Conformational Analysis of the Cyclopropylacyl, Oxiranylacyl, and Aziridinylacyl Radicals by Electron Spin Resonance Spectroscopy

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A series of ring-substituted cyclopropylacyl, oxiran-2-ylacyl, and aziridin-2-ylacyl radicals have been prepared principally by the reaction of photolytically generated t-butoxyl radicals with the corresponding aldehydes. The e.s.r. spectra show that the cyclopropylacyl σ-radicals exist in *s-cis-* and *s-trans*-conformations of approximately equal stability, in which the plane of the acyl group bisects the ring (as it does in the parent aldehyde), and simulation of the spectra through the region of intermediate rates of exchange show that the barrier to rotation is *ca.* 17.5 kJ mol^{-1}. The behaviour of the *trans*-2-ethoxycarbonylcyclopropylacyl and 2,2-dimethylcyclopropylacyl radicals is similar. The oxiranylacyl and *trans*-3-methyloxiranylacyl radicals exist in the same two conformations with a rather lower barrier, and the *N*-alkylaziridinylacyl radicals appear to have a lower barrier still.

Our previous studies of acyl radicals were concerned largely with the correlation of the structure and the n.m.r. spectrum of the parent aldehyde with the structure and the e.s.r. spectrum of the product acyl radical.[1,2] Intramolecular interactions are largely unchanged when the σ-CH bond in the parent is replaced by the unpaired electron in the σ-orbital in the product, and the conformations of the two structures, particularly about the C(1)–C(2) bond, correspond. As the ^{1}H n.m.r. coupling constant, ^3J(HC–CHO), and the e.s.r. coupling constant, $a(H_\beta)$, show a similar dependence on the dihedral angle between the H–C(2) bond and the σ-orbital occupied by the two electrons in the C(O)–H bond of the aldehyde or by the unpaired electron in the radical, the two constants are linearly related.

Cyclopropanecarbaldehyde differs from the acyclic aldehydes in that it has two conformations (I) and (II) of approximately equal stability and in which the plane containing the CHO group bisects the ring, with a relatively high rotational barrier. On the above model, one might expect to detect under suitable conditions, two corresponding cyclopropylacyl radicals, and in a preliminary communication we reported the identification in this system of the first example of isomeric σ-radicals related by rotation about a formal σ-bond.[3]

We describe here an e.s.r. study of a series of cyclopropyl-, oxiranyl-, and aziridinyl-acyl radicals with the particular aim of investigating the rotational barrier about the C–ĊO bond.

Results and Discussion

A series of cyclopropane-, oxiran-, and aziridine-carbaldehydes were prepared, and were caused to react with photolytically generated t-butoxyl radicals in the cavity of an e.s.r. spectrometer (*cf.* ref. 1). The radicals which were detected, and their e.s.r. parameters, are listed in the Table.

Cyclopropylacyl Radicals.—Photolysis of a mixture of di-t-butyl peroxide and cyclopropanecarbaldehyde in cyclopropane below 183 K showed the spectra of two radicals, one consisting of a widely spaced doublet, a(H) 18.2 G, and the other a broad singlet, each with further hyperfine splitting observable at lower temperatures. Within an experimental error of *ca.* ±5%, the relative concentrations of the two radicals was 60 : 40.

As the temperature was raised, the lines broadened and then resolved into a simple doublet, a(1H) 11.0 G; the temperature dependence of the hyperfine coupling constant and linewidth of the outer pair of lines is illustrated in Figure 1. The spectra at low resolution are shown in our preliminary communication.[3]

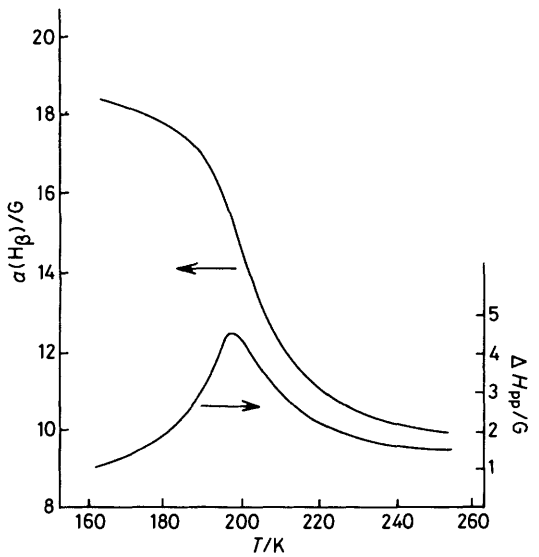
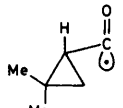
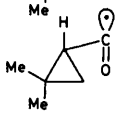
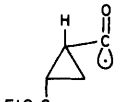
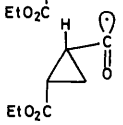
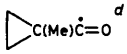
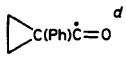
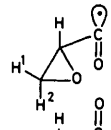
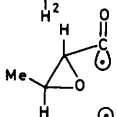
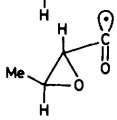
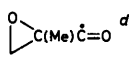
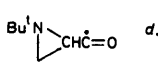
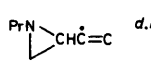


Figure 1. Temperature dependence of the hyperfine coupling constant, $a(H_\beta)$, and the width of the low-field line ΔH_{pp}, for the doublet of the cyclopropylacyl radical

Identical spectra were obtained when a mixture of cyclopropylacyl bromide, di-t-butyl peroxide, and hexabutylditin were photolysed in cyclopropane, or when t-butyl cyclopropyl ketone was photolysed in dichlorofluoromethane; the latter reaction showed also the spectrum of the t-butyl radical, as illustrated in Figure 2.

The low g factors and high ^{13}C hyperfine coupling constants, and the fact that identical results are obtained using three standard routes to acyl radicals, unambiguously identify both radicals as σ-acyl radicals. Electron diffraction [4] and microwave [5] spectroscopy established that cyclopropanecarbaldehyde (and related cyclopropylcarbonyl compounds) exist in the gas phase in the conformations (I) and (II) which have approximately equal stabilities and are separated by an appreciable rotational barrier (>10 or 18 kJ mol^{-1}, respectively, by the two techniques). ^{1}H N.m.r. spectroscopy of the aldehyde in solution is compatible with those conclusions but cannot decide unambiguously between a two- or three-fold barrier.[6,7] MO calculations suggest that the *cis*-conformation is more stable than the *trans*, with a barrier height of *ca.* 23 kJ mol^{-1}.[8] Applying our principles that the structures of the acyl radicals

E.s.r. parameters of cyclopropyl-, oxiranyl-, and aziridinyl-acyl radicals in cyclopropane

Radical	Hyperfine coupling constants (G) $a(H_\beta)$	$a(H_\gamma)$	$a(^{13}C_\alpha)$	g	T/K
 [a]	18.2	0.2 (2 H)	120.5	2.0009	172
 [b,c]	0.5	0.95 (2 H) 0.6 (2 H)	123.6	2.0008	172
	18.6	0.36 (1 H) [i]	121.5	2.0008 [s]	139
			122.5	2.0007	139
	17.9	0.2 (2 H)		2.0006	139
	0.8	1.5 (2 H) 1.0 (1 H)		2.0007	139
 [d]		0.85 (3 H)		2.0009	163
 [d]			126.0	2.0009	163
 [c]	14.2			2.0005	148
 [e]	1.6	3.2 (H^1)		2.0004	148
 [f]	11.0			2.0009	148
 [f]				2.0005	148
 [d]		1.2 (3H)		2.0001	176
 [d,g]		*j*		2.0006	151
 [d,h]		*k*		2.0007	151

[a] Calc. (INDO): $a(H_\beta)$ 25·2, a(2 H_γ), 0.25, a(2 $H_{\gamma'}$) 0.02, $a(^{13}C_\alpha)$ 125.0 G, assuming C–C=O 122°, and a normal geometry for the rest of the molecule. [b] Calc. (INDO): $a(H_\beta)$ −0.2, $a(2H_\gamma)$ 2.5, $a(2H_{\gamma'})$ 0.8, $a(^{13}C_\alpha)$ 124.5 G. [c] Analysed by computer simulation. [d] Conformation uncertain. [e] In dichlorodifluoromethane solvent. [f] In dimethoxyethane–cyclopropane mixture. [g] $da/dT = -35$ mG K^{-1} from 143 to 223 K; see Figure 4. [h] $da/dT = -33.5$ mG K^{-1} from 143 to 223 K. [i] a(3 H_δ) 0.36 G. [j] At higher temperatures a further triplet splitting of 0.48 G was observed. [k] At higher temperatures a further triplet splitting was observed.

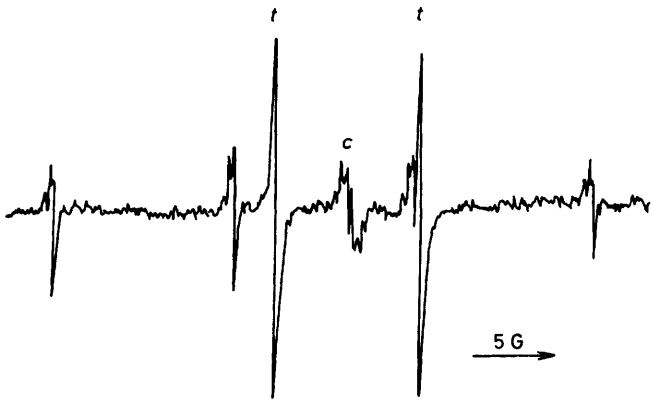
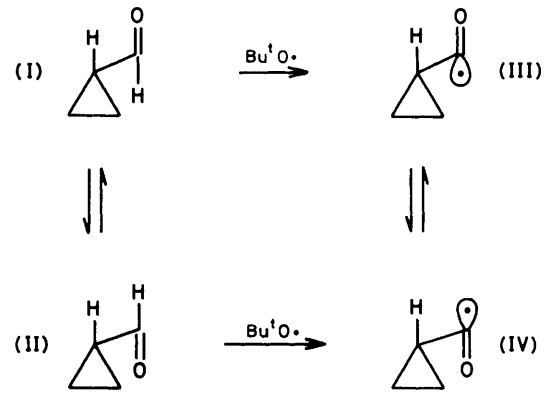


Figure 2. E.s.r. spectrum observed from the photolysis of cyclopropyl t-butyl ketone in CF_2Cl_2 at 143 K, showing the doublet of the *trans*-cyclopropylacyl radical (*t*) and the multiplet of the *cis*-cyclopropylacyl radical (*c*) superimposed in the signals of the t-butyl radical



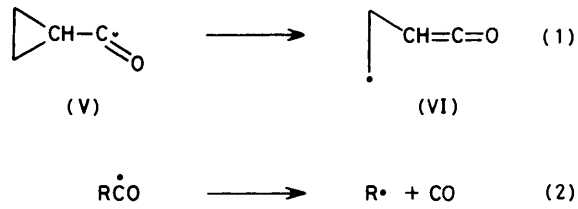
and the parent aldehydes should correlate, and that $a(H_\beta)$ is largest when the conformation about the C(1)–C(2) bond is *trans*,[1] we conclude that the doublet and the singlet which we observe at low temperature represent respectively the *trans*- and the *cis*-conformations of the cyclopropylacyl radical (III) and (IV). This assignment is supported by INDO calculations of the hyperfine coupling constants (see Table).

Above *ca.* 183 K, rotation about the C(1)–C(2) bond in the acyl radicals is rapid on the e.s.r. time scale, and a time-averaged spectrum is observed. Computer simulation of the spectra in the region of intermediate rates of exchange gives the approximate values at 186 K of k_1 1.8×10^7 s^{-1}, k_2 2.6×10^7 s^{-1}, E_a 17.5 kJ mol^{-1}, A 3.2×10^{12} s^{-1}, and ΔG 500 J mol^{-1}.

2,2-Dimethylcyclopropanecarbaldehyde behaved in the same way as the unsubstituted compound, showing a spectrum consisting of a doublet and a singlet at low temperature with relative intensities 70 : 30, and a singlet at high temperature. Further hyperfine splitting of the doublet could be resolved at low temperatures, INDO calculations suggesting that it is caused by coupling to the γ-proton and the γ-methyl group which lie *cis* to the carbonyl group in the *s-trans*-radical.

The behaviour of *trans*-2-ethoxycarbonylcyclopropanecarbaldehyde was again similar, but the relative intensity of the doublet and singlet was *ca.* 40 : 60. Details of the spectra of these two radicals are given in the Table.

We were unable to simulate satisfactorily the dynamic behaviour of these two radicals on the assumption of a simple two-fold barrier to rotation about the C(1)–C(2) bond, probably because the substituents in the ring interact with the carbonyl group to impose a more complicated energy profile on the rotation. However, since the spectral changes occur over a similar temperature range, and involve similar hyperfine coupling constants, as for cyclopropanecarbaldehyde, the Arrhenius parameters must be similar, *i.e.* E_a *ca.* 17 kJ mol^{-1} and log A *ca.* 12.



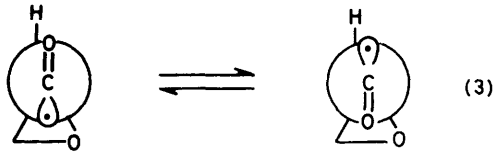
1-Methylcyclopropanecarbaldehyde showed the spectrum of only one radical, with no significant temperature effect. The large value of $a(3H_\gamma)$ of 0.85 G, suggests that the orbital containing the unpaired electron is located *trans* with respect to the methyl group [*cf.* EtCH=CMeĊO, where $a(3H_\beta)$ is 1.1 G],[1] but the above examples, and INDO calculations, indicate that, if the corresponding *cis*-isomer were present, its spectrum would consist of a single broad line beneath that of the *trans*-radical.

1-Phenylcyclopropanecarbaldehyde showed a spectrum of an acyl radical consisting of a single broad line throughout the temperature range which was examined. With no information from proton coupling constants, the conformation of the radical cannot be assigned.

Two familiar fragmentation reactions are not observed under our conditions. First, the ring-opening of cyclopropylmethyl radicals has attracted a lot of attention,[9] largely because ring-substituted compounds may show a contrathermodynamic regioselectivity.[10] Such a reaction with the cyclopropylacyl radicals (V) would lead to a keten (VI) [equation (1)], and the spectrum of (VI) is not observed, up to *ca.* 270 K even when the cyclopropyl ring carries 1-methyl, 1-phenyl, or 2,2-dimethyl substituents.

This accords with studies of the thermolysis of di-t-butyl peroxide in the presence of cyclopropanecarbaldehyde, 1-methylcyclopropanecarbaldehyde, and 1-phenylcyclopropanecarbaldehyde at *ca.* 410 K, when no ring-opened products were detected;[11,12] similarly, when cyclopropylacyl chloride was reduced with tributyltin hydride, no products resulting from the ring-opening of the intermediate cyclopropylacyl radical were obtained.[13] Whereas the ring-opening of the cyclopropylmethyl radical is probably exothermic by *ca.* 21 kJ mol^{-1}, the enthalpy of formation, $\Delta H_f°$, of both radicals (V) and (VI) can be estimated to be *ca.* +92 kJ mol^{-1}, and the reaction (V) ⟶ (VI) will be approximately thermally neutral.[14,15]

Secondly, acyl radicals undergo decarbonylation [equation (2)] at rates which are strongly dependent on the nature of the alkyl group. When R is primary alkyl, the spectra of the acyl radicals RĊO have been observed up to *ca.* 240 K, at which temperatures no signals of the alkyl radical R• are apparent,[1] but the pivaloyl radical (R = Bu^t) undergoes decarbonylation at 200 K at a rate such that the spectrum of the t-butyl radical which is formed can be observed.[16] Similarly, product analysis shows that little or no decarbonylation of the intermediate cyclopropylacyl occurs when it is formed from the aldehyde in carbon tetrachloride or diphenyl ether at *ca.* 410 K,[11,12] or from the acyl chloride and tributyltin hydride at room temperature.[13]



(VII) (VIII) (3)

None of the cyclopropylacyl radicals studied here showed any spectrum that could be assigned to the corresponding cyclopropyl radical up to *ca.* 270 K, and experiments in which the intensity of the photolysing light was varied with screens, showed that the decay of the cyclopropylacyl radical was second order (like that of the benzoyl radical [17]), presumably to give the 1,2-dione. This is in accord with the familiar strength of bonds to the cyclopropane ring.[11,12,18,*]

Oxiranylacyl Radicals.—At 148 K the spectrum observed from oxirancarbaldehyde consisted of a widely spaced broad-lined doublet, together with a central broad line. As the temperature was raised, the central line disappeared and the two outer lines sharpened and moved together (see Figure 3). 3-Methyloxiran-2-carbaldehyde behaved in the same way, but 2-methyloxiran-2-carbaldehyde showed a closely spaced quartet which was independent of the temperature (see Table).

With the first two compounds, an exchange process is clearly being observed, but at the lowest temperatures at which we could observe the radicals we have not reached the slow exchange limit spectra and so cannot measure the H hyperfine splitting constants required to simulate and estimate the barrier to rotation. However, comparison of the linewidths and hyperfine couplings with those observed with cyclopropanecarbaldehyde (Figures 1 and 2) suggests that exchange broadening of the spectra of (VII) and (VIII) [equation (3)] is already taking place at the lowest temperature (148 K) where spectra could be observed, implying that the rotational barrier between (VII) and (VIII) is now less than 17.5 kJ mol^{-1}.

The structure of oxirancarbaldehyde has been studied by microwave spectroscopy.[19] Only the *trans*-rotamer was detected, and the concentration of any other isomer at 195 K was estimated to be $<5\%$, corresponding to an energy difference of *ca.* 4.5 kJ mol^{-1}. The n.m.r. technique is less powerful for determining the structure, but, from the similarity of the vicinal coupling constants in cyclopropanecarbaldehyde and oxirancarbaldehyde under a variety of conditions, it was concluded that both compounds had a two-fold barrier to rotation.[7] On the other hand, from the results of a variety of measurements (i.r. and n.m.r. spectra, dipole moment, and Kerr constant) it was concluded that, in solution, only one conformation was important, in which the O–C–C=O moiety was approximately *s-trans* about the C–C bond.[20]

Aziridinylacyl Radicals.—Photolysis of di-t-butyl peroxide in the presence of *N*-t-butyl-2-formylaziridine (IX; R = Bu^t) in cyclopropane showed a spectrum consisting of a doublet, with a large negative temperature dependence, over the range

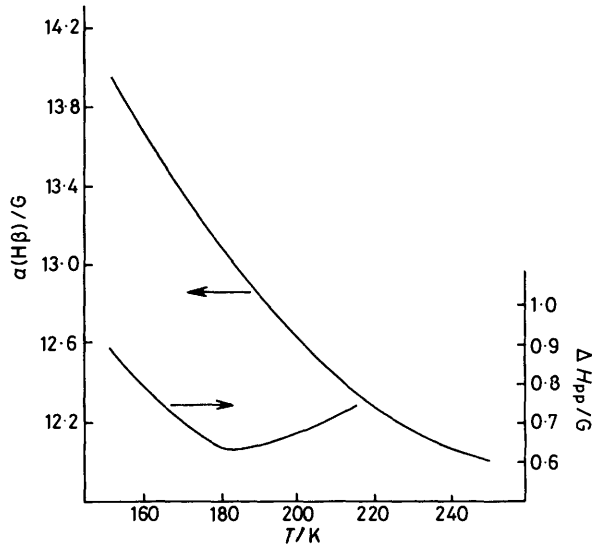


Figure 3. Temperature dependence of the hyperfine coupling constant, $a(H_\beta)$, and the width of the low-field line, ΔH_{pp}, for the doublet of the oxiranylacyl radical

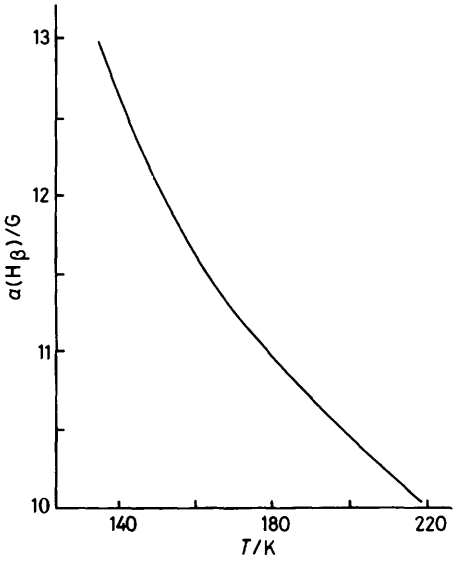
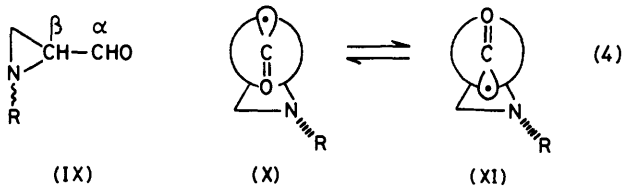


Figure 4. Temperature dependence of the hyperfine coupling, $a(H_\beta)$, for the *N*-t-butylaziridinylacyl radical

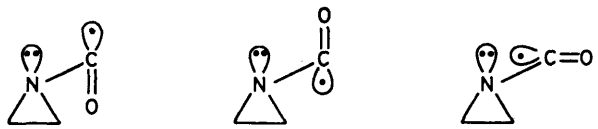


(IX) (X) (XI) (4)

143—223 K, as shown in Figure 4. At the higher temperatures, a further small triplet splitting was apparent, but the resolution was insufficient to show whether this was caused by the nitrogen or the two protons on C(3). The behaviour of *N*-propyl-2-formylaziridine (IX; R = Pr) was the same.

Studies by ^{1}H n.m.r. spectroscopy [21] have shown *N*-alkyl-2-formylaziridines (IX) undergo inversion at the nitrogen

* There is some question about the effect of 1-substituents in the cyclopropane ring on the bond strengths. The relative yields of products from the decarbonylation of the acyl radicals from cyclopropanecarbaldehyde and 1-methylcyclopropanecarbaldehyde at 408 K were 1 : 45,[12] whereas the relative yields from the decarboxylation of the acyloxyl radicals from cyclopropane t-butylperoxycarboxylate and 1-methylcyclopropane t-butylperoxycarboxylate were 1 : 1.7.[18] It has been suggested that the fragmentation of the peroxycarboxylate may involve synchronous rather than stepwise fission of the O–O and C–C bonds.[12]



(XII) (XIII) (XIV)

(XV) (XVI)

centre, with the *trans*-configuration predominating as the size of the alkyl group, R, increases: the *s-trans* conformation about the C_α–C_β bond is favoured. We interpret our results to imply that the barrier to rotation about the C_α–C_β bond in the corresponding acyl radical is lower than that in either the oxiran or cyclopropane analogues, so that only the region of fast exchange between the *s-cis* and *s-trans* radicals (X) and (XI) is being observed; the *s-cis* conformation (X) is less favourable, and the temperature dependence results from the radical preferring the *s-trans* conformation (XI) at low temperature.

On the principles that the structures of the aldehydes and acyl radicals, and the values of the n.m.r. and e.s.r. couplings should correlate,[1] the magnitude of ^3J(CH–CHO) in the aldehyde should show a similar negative temperature dependence, and a small effect is indeed observed. This is consistent with rotational isomerism taking place, with a low barrier.

The aziridin-1-ylacyl radicals would be interesting because they might adopt either the bisecting conformations (XII) and (XIII) analogous to the cyclopropyl, oxiran-2-yl, or aziridin-2-yl radicals reported here, or the perpendicular conformation (XIV) similar to that which is observed for the dialkylformamidyl radicals.

Unfortunately *N*-formylaziridine has never been properly characterized, and our attempts to synthesize it by a variety of methods, including the reaction of aziridine with methyl formate in methanol containing sodium methoxide,[22] were unsuccessful. *N*-Pivaloylaziridine was prepared in the hope that it might show a Norrish I fragmentation like cyclopropyl t-butyl ketone, but no t-butyl or acyl radical was observed on photolysis.

Conclusion

We conclude that the cyclopropylacyl, oxiranylacyl, and aziridin-2-ylacyl radicals are σ radicals in which the plane of the acyl moiety bisects the three-membered ring, and that the rotational barriers decrease in the sequence cyclopropyl (17.5 kJ mol^{-1}) > oxiranyl > aziridinyl. The origin of this barrier is probably best understood in terms of the interaction of the Walsh π-orbital [23] of the ring with the carbonyl π-orbital, as has been assumed in the corresponding aldehydes.[4,19] A similar but stronger interaction between the π-orbitals of the C=C and C=O groups is probably involved in holding the propenoyl radical more rigidly in the *s-trans* conformation (XV),[1] and a weaker interaction between the singly occupied *p*-orbital and the Walsh π-orbital may be responsible for the lower barrier (≯8—12 kJ mol^{-1}) to rotation between the degenerate conformations of the cyclopropylmethyl radical (XVI).[24]

Experimental

E.s.r. spectra were recorded and simulated by the methods already described; [1] we are grateful to Dr. A. R. Gregory for allowing us to use his modification of the computer program for simulations. Compounds which are not described below were commercially available, and were purified as necessary before use.

Cyclopropanecarbaldehyde.—This was prepared by oxidising cyclopropylmethanol with cerium(IV) ammonium nitrate,[25] and also by reducing cyclopropanecarbonitrile with tri-n-butoxyaluminium hydride,[26] and was purified by preparative g.l.c. on a C20M Carbowax column at 100 °C; τ (CCl_4) 1.08 (1 H, d, *J* 6.0 Hz, CHO), 7.99—8.57 (1 H, m, C*H*CHO), and 8.90—9.1 (4 H, m, CH_2CH_2CH).

Cyclopropanecarbonyl Bromide.—A mixture of cyclopropanecarboxylic acid (10.4 g) and phosphorus tribromide (10.8 g) was stirred at 50 °C under nitrogen for 1 h. Material with b.p. >70 °C at 20 mmHg was distilled off, then fractionated through a short column yielding the acyl bromide (4.57 g; 25%), b.p. 45—47 °C at 20 mmHg.[27]

Cyclopropyl t-Butyl Ketone.—Cyclopropanecarbonitrile (5.0 g) was slowly added at 0 °C to the Grignard reagent from t-butyl chloride (9.26 g) and magnesium (2.68 g) in ether (52 cm^3). The mixture was heated under reflux for 2 h, and hydrolysed with aqueous ammonium chloride yielding the ketone, b.p. 140—145 °C, τ (CCl_4) 8.5—9.45 (5 H, m, CH_2CH_2CH) and 8.84 (9 H, s, Bu^t); ν 1 700 cm^{-1} (C=O).[28]

1-*Methylcyclopropanecarbaldehyde*.—Methyl 1-methylcyclopropanecarboxylate was prepared by methylenation of methyl methacrylate with di-iodomethane in the presence of a zinc–copper couple,[29] or with diazomethane,[30] then reduced to 1-methylcyclopropylmethanol with lithium aluminium hydride, and oxidised to the aldehyde with chromium(VI) oxide and pyridine.[31] The product was purified by g.l.c. on a C20M Carbowax column at 150 °C; τ ($CDCl_3$) 1.33 (1 H, s, CHO), 7.92—9.35 (4 H, m, CH_2CH_2C), and 8.76 (3 H, s, CH_3).

2,2-*Dimethylcyclopropanecarbaldehyde*.—2,2-Dimethylcyclopropanecarbonitrile was prepared by treating the bis-(toluene-*p*-sulphonate) of 2,2-dimethylpropane-1,3-diol with potassium cyanide,[32] then it was reduced to the aldehyde with lithium aluminium hydride.[11] The product was purified by g.l.c. on a C20M Carbowax column at 120 °C, τ ($CDCl_3$) 0.57 (1 H, d, *J* 5.3 Hz, CHO), 8.06—9.04 (3 H, m, CCH_2OH), 8.72 (3 H, s, CH_3), and 8.80 (3 H, s, CH_3).

1-*Phenylcyclopropanecarbaldehyde*.—This was prepared from the nitrile by Roberts' method; [11] b.p. 58—60 °C at 0.5 mmHg, τ ($CDCl_3$) 0.68 (1 H, s, CHO), 2.69 (5 H, s, C_6H_5), and 8.24—8.66 (4 H, m, CH_2); ν 1 700 cm^{-1} (C=O).

Oxirancarbaldehyde.[33]—1M-Sodium hydroxide solution was added to a mixture of methanol (75 cm^3), water (75 cm^3), and 70% t-butyl hydroperoxide (0.275 mol) to bring the pH to 8—9 (Universal indicator paper). Acrolein (0.25 mol) was added dropwise over 20 min to this mixture at 35—38 °C, keeping the pH between 10 and 10.5 by adding alkali as needed. The mixture was stirred for 1 h, then it was cooled and saturated with ammonium sulphate, and extracted with cyclohexanone. The extract was distilled, collecting material boiling up to 70 °C at 50 mmHg. This fraction was diluted with benzene, dried ($MgSO_4$), and distilled. The fraction b.p. 70 °C at 50

mmHg consisted of oxirancarbaldehyde containing a little cyclohexanone; τ (neat) 2.18 (1 H, d, *J* 6.0 Hz, CHO) and 7.88—8.06 (3 H, m, CH_2CHO).

2-Methyloxiran-2-carbaldehyde.[33]—This was prepared in the same way as oxirancarbaldehyde, except that the reaction was strongly exothermic and required cooling, and the product was extracted into ether, and recovered with b.p. 51—56 °C at 80 mmHg; τ (neat) 1.06 (1 H, s, CHO), 6.70—7.02 (2 H, m, CH_2), and 8.58 (3 H, s, CH_3).

3-Methyloxiran-2-carbaldehyde [33]—This was prepared in the same way as 2-methyloxiran-2-carbaldehyde. The fraction boiling in the range 50—70 °C at 50 mmHg was collected, τ (CCl_4) 0.99 (1 H, d, *J* 6.5 Hz, CHO), 6.54—7.09 (2 H, m, CH–CH–O), and 8.06 (3 H, d, *J* 4.2 Hz, CH_3).

N-t-Butyl-2-formylaziridine.—t-Butylamine (2.33 g) and triethylamine (6.10 g) in benzene (50 cm^3) were added to a stirred solution of methyl 2,3-dibromopropionate (7.5 g) in benzene (15 cm^3) below 15 °C. This mixture was allowed to warm to room temperature over 1 h, then heated under reflux for 3 h, cooled, filtered free from triethylammonium bromide and passed down an alumina column to remove any residual salt, water, and acid. The solvent was removed leaving crude *N*-t-butyl-2-methoxycarbonylaziridine (2.88 g).[34]

A solution of 2M-di-isobutylaluminium hydride in hexane (10 cm^3) was added over 15 min to the crude ester (2.8 g) in ether (130 cm^3) at −78 °C under nitrogen. The mixture was stirred for 30 min, then was hydrolysed by adding methanol (2 cm^3) followed by a saturated solution of sodium hydrogencarbonate and allowed to warm slowly to room temperature. 10% Sodium hydroxide solution (7.9 cm^3) was then added and the resulting precipitate was filtered off. The filtrate was distilled giving a mixture of the aldehyde [35] and the corresponding alcohol from which the aldehyde was isolated by g.l.c. on a 15% silicone oil column at 125 °C; τ ($CDCl_3$) 1.1 (1 H, d, *J* 5.5 Hz, CHO), 7.64—8.24 (3 H, m, CH_2CHN), and 8.97 (9 H, s, Bu^t).

The temperature dependence of ^3J(CH–CHO) for the neat aldehyde was determined under the same temperature conditions which Karabatsos used for cyclopropane- and oxirancarbaldehydes: [6] τ/°C, ^3J/Hz, −30, 6.6; 0, 6.5; +30, 6.6; +70, 6.2.

N-Propyl-2-formylaziridine.—*N*-Propyl-2-methoxycarbonylaziridine, b.p. 50—52 °C at 0.1 mmHg, was prepared in 75% yield from n-propylamine and methyl 2,3-dibromopropionate. The ester (7.3 g) was reduced in ether with lithium aluminium hydride (0.88 g) at —78 °C, and the resulting aldehyde was separated from the alcohol by g.l.c.; τ (CCl_2FCClF_2) 1.20 (1 H, d, *J* 5.5 Hz, CHO) and 7.54—9.19 (10 H m, Pr and CH_2CHN).

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