 - a_3M_3 \quad (3)$$

where $M_{2,3} = 3/2, 1/2, -1/2, -3/2$ are the total magnetic spin quantum numbers of the two groups of CH₃-protons. An exchange not affecting the M_1 [16] but the coupling constants shifts the line to

$$H_{\mathbf{r}'} = -a_3M_2 - a_2M_3 \quad (4)$$

i.e. by a distance

$$\Delta H_{\mathbf{r}} = -(a_2 - a_3) (M_2 - M_3) \quad (5)$$

In the *slow* exchange limit this leads to a line broadening of lines with $M_2 \neq M_3$, the excess peak to peak width of a Lorentzian derivative line in frequency units [16] given by

$$\Delta\nu = \frac{k_1}{\pi\sqrt{3}} \quad (6)$$

if $k_1 = \bar{k}_1$ is the rate constant of inversion of the trimethyloxiranyl radical. For *intermediate* exchange the lines at positions H_r and H_r' coalesce at the average position

$$\bar{H}_r = -\frac{1}{2}(a_2 + a_3)(M_2 + M_3) \quad (7)$$

if

$$k_1 = \frac{\pi}{\sqrt{2}} |\Delta H_r| \quad (8)$$

(ΔH_r in frequency units), and for *fast* exchange one expects lines at \bar{H}_r with excess widths

$$\Delta\nu = \frac{\pi}{2\sqrt{3}} \Delta H_r^2 \quad (9)$$

Obviously, the observed line broadening effects of fig. 1 correspond to the slow and intermediate exchange cases. The lines remaining sharp are identified as lines with $M_2 = M_3$. Fig. 2 shows a schematic representation of one quartet of quartets and the correlation of the lines connected by the exchange process. We distinguish the cases of like and unlike signs of a_2 and a_3 , for both of which 4 equidistant lines

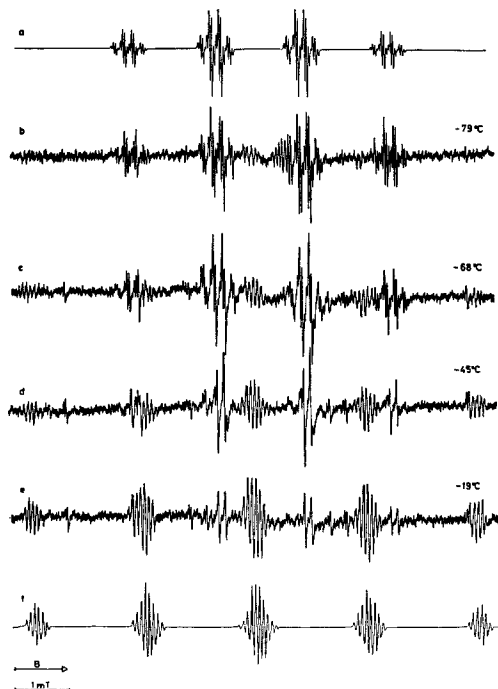


Fig. 1. ESR-Spectra of Radicals Derived from Trimethyloxirane: a) and f) simulated, b)-e) observed

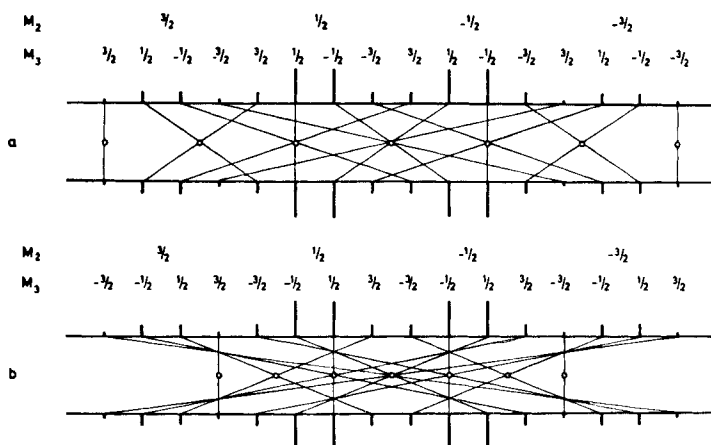


Fig. 2. Correlation Diagram for the ESR-Lines of 2,3,3-Trimethyloxiranyl: a) like signs, b) unlike signs of a_γ

with intensity ratios 1:9:9:1 do not shift and will remain sharp. Like signs yield a distance of these lines $|a_2| + |a_3| = 0.202$ mT, whereas for unlike signs a distance $|a_2| - |a_3| = 0.122$ mT is expected. The observed value of 0.120 mT clearly corresponds to the latter case. Thus the *syn*- and *anti*-CH₃-groups of the trimethyloxiranyl radical must have coupling constants with unlike signs. We will discuss this finding in a later section.

For $T = -19^\circ$ (fig. 1e) no lines except those not subject to exchange are observable. This indicates that this temperature corresponds to near coalescence of the shifting lines. $|\Delta H_T|$ of eq. (8) is of the order of 0.2 mT, thus $k_1 \approx 10^7$ s⁻¹ at $T = -19^\circ$.

2.2. *cis*- and *trans*-2,3-Dimethyloxirane. Photolysis of DTBP in both compounds yields for $T \geq -71^\circ$ identical ESR.-spectra. Fig. 3b shows a spectrum obtained

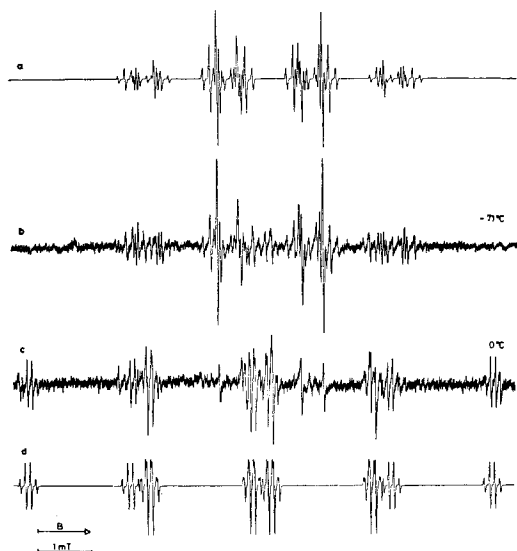


Fig. 3. ESR.-Spectra of Radicals Derived from *cis*- and *trans*-Dimethyloxirane: a) and d) simulated, b) and c) observed

from the *cis*-compound at $T = -71^\circ$, and the simulation (fig. 3a) demonstrates that the spectrum represents a superposition 1:1 of two radicals with coupling constants $|a_1| = 1.550$ mT (quartet), $|a_2| = 0.530$ mT (doublet), $|a_3| = 0.130$ mT (quartet) and $|a_1| = 1.505$ mT (quartet), $|a_2| = 0.380$ mT (doublet), $|a_3| = 0.050$ mT (quartet), respectively. Comparison of these data with the constants of trimethyloxiranyl (section 2.1.) shows that they evidently belong to the two magnetically inequivalent isomers of the 2,3-dimethyloxiran-2-yl radical and that $|a_1|$ belongs to the protons of the 2-CH₃-group, $|a_2|$ to the CH-proton and $|a_3|$ to the γ -CH₃-protons. At this stage an assignment of the two sets of coupling constants to the specific isomers is impossible but it will be given in section 2.7.

The observation of two inequivalent isomers demonstrates the pyramidal configuration of C(2), whereas the finding of the isomer ratio 1:1 from both parent compounds shows that at -71° geometrical isomerization by inversion (2) effectively competes with the radical termination reactions, and that $k_1 = \bar{k}_i$, thus $k_1 > 10^3$ s⁻¹ at -71° .

For $T \geq -50^\circ$ the oxiranyl radicals undergo ring opening (1) as evident from the appearance of the spectrum of the α -keto radical $\text{CH}_3\dot{\text{C}}\text{HCOCH}_3$. A spectrum observed at $T = 0^\circ$ is given in fig. 3c, and fig. 3d represents a simulation of the spectrum of the α -keto radical, parameters given in table 1. At $T \simeq -35^\circ$ oxiranyl and α -keto radical are present in roughly equal concentrations, thus, here $k_r \simeq 10^3$ s⁻¹.

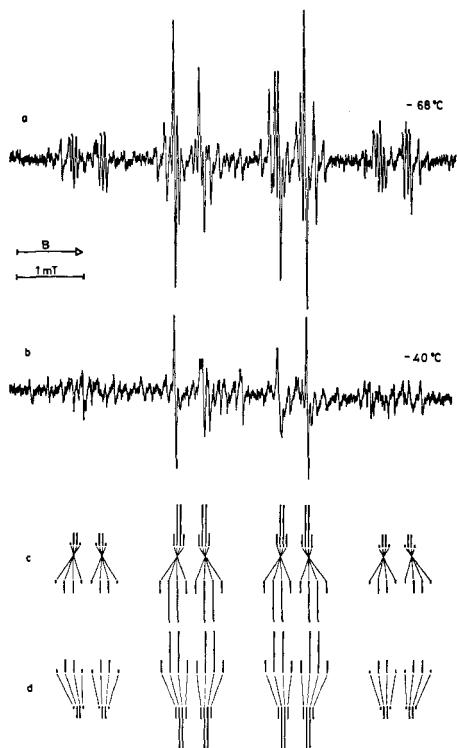


Fig. 4. Inversion Effects in the ESR.-Spectrum of 2,3-Dimethyloxiranyl: a) and b) ESR.-spectra, c) and d) correlation diagram for unlike and like signs of a_i .

Line broadening effects due to inversion of the 2,3-dimethyloxiran-2-yl radicals are observed for $T \geq -70^\circ$ (fig. 4). Since the two isomers are not equivalent the effects are expected to be more complicated than those observed in section 2.1. However, certain lines which accidentally appear at the same resonance positions for both isomers remain sharp, and the correlation diagrams of fig. 4c and d demonstrate that this behaviour is easily explained if $|a_3|$ changes sign on inversion whereas $|a_1|$ and $|a_2|$ have the same signs for both isomers.

In the temperature range $-71^\circ \leq T \leq -54^\circ$ the spectra are describable within the slow exchange limit. Since $k_1 = \bar{k}_1$ the excess line width of shifting lines is given by eq. (6). Analysis of the width of two strong lines of the spectrum by eq. (6) lead to the Arrhenius plot of k_1 given in fig. 5 from which $k_1 \simeq 10^7 \text{ s}^{-1}$ at -55° and $E_a = (5.8 \pm 1.4) \text{ kcal/mol}$, $\log (A/\text{s}^{-1}) = 12.6 \pm 0.8$ follow. These values are compatible with the previous estimate $k_1 > 10^3 \text{ s}^{-1}$ at -71° , with the order of magnitude of k_1 given by Altman [11] and with a normal frequency factor for the inversion ($T = -60^\circ$, $A = kTe/h = 1.2 \cdot 10^{13} \text{ s}^{-1}$) [24].

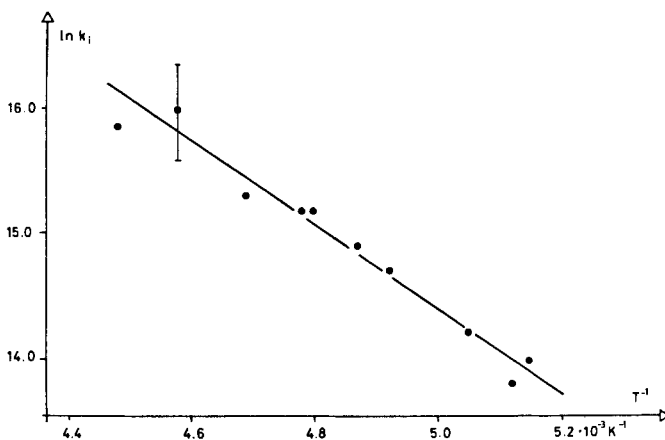


Fig. 5. 2,3-Dimethyloxiranyl: Arrhenius Plot of the Inversion Rate

2.3. 3,3-Dimethyloxirane. Photolysis of DTBP in this compound ($-80^\circ \leq T \leq 0^\circ$) leads to fairly weak ESR.-spectra with many lines which were not fully analyzed (fig. 6). Present under all conditions is a radical with a doublet (a_1) and a septet (a_2) splitting which we identify as the 3,3-dimethyloxiran-2-yl radical ($|a_1| = 2.33 \text{ mT}$, $|a_2| = 0.084 \text{ mT}$ at $T = -20^\circ$). a_1 is attributed to the CH-proton, a_2 to the six CH_3 -protons. Fig. 7 demonstrates alternating line width effects within the septets at $T \leq -30^\circ$. For $T \geq -20^\circ$ the intensity distribution is nearly binomial. Such effects are expected for a radical with two groups of non-equivalent CH_3 -protons undergoing exchange by inversion at the non-planar radical center within the fast exchange limit. Unfortunately, a full analysis of the line widths *via* eq. (9) was not possible because we were not able to obtain the low temperature limiting form of the spectrum which would reveal the difference of the CH_3 -coupling constants and thus ΔH_r . The solution solidified for $T < -80^\circ$. Yet, for an estimate of the inversion frequency we note that $|a_2| = 0.084 \text{ mT}$ is similar to the average of the γ - CH_3 -couplings of tri-

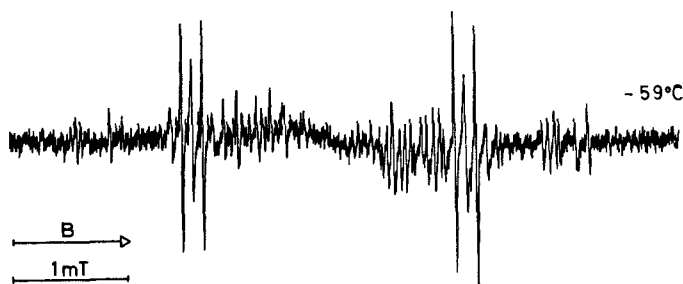


Fig. 6. ESR.-Spectrum of Radicals Derived from 3,3-Dimethyloxirane



Fig. 7. Inversion Effects in the ESR.-Spectrum of 3,3-Dimethyloxiran-2-yl

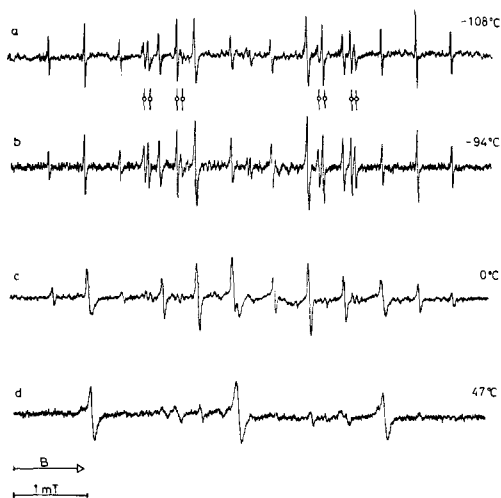


Fig. 8. ESR.-Spectra of Radicals Derived from Methyloxirane: a) and b) modulation amplitude 0.01 mT, c) and d) 0.04 mT

methyloxiranyl (0.061 mT) and of the two isomers of 2,3-dimethyloxiran-2-yl (0.040 mT). Therefore, the individual CH_3 -coupling constants are expected to be similar to those of the two other radicals. If this is true 3,3-dimethyloxiran-2-yl inverts more facile than trimethyloxiranyl and 2,3-dimethyloxiran-2-yl since the spectra are of the fast exchange type, and the inversion frequency may be about 10^7 s^{-1} already at $T = -79^\circ$ (fig. 7a).

Weak lines of the ring opened radical $(\text{CH}_3)_2\dot{\text{C}}\text{CHO}$ are also observable for $T > -40^\circ$, and for $T \simeq -10^\circ$ oxiranyl and α -keto radicals had about equal concentrations. Thus, by the same reasoning as above, $k_r \simeq 10^8 \text{ s}^{-1}$ at $T = -10^\circ$.

2.4. *Methyloxirane*. Fig. 8 shows ESR.-spectra taken during photolysis of DTBP in methyloxirane. For $T = -108^\circ$ and -94° they are similar to the spectrum published by *Behrens & Schulte-Frohlinde* for -40° [15] and are attributed to the 2-methyloxiran-2-yl ($|a_1| = 1.48 \text{ mT}$, quartet, CH_3 , $|a_2| = 0.47 \text{ mT}$, triplet, CH_2) and to the 3-methyloxiran-2-yl radicals (lines $\frac{1}{2}$).

The spectrum of 2-methyloxiran-2-yl shows line broadening within the CH_3 -quartet comparable to that of trimethyloxiranyl (section 2.1.) and similarly ascribed to restricted rotation. This indicates a non-planar radical site. However, we did not observe line broadening effects due to inversion for $-108^\circ \leq T \leq 0^\circ$, and the CH_2 -protons were equivalent under all conditions. Since all other oxiranyls with 2- CH_3 -groups did invert rapidly in this temperature range and since the restricted rotation indicates a pyramidal radical center we believe that the 2-methyloxiranyl radical also inverts rapidly and that the missing line broadening arises from a near equivalency of the CH_2 -protons in the equilibrium geometry.

At first sight the spectrum of the 3-methyloxiran-2-yl radical (lines $\frac{1}{2}$ in fig. 8) appears to consist of two sets of doublets of doublets. These were assigned to the magnetically distinguishable non-planar isomers by *Behrens & Schulte-Frohlinde* [15] which were assumed to be separately detectable at $T = -40^\circ$. This interpretation severely conflicts with the findings described for other oxiranyls in sections 2.1. to 2.4. Firstly, we expect the radicals to exhibit a γ - CH_3 -splitting of about 0.04–0.08 mT which should be easily detectable if the radicals were configurationally stable.

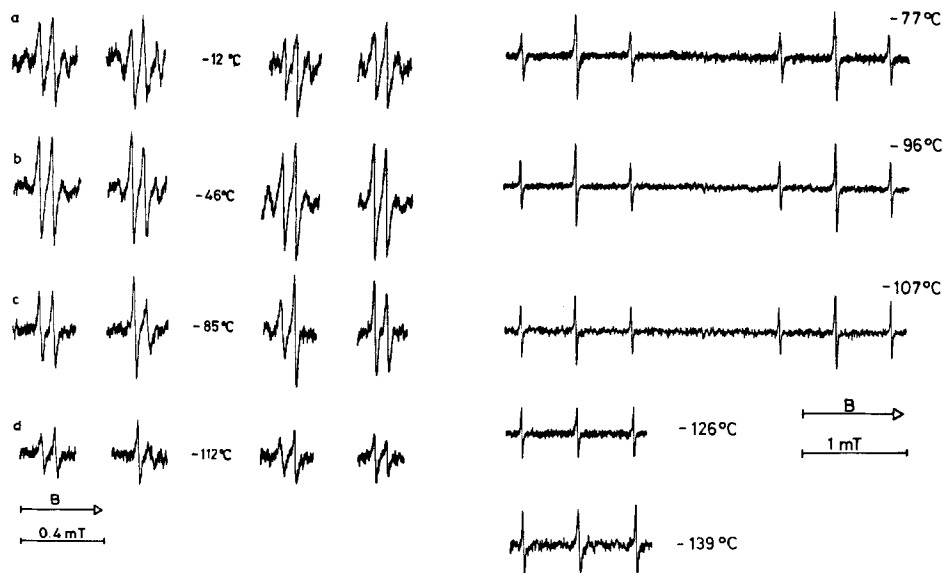


Fig. 9. Inversion Effects in the ESR.-Spectrum of 3-Methyloxiran-2-yl

Fig. 10. ESR.-Spectra of Oxiranyl (30% by vol. epoxide, 10% by vol. DTBP in Frigen 11 S)

Secondly, by analogy with 3,3-dimethyloxiran-2-yl we expect rapid inversion at $T = -40^\circ$ leading to severe line broadening. Now, in fact, on expansion of the spectral range of the lines attributed to 3-methyloxiran-2-yl one finds (fig. 9) that the radicals do show more than the 8 lines discussed by the previous authors [15]. At $T = -12^\circ$ a doublet of doublets of quartets ($|a_1| = 2.44$ mT, $|a_2| = 0.49$ mT, $|a_3| = 0.062$ mT) is seen, and for $T < -12^\circ$ the outer lines of the quartets broaden, and the pattern becomes unsymmetrical. This is exactly what would be expected for inversion in the fast and intermediate exchange limits where the two isomers cannot be observed separately, and where the above coupling constants are the average couplings of the 2-CH₃-, 3-CH- and 3-CH₃-protons, respectively. Full analysis of the line broadening effects was not possible since we were unable to obtain the slow exchange low temperature limiting spectra, but from the line coalescence even at -112° we may infer that $k_1 \simeq 10^7$ s⁻¹ at this temperature.

Figs. 8c and d present evidence for the rearrangement (1) of the 2-methyloxiran-2-yl radical to the acetyl radical $\dot{\text{C}}\text{H}_2\text{COCH}_3$. With increasing temperature the lines of the former radical become weaker whereas those of the latter become stronger. For $T \approx 0^\circ$ both radicals are present in equal concentrations, thus $k_r \simeq 10^3$ s⁻¹. Rearrangement radicals formed from the 3-methyloxiran-2-yl radical are not detected, and this radical seems to persist at $T > 0^\circ$. Section 3 will present a more detailed study of the ring opening of 2-methyloxiran-2-yl.

2.5. Oxirane. The spectrum of the oxiranyl radical reported by others for $T = 20^\circ$ [14], 2° [13] and -30° , -60° , -70° [15] is a doublet (CH-proton) of triples (CH₂-protons). No line broadening effects were mentioned, and all authors assumed a pyramidal radical carbon atom and very fast inversion which causes an apparent equivalency of the CH₂-protons. That the radical carbon atom is non-planar and that the CH₂-protons are non-equivalent in the equilibrium configuration but undergo exchange due to inversion is now confirmed by the spectra of fig. 10. For temperatures lower than those used previously we find line broadening of the center lines of the CH₂-triplets as expected for a slower inversion at lower temperatures. Since we always observe CH₂-triplets the inversion is rapid even at $T = -139^\circ$, and the excess line width of the center-lines should be given by eq. (8). Unfortunately, the value of ΔH_r , *i.e.* the difference of the coupling constants of the *syn*- and *anti*-CH₂-protons could not be determined experimentally, and an exact determination of the inversion rate is impossible. For an estimation we assume an *Arrhenius* law for k_1 . This should lead to a linear dependence of the logarithm of the excess line width on T^{-1} from which the activation energy can be determined. Evaluation of the data yielded $E_a = (2 \pm 1)$ kcal/mol, and, as expected (see Introduction), this value is considerably smaller than those predicted from the CNDO/2 [12] and INDO [13] calculations. For a further crude approximation of the frequency factor we use the observed excess line width of 0.005 mT at $T = -127^\circ$ and the value of $\Delta H_r = 0.39$ mT obtained by INDO [13]. This gives $\log (A/\text{s}^{-1}) = (11.9 \pm 2.0)$, *i.e.* roughly identical to a normal value (12.9) for this temperature. Thus, tunneling is not effectively contributing to the inversion.

At this point we wish to add that we have repeated the INDO calculation [13] using an available programme [25] and the molecular geometries given by *Norman et al.* [13] or, alternatively, a set derived from the geometry of oxirane [26] (CH:1.083 Å, CC:1.470 Å, CO:1.435 Å,

HCH:116.3°, CCH₂:158.1°, H_αC-plane:variable (ϕ). For both geometries we find the energy minimum at $\phi = 40^\circ$ and an inversion barrier of 7.5–8.0 kcal/mol. The ¹³C- and CH-coupling constants agree with those given in [13] but the coupling constants of the CH₂-protons differ. We find for $\phi = 40^\circ$ for the proton *cis* to H_α +1.316 mT and +1.322 mT and for the proton *trans* to H_α +0.850 mT and +0.844 mT, respectively, whereas the values +0.84 mT and +0.45 mT have been reported. The reason for this discrepancy is unclear but the difference of the coupling constants is nearly the same for both calculations (0.45 *vs.* 0.39 mT)¹⁾.

At no temperature radicals derived from ring opening could be detected. This implies that $k_r < 10^3 \text{ s}^{-1}$ even at room temperature and is in accord with previous findings [7].

2.6. *t*-Butyl- and *trans*-2,3Di-*t*-butyloxirane. Photolysis of DTBP in *t*-butyloxirane leads to the ESR-spectra of fig. 11. For $T < -50^\circ$ the spectrum is a doublet ($|a_1| = 0.48 \text{ mT}$) of doublets ($|a_2| = 0.46 \text{ mT}$) of decets ($|a_3| = 0.02 \text{ mT}$) and is attributed to the 2-*t*-butyloxiran radical. The two CH₂-protons ($|a_1|$ and $|a_2|$) are slightly inequivalent, and we have not found drastic line broadening effects. Thus,

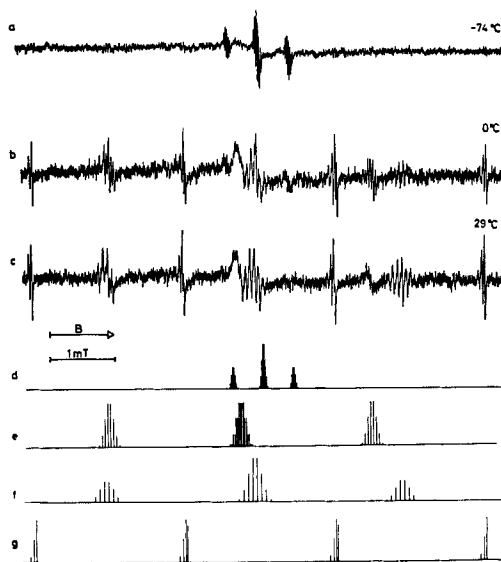
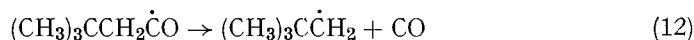
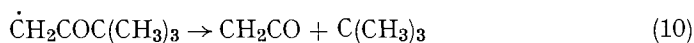


Fig. 11. ESR-Spectra of Radicals Derived from *t*-Butyloxirane: a), b), c) observed, d)–g) simulated

the radical has a pyramidal radical site, and the inversion rate must be lower than $5 \cdot 10^5 \text{ s}^{-1}$ at $T < -50^\circ$. For $T > -50^\circ$ many new lines appear which could be ascribed by comparison of their coupling constants with literature values to $\cdot \text{CH}_2\text{COC}(\text{CH}_3)_3$ [27], $\cdot \text{CH}_2\text{C}(\text{CH}_3)_3$ [28] and $\dot{\text{C}}(\text{CH}_3)_3$ [17] [21]. The α -keto radical is expected from the rearrangement of 2-*t*-butyloxiran-2-yl, but the appearance of the two other radicals is noteworthy. A possible route to these radicals would be

1) Note added in proof: Prof. Norman has kindly informed us of a typographic error in [13]. His original values agree with ours.



however, a decomposition of the α -keto radical has not been reported in an adamantane matrix study even up to $T = 30^\circ$ [27]. Nevertheless, 2-*t*-butyloxiran-2-yl radicals do rearrange and using the same reasoning as outlined for other systems we have $k_r \simeq 10^8 \text{ s}^{-1}$ at $T \simeq -30^\circ$.

Photolysis of DTBP in *trans*-2,3-di-*t*-butyloxirane yielded a radical formed by H-abstraction from one of the *t*-butyl groups. No oxiranyl radicals were detected.

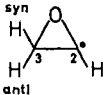
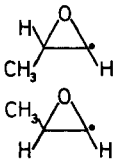
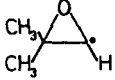
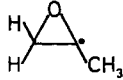
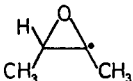
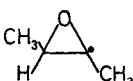
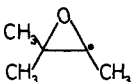
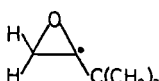
2.7. Discussion of the Coupling Constants. Table 1 lists the coupling constants of the oxiranyl and α -keto radicals and their assignment to specific protons as well as their probable signs. The experimental errors are approximately 0.01 mT. The coupling constants of the α -keto radicals are of normal magnitudes [21] [27] [29] and deserve no discussion. However, those of the oxiranyl radicals are noteworthy and allow further conclusions:

1. Hydrogen atoms bonded to the radical carbon atom H-C(2): It is well known that the coupling constant is negative for planar carbon center but may become positive as the radical carbon atom adopts a pyramidal configuration [5] [13] [29–31]. The absolute values of the coupling constants of H-C(2) observed for oxiranyl, 3-methyloxiran-2-yl and 3,3-dimethyloxiranyl (2.46, 2.44, 2.33 mT) are larger than that of the planar CH_3 -radical (2.304 [17]). This indicates positive values and a large degree of out-of-plane bending as confirmed by the INDO calculations ($\phi = 40^\circ$) [13]. The coupling constants decrease with methyl substitution at C(3). This is expected since steric repulsion will decrease ϕ . Interestingly, the oxiranyl radical observed in water at 2° and 20° [13] [14] showed a CH-coupling constant of 2.34 mT, more than 0.1 mT less than that observed here (2.46 mT) and in [15] for non-aqueous solution and at lower temperatures. While part of the difference may be due to vibrational effects we believe that it is mostly due to a solvent effect, since 2.46 mT were found at -100° and 2.45 mT at -30° .

2. Hydrogen atoms of CH_3 -groups bonded to the radical carbon atom ($\text{H}_3\text{C}-\text{C}(2)$): The values observed for 2-methyloxiran-2-yl (1.48 mT), the two isomers of 2,3-dimethyloxiran-2-yl (1.505 and 1.55 mT) and trimethyloxiranyl (1.55 mT) are close to that of the pyramidal radical $\text{CH}_3\dot{\text{C}}\text{F}_2$ (1.399 mT) [5] [18] for which INDO calculations predict +1.431 mT [5] [18]. The data available for non- π -radicals [5] [29] indicate that the coupling constants remain positive on bending but decrease in magnitude. Since we expect trimethyloxiranyl to be less bent than 2-methyloxiran-2-yl because of steric hindrance our findings of 1.55 mT for the former and 1.48 mT for the latter radical agree with all available information. The same argument allows to attribute the CH_3 -coupling of 1.505 mT to the *trans*-(*syn*)-isomer and of 1.55 mT to the *cis*-(*anti*)-isomer of 2,3-dimethyloxiran-2-yl (Table 1).

3. Hydrogen atoms bonded to C(3): From the INDO calculations the coupling constants are certainly positive and decrease with increasing out-of-plane angle ϕ at C(2). Further, the coupling constant of the *cis*-(*anti*)-hydrogen atom of oxiranyl is

Table 1. ESR.-Data of Oxiranyl and α -keto Radicals

Radical	T	Coupling constants [mT]
	-100°	2-H: +2.46; 3-H(anti), 3-H(syn), av: +0.52
	-62°	2-H: +2.44; 3-H(anti), 3-H(syn), av: +0.49 CH ₃ (anti), CH ₃ (syn), av: +0.062
	-20°	2-H: +2.33, CH ₃ (anti), CH ₃ (syn), av: +0.084
	-40°	CH ₃ : +1.48; 3-H(anti), 3-H(syn), av: +0.47
	-62°	2-CH ₃ : +1.55; H: +0.53; 3-CH ₃ : +0.13
	-62°	2-CH ₃ : +1.505, H: +0.38; 3-CH ₃ : -0.05
	-75°	2-CH ₃ : +1.55; 3-CH ₃ (anti): +0.162; 3-CH ₃ (syn): -0.04
	-64°	3-H(anti): +0.46; 3-H(syn): +0.48; C(CH ₃) ₃ : 0.02
CH ₃ \dot{C} HCOCH ₃	-20°	H _{α} : -1.88; H _{β} : +2.23; H _{γ} : 0.118
(CH ₃) ₂ \dot{C} COCH ₃	-20°	H _{β1} : +1.89; H _{β2} : +2.03; H _{γ} : 0.13:
\dot{C} H ₂ COC(CH ₃) ₃	-20°	H _{α1} : -1.99; H _{α2} : -2.20; H _{γ} : 0.045

calculated to be larger than that of the *trans*-(*syn*)-hydrogen atom (section 2.5.). For most of the cases studied in this paper only the average of the coupling constants could be observed, but for the two isomers of 2,3-dimethyloxiran-2-yl we obtained two different values (0.53 and 0.38 mT). Adopting the assignment of coupling constants to isomers as derived from the 2-CH₃-coupling the 0.53 mT belong to the *cis*-isomer (hydrogen atom *syn*) and the 0.38 mT belong to the *trans*-isomer (hydrogen atom *anti*). The order of the two coupling constants is inverse to that calculated for the unsubstituted radical. This may be caused by the difference of ϕ for the two isomers.

4. γ -CH₃-protons (H₃C–C(3)): For trimethyloxiranyl two different coupling constants (0.162 mT, 0.04 mT) with opposite signs were found, and the two isomers of 2,3-dimethyloxiran-2-yl had γ -CH₃-couplings of 0.13 and 0.05 mT again with opposite signs. From the assignment of the 2-CH₃-couplings obviously the larger value belongs to the *cis*-(*anti*)-CH₃-group. It is known that large and positive γ -proton coupling constants arise if a «*W*-plan» arrangement of the bonds between the γ -hydrogen and the orbital axis of the unpaired electron is part of the radical structure [32]. For our radicals such an arrangement is realized only for the *cis*-(*anti*)-CH₃-group in perfect agreement with our assignment of the larger γ -CH₃-coupling to that group. Recent *ab-initio*-calculations [33] have confirmed the *W*-plan rule and have shown that for other γ -CH-conformations mostly small and negative couplings result. This again confirms our assignments.

For 3-methyloxiran-2-yl and for 3,3-dimethyloxiranyl only average coupling constants of the γ -CH₃-protons of 0.062 and 0.084 mT could be observed. Since these values are close to the averages for trimethyloxiranyl ((+0.162 – 0.04)/2) and 2,3-dimethyloxiran-2-yl (+0.13 – 0.05)/2) we assume their signs as positive.

As we have shown our results confirm all present theories on proton coupling constants of non- π -radicals and contribute many new examples. Any more quantitative correlation of coupling constants with the radical configurations has to wait for more detailed theoretical calculations. In particular we feel that substituent effects have to be considered. Further, steric effects in most of the radicals will cause considerable geometrical distortions at C(2) and C(3), and we are at present investigating their influence on calculated coupling constants.

2.8. *Discussion of the Rates of Inversion and Rearrangement.* From the ESR-spectra characteristic temperatures T_i and T_r have been obtained for most of the oxiranyl radicals. At these temperatures $k_i \simeq 10^7$ s⁻¹ and $k_r \simeq 10^3$ s⁻¹, respectively. As Table 2 shows, T_i and T_r vary considerable with substitution at both carbon atoms of the oxiranyl ring:

a) For equal substitution at C(3) T_i increases by approximately 60° if the hydrogen atom at the radical carbon atom is replaced by a CH₃-group. *t*-Butyl substitution further increases T_i;

b) For equal substitution at the radical carbon T_i increases by about 70° if one of the hydrogen atoms at C(3) is replaced by a CH₃-group. Further substitution of the second hydrogen at C(3) increases T_i by another 30–40°;








c) Methyl substitution at both C(2) and C(3) decreases T_r, *i.e.* facilitates the ring opening rearrangement.

We believe that the first effect a) can at least partly be ascribed to differences of zero point vibration energies. Assuming that substitution at the radical carbon does not change the barriers to inversion and that the frequency factors are the same for all radicals (compare footnotes a and c of table 2) the difference of the activation energies for inversion of any pair of radicals equally substituted at C(3) is given by

$$E_a(1) - E_a(2) = E_v(2) - E_v(1) \quad (13)$$

where $E_v = \frac{1}{2} h (f/\mu)^{1/2}$ is the zero point vibration energy of the bending vibration in the energy minimum configuration. This is estimated with the further assumption

Table 2. Characteristic Temperatures for Inversion and Rearrangement of Oxiranyl Radicals

Radical	$k_i \simeq 10^7 \text{ s}^{-1}$ at T_i	$k_r \simeq 10^3 \text{ s}^{-1}$ at T_r
	$-180 \pm 20^a)$	> 70
	$-^b)$	0 ± 5^c
	> -50	-30 ± 5
	-110 ± 10	> 0
	-55 ± 5^d	-35 ± 5
	-80 ± 5	-10 ± 10
	-15 ± 5	-45 ± 5

a) $E_a = (2 \pm 1)\text{kcal/mol}$, $\log (A/\text{s}^{-1}) = 11.9 \pm 2$

b) not observed, may be < -100

c) $E_a = (15 \pm 2)\text{kcal/mol}$, $\log (A/\text{s}^{-1}) = 15 \pm 1$ (section 3)

d) $E_a = (5.8 \pm 1.4)\text{kcal/mol}$, $\log (A/\text{s}^{-1}) = 12.6 \pm 0.8$

of the force constants being equal for all radicals and given by the INDO energy profile. Our INDO energies as function of ϕ yield $f = 0.85 \cdot 10^{-4} \text{ dyn/\AA}$ which seems reasonable (*cf.* $f(\text{CH}_3) = 0.56 \cdot 10^{-4} \text{ dyn/\AA}$ [34]) and leads to $E_\nu = 0.54 \text{ kcal/mol}$ for oxiranyl and to $E_\nu = 0.16 \text{ kcal/mol}$ for 2-methyloxiran-2-yl. From the Arrhenius law we have

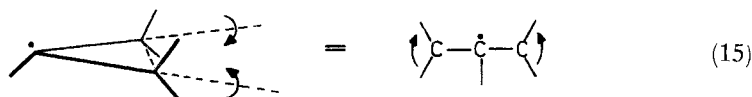
$$\frac{E_a(1) - E_a(2)}{E_a(2)} = \frac{T_i(1) - T_i(2)}{T_i(2)} \quad (14)$$

Insertion of $E_a(1) - E_a(2) = 0.38 \text{ kcal/mol}$ and $E_a(2)$ and $T_i(2)$ from table 2 then leads to the prediction that T_i should be about 10 to 50° higher for radicals carrying CH_3 -groups at C(2) than for radicals carrying hydrogen atoms. The experimental difference in T_i is about 60°.

The large effects b) of methyl substitution at C(3) on T_i must be due to an increase of the inversion barrier. Since the zero point vibration energies are small compared with the observed activation energies this statement is confirmed by the activation energies of 5.8 kcal/mol for 2,3-dimethyloxiranyl and of 2 kcal/mol for oxiranyl. Any quantitative discussion has to wait for results of quantum chemical calculations.

Facilitation of the ring opening rearrangement by substitution at C(2) and C(3) has also been demonstrated in the previous chemical studies [7–12]. We believe that

steric effects play a major role as evident from the data of table 2. In contrast to the cyclopropyl radical where the mode of ring opening is now being extensively discussed [35] we do not know of any theoretical treatment of the oxiranyl rearrangement (2) and therefore again delay quantitative statements. However, qualitatively, the effects of substitution may easily be explained if the ring opening of oxiranyl takes the same stereochemical course as cyclopropyl. This radical rearranges in a disrotatory fashion starting from a bent structure [35]. Now, we expect that highly substituted



oxiranyl radicals will be distorted by steric repulsions of the substituents as in (16), *i.e.* similar to the required approach to the transition state. Thus, as observed, substitution at C(2)



and C(3) will facilitate the ring opening.

3. Rearrangement Kinetics of 2-Methyloxiran-2-yl. – 3.1. *A Solvent Dependence of the ESR-Spectrum of Acetonyl Radicals.* In section 2.4, it was shown that photolysis of DTBP in methyloxiran \geq T at 0° leads to the appearance of a radical with three broad lines (1:2:1) which we, as others [15], attributed to the acetonyl radical $\dot{\text{C}}\text{H}_2\text{COCH}_3$ formed by ring opening of 2-methyloxiran-2-yl (fig.8). This radical has previously been observed by many authors. Comparison of the published ESR.-data reveals a consistency of the coupling constants of the inequivalent CH_2 -protons but a marked discrepancy between the observed CH_3 -couplings and g -factors. For instance, in aqueous solution $g = 2.0041$, $a(\text{CH}_3) = 0.10$ mT [36] [37], in acetone/water mixture $a(\text{CH}_3) = 0.083$ mT [38] and in acetone $g = 2.00441$, $a(\text{CH}_3) = 0.027$ mT [39] have been measured. To be certain that this is due to a solvent effect and not to a wrong assignment of the spectrum to acetonyl we remeasured the CH_3 -coupling constant and

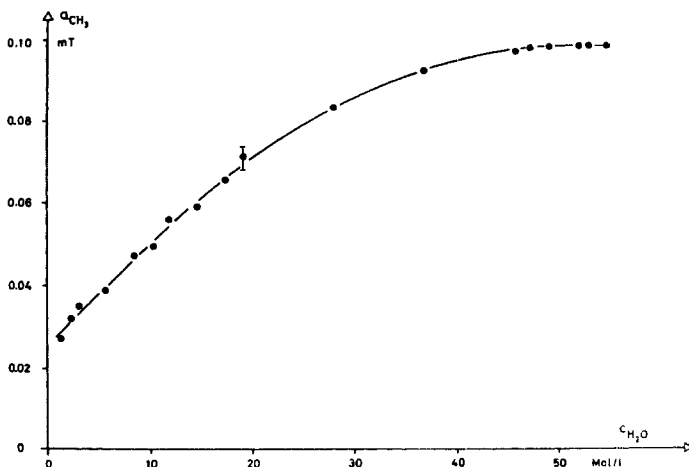
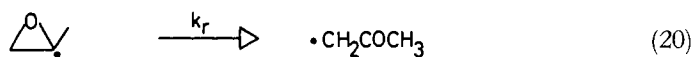
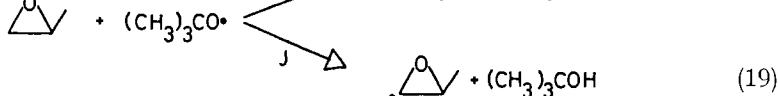
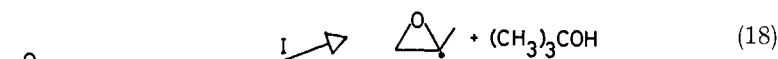
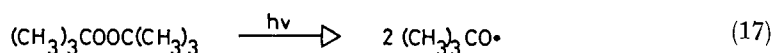


Fig. 12. a_{CH_3} of $\dot{\text{C}}\text{H}_2\text{COCH}_3$ vs. $\text{C}_2\text{H}_5\text{O}$

g-factor in acetone/water mixtures as function of the solvent decomposition. The radicals were produced by photolysis of H₂O₂ (3% by vol.) in these mixtures. Fig. 12 gives *a*(CH₃) at T = 25° as a function of the water concentration. The steady increase from 0.027 mT to 0.10 mT confirms that the spectra are not due to different radicals and that the differences of *a*(CH₃) are due to solvent effects. *g* shows a steady decrease from *g* = 2.00453 in acetone to *g* = 2.00417 in water. Solvent effects changing coupling constants by factors close to 4 are rare in ESR. Large effects are, for instance, known for nitroxide radicals where a solvent dependent stabilization of dipolar resonance structures is assumed responsible [40]. The solvent dependence of *a*(CH₃) and *g* observed here may be due to a similar contribution of the structure $\overset{\cdot}{\text{C}}\text{HC}_2(\text{O}^-)\text{CH}_3$, in water, probably favoured by hydrogen bonding effects. In other polar aprotic solvents coupling constants as in acetone are found, so in methyloxirane.

3.2. Rate Constants of the Rearrangement. Having established that the triplet observed for T ≥ 0° in methyloxirane (section 2.4.) is due to acetylonyl we measured the ratio of the concentrations of acetylonyl [K] and 2-methyloxiran-2-yl radicals [O] during photolysis of DTBP in methyloxirane by integration of the spectra. Details are given in the experimental section, an *Arrhenius* plot of [K]/[O] is shown in fig. 13. From the slope of the straight line the activation energy of the rearrangement is obtained following a kinetic analysis used previously for the neophyl rearrangement [3]: The reaction scheme is



where *I* and *J* denote the rates of formation of the oxiranyl radicals and *k_{ij}* are the termination rate constants for all the radicals of the scheme. As discussed earlier we neglect termination of the *t*-butoxy radicals and assume that *I* and *J* are temperature independent. Further, *k_{ij}* is approximated by 2(*k_{ii}k_{jj}*)^{1/2}. For steady state conditions this leads to

$$\frac{[K]}{[O]} = \frac{k_r}{(2k_{KK} [I + J])^{1/2}} \quad (22)$$

from which

$$\ln \frac{[K]}{[O]} = -\frac{E_a - 1/2 E_K}{RT} + \text{const} \quad (23)$$

where *E_K* is the activation energy of termination of the acetylonyl radical. This is approximated by the activation energy of the fluidity of methyloxirane (*E_F* = 1.8

kcal/mol [41]), since the terminations of transient radicals are close to diffusion control. From fig. 13 we then obtain the activation energy of the rearrangement $E_a = (15 \pm 2)$ kcal/mol, and from the absolute radical concentration we estimate $k_r = 10^3 \text{ s}^{-1}$ at 0° and combining this value with E_a arrive at a frequency factor of $\log (A/\text{s}^{-1}) = 15 \pm 1$. Transition state theory [24] predicts a frequency factor larger than $kT_e/h \simeq 10^{13}$ since the radical will gain entropy at ring opening, thus our result seems very reasonable.

To further characterize the rearrangement we have carried out a thermochemical analysis following known procedures [24]. The standard enthalpy of formation of acetylonyl is known ($\Delta H^\circ = -5.7$ kcal/mol [42]), that of 2-methyloxiran-2-yl was estimated from group increments and from ΔH° of cyclopropyl [43] as $\Delta H^\circ = 33.4$ kcal/

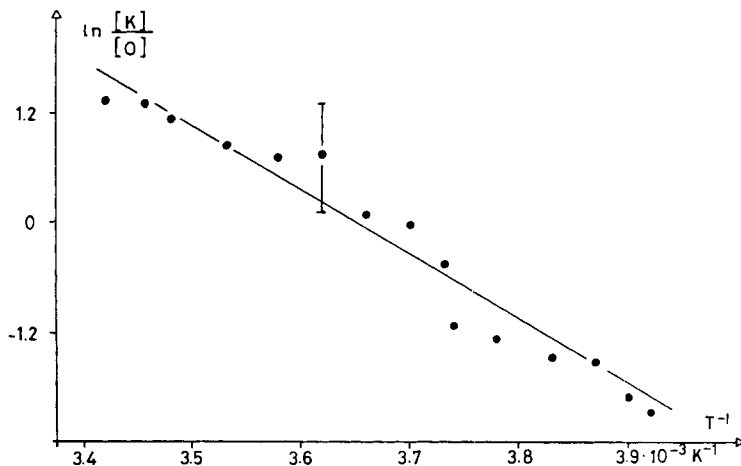


Fig. 13. 3-Methyloxiranyl Rearrangement: Arrhenius Plot of the Ratio of Radical Concentrations

mol. Thus the ring opening is exothermic by 39.1 kcal/mol. Absolute entropies determined by difference methods [43] show a slight (3.3 e. u.) entropy gain on rearrangement. The large enthalpy gain makes reaction (1) appear completely irreversible at normal temperatures, and in fact the ring closure reaction of α -keto alkyl radicals has never been reported.

4. Conclusions. - A series of alkyl substituted oxiranyl radicals has been studied by ESR-spectroscopy. The radicals have pyramidal configurations at the radical carbon atom and undergo inversion. The inversion rate constants and activation energies depend on substitution. In general, the inversion rates decrease with increasing degrees of alkyl substitution. Ring opening rearrangement of oxiranyl to α -keto alkyl radicals is found for several cases. The rearrangement is strongly favoured by alkyl substitution. For 2-methyloxiran-2-yl the kinetic and thermochemical data of the ring opening have been obtained.

To our opinion these results demonstrate the great potential of ESR, in the elucidation of radical structure and reaction kinetics and its advantages over conventional chemical methods relying on product analyses [2]. It will be interesting to compare the inversion and rearrangement behaviour of oxiranyls with detailed mo-

lecular energy calculations and with the behaviour of the structurally and electronically related radicals derived from cyclopropanes and aziridines, and we plan to study these subjects in the future.

5. Experimental. – The radicals were produced by photolysis of solutions within the cavity of a *Varian-E-4* ESR.-spectrometer. The light source was a *Hanovia* 1000W/Xe/Hg-lamp (977 B-1) the light of which was focussed on the sample by two *Suprasil* lenses ($\varnothing = 10$ cm, $f = 20$ cm) and filtered by a Ni/Co-sulfate solution [21]. The sample arrangement is shown in fig.14. It consists of a flat cuvette *K* through which the solution is slowly driven from a syringe and which is inserted into the dewar system *A* in the cavity *H*. Parts *B–G*, *I*, *L* and *M* of fig.14 serve to fix *A* and *K* and are self-explanatory. *A* and *K* were fabricated from *Suprasil* quartz. Typical flow rates and the procedures for measurements of coupling constants were as described earlier [21].

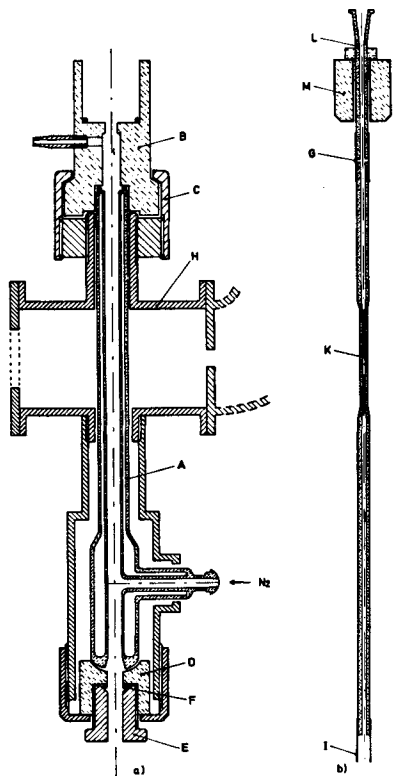


Fig.14. Cavity Arrangement: a) Dewar system, b) cuvette

To simulate and integrate ESR.-spectra on an on-line computer (*Varian* 620i, 8K) several computer programmes were developed:

a) A programme for spectrum simulation including second order shifts which is capable to handle up to 12 groups of up to 2^{15} equivalent protons.

b) Two programmes for integration starting either from noiseless simulated lines or from individual lines stored in the memory.

Commercially available chemicals were obtained from *Fluka* AG. *2-t*-Butyl- and *2,3-di-t*-butyloxirane were prepared following [44] from the corresponding olefins and *m*-chloroperbenzoic acid. Trimethyloxirane was obtained from the olefin *via* 2-bromo-2,3-dimethyl-butan-3-ol [45], and 3,3-dimethyloxirane from 1-chloro-2-methyl-propan-2-ol [46]. *Cis*- and *trans*-2,3-dimethyloxirane were prepared from the olefins by procedures [45] modified for gaseous starting compounds and low boiling points of the oxiranes. All compounds were characterized by NMR. and

boiling points. Gas-chromatography showed purities $\geq 90\%$, for the *cis*- and *trans*-dimethyloxiranes $\geq 98\%$. Solutions for ESR. measurements were purged with helium for 10–20 min before use.

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91. Kristalline Derivate des D,L- γ -Carboxyglutaminsäure- γ, γ' -di-*t*-butylesters

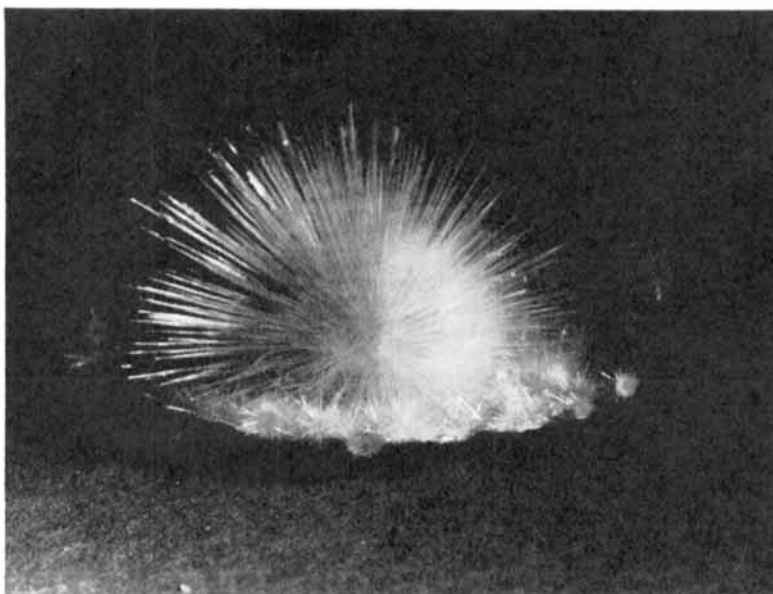
Vorläufige Mitteilung¹⁾

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(17. III. 76)

Kürzlich hatten wir über die Herstellung einiger für die Peptidsynthese geeigneter Derivate der im Prothrombin vorkommenden γ -Carboxyglutaminsäure



Figur. Kristalle von D,L-Z · Gla(OBu^t)₂ · OMe. Nadellänge ca. 1 cm. Aufnahme von Frau M. Bischof, Laboratorium für Festkörperphysik, ETH Hönggerberg, 8093 Zürich. Kamera: Hasselblad 500C, Objektiv: 3,5/100 mm mit Balg. Film: Kodak EHB 120, Kunstlicht 3200K (Leitz Aufnahmelampen)

¹⁾ Diese Arbeit wurde vom Schweizerischen Nationalfonds zur Förderung der Wissenschaftlichen Forschung unterstützt und ist ein Teil der Dissertationen von W. M. und M. O. Nomenklatur und Abkürzungen entsprechen den üblichen Normen, vgl. E. Wünsch: «Synthese von Peptiden», Bd. 15 von «Houben-Weyl, Methoden der organischen Chemie», E. Müller, Herausgeber, Georg Thieme Verlag, Stuttgart 1974. MSOC- ist 2-Methylsulfonyl-äthoxycarbonyl.