Experimental Section

Dibromoacetaldehyde was prepared according to the procedure of Shchukina.[21] The following is a typical preparation. To 44 g of freshly distilled acetaldehyde maintained at 0° and stirred with a magnetic stirrer was added dropwise 80 g of bromine. At the end of the addition, the reaction mixture was allowed to warm up to room temperature. After dropwise addition of another 80 g of bromine, the reaction mixture was stirred for 20-25 hr. The resultant two layers were separated and the upper layer was discarded. Prepurified nitrogen was bubbled through the lower layer for about 1 hr in order to purge it of any hydrogen bromide present. After three vacuum distillations (3 mm of Hg, 26°) pure dibromoacetaldehyde was obtained.

Commercially available dichloroacetaldehyde was purified by preparative gas chromatography prior to use.

Nmr spectra were determined at 60 Mc on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.), equipped with a variable-temperature probe and a V-6040 variable-temperature controller. Temperatures were controlled to ±2°.

Acknowledgment. We thank the National Science Foundation for generous financial support. We also thank Dr. N. Hsi for his assistance in the studies of dichloroacetaldehyde.

[21] M. N. Shchukina, *Zh. Obshch. Khim.*, **18**, 1653 (1948).

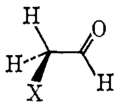
Structural Studies by Nuclear Magnetic Resonance. XXII. Conformational Analysis of Glycidaldehyde, Phenoxyacetaldehyde, Methoxyacetaldehyde, and Methylmercaptoacetaldehyde

Gerasimos J. Karabatsos and David J. Fenoglio

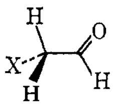
Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. Received September 11, 1968

Abstract: The vicinal spin-spin coupling constants between aldehydic and α-protons of methoxyacetaldehyde, phenoxyacetaldehyde, methylmercaptoacetaldehyde, glycidaldehyde, and cyclopropanecarboxaldehyde were studied at 60 Mc as a function of temperature and solvent. The following conclusions were drawn. (1) A threefold barrier to rotation about the carbon-carbon bond best fits the data from the first three compounds. No unambiguous decision could be made regarding the analogous barrier to rotation of the last two compounds. (2) The most stable rotamer of methoxyacetaldehyde and phenoxyacetaldehyde is the one where the C-X bond eclipses the carbonyl group, and the most stable rotamer of the other three compounds is the one where the C-H bind eclipses the carbonyl. (3) The free energy and enthalpy values for I $\rightleftharpoons$ II (X = OCH_3, OC_6H_5) are strongly solvent dependent, being much more negative in solvents of high dielectric constant. Those of methylmercaptoacetaldehyde and glycidaldehyde are solvent insensitive. (4) Whereas the cyclopropyl group acts as an electron donor, the oxirane group acts as an electron withdrawer. This difference notwithstanding, the oxirane resembles more the cyclopropyl than it does the methoxy.

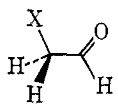
We have recently discussed the conformational analysis of chloro- and bromoacetaldehyde,[1] and of dichloro- and dibromoacetaldehyde.[2] As part of our program designed to probe into the nature of the factors controlling the relative stabilities of I and II, when X is a heteroatom, we have studied phenoxyacetaldehyde (X = OC_6H_5), methoxyacetaldehyde (X = OCH_3), and methylmercaptoacetaldehyde (X = SCH_3). Since there was some question from the nmr results[3] as to whether in the liquid phase cyclopropanecarboxaldehyde was best described in terms of a twofold barrier to rotation (III and IV as the minimum energy configuration), as found in the gas phase,[4] or in terms of a threefold barrier to rotation (III and V as the minimum energy configurations), we have studied this problem further. The obvious relation of glycidaldehyde to both systems under consideration, prompted us to study it, to see if a twofold (VI and VII) or a threefold (VI, VIII, and IX) barrier to rotation best describes this system.



Ia



Ib



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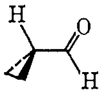
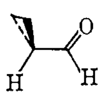
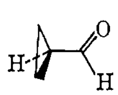


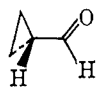
III



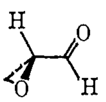
IV



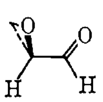
Va



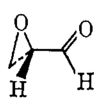
Vb



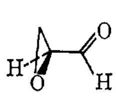
VI



VII



VIII



IX

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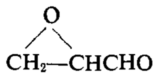
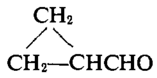
[1] G. J. Karabatsos and D. J. Fenoglio, *J. Am. Chem. Soc.*, **91**, 1124 (1969).

[2] G. J. Karabatsos, D. J. Fenoglio, and S. S. Lande, *ibid.*, **91**, 3572 (1969).

[3] G. J. Karabatsos and N. Hsi, *ibid.*, **87**, 2864 (1965).

[4] (a) L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Letters*, No. **13**, 705 (1964); *J. Chem. Phys.*, **43**, 647 (1965); (b) R. N. Schwendeman and H. N. Volltrauer, private communication.

Table I. Vicinal Spin–Spin Coupling Constants[a] of Some Heteroacetaldehydes

	J_{HH}, cps				
Solvent[b]	$C_6H_5OCH_2CHO$	CH_3OCH_2CHO	CH_3SCH_2CHO		
$CH_3(CH_2)_3CH_3$	1.52	1.37	3.63		4.63
Cyclohexane	1.49	1.34	3.63	6.26	4.70
trans-Decalin	1.45	1.29	3.63	6.28	4.74
CCl_4	1.48	1.27	3.63	6.22	4.94
$CHCl_3$	1.16	0.80	3.54		
CH_2Br_2	1.05	0.78	3.51	6.08	5.75
CH_2Cl_2	0.94	0.77	3.46	6.06	5.75
CH_3COCH_3	0.73	0.76	3.35	5.90	5.80
$(CH_3)_2NCHO$	*Ca.* 0.49	*Ca.* 0.47	3.25	5.85	5.95
CH_3CN	*Ca.* 0.44[c]	*Ca.* 0.41	3.25	5.94	6.00
$(CH_3)_2SO$			3.18	5.79	6.15
H_2NCHO			3.10	5.48	6.20
C_6H_6	1.15	0.99	3.51	6.41	5.30
$C_6H_5CH_3$	1.22	0.99	3.51	6.40	5.25
C_6H_5Cl	1.14	0.92	3.48	6.23	5.80
C_6H_5CN	0.71	0.69	3.33	6.06	5.73
$C_6H_5NO_2$	0.71	0.59	3.39	6.04	5.60
Neat	0.73		3.42		

[a] Values at 36 ± 2°. [b] 2.5–4% solutions. [c] Poor resolution.

Results and Discussion

Spin–Spin Coupling Constants. In Table I are summarized the vicinal spin–spin coupling constants between the aldehydic proton and the proton(s) on the α-carbon of phenoxyacetaldehyde, methoxyacetaldehyde, methylmercaptoacetaldehyde, glycidaldehyde, and cyclopropanecarboxaldehyde, in 2.5–4% solutions in various solvents. All values are averages of seven to ten measurements with a precision of ±0.03 cps. They were always checked against known values of acetaldehyde.[1,2]

The coupling constants of phenoxyacetaldehyde and methoxyacetaldehyde are the smallest vicinal coupling constants observed for substituted acetaldehydes.[1–3] Their dependence on solvent polarity, *i.e.*, sharp decrease with increasing dielectric constant of solvent, closely parallels that of the vicinal coupling constants of haloacetaldehydes.[1,2] On this observation alone, we conclude that the more polar rotamer must be the one with the smaller coupling constant. This conclusion is consistent with I and II being the minimum energy configuration of these two compounds.

The vicinal coupling constant of methylmercaptoacetaldehyde is considerably larger than those just discussed. In fact, it is even larger, in all solvents, than that of acetaldehyde (2.85 cps). It decreases with increase of solvent polarity, but to a much lesser extent than those of phenoxy- and methoxyacetaldehydes. The polarities of the rotamers of methylmercaptoacetaldehyde must, therefore, be quite similar. In view of the small differences between the electronegativities of hydrogen and sulfur, this conclusion is reasonable and again consistent with I and II being the minimum energy configurations of this aldehyde.

In contrast to the small values of the vicinal coupling constants of the above three aldehydes, those of the corresponding coupling constants of glycidaldehyde and cyclopropanecarboxaldehyde are quite large. In fact, the coupling constant of glycidaldehyde is the largest observed of any aldehyde, other than those of α,β-unsaturated aldehydes, whose values are[5] about 7.7 cps. From the fact that the coupling constant of glycidaldehyde decreases with increase of solvent dielectric constant, whereas that of cyclopropanecarboxaldehyde increases, we conclude that the rotamer with the high coupling constant of glycidaldehyde and cyclopropanecarboxaldehyde is, respectively, the less and the more polar rotamer. In more specific terms, III is more polar than IV, or V, and VI is less polar than VII, or VIII and IX.

Table II demonstrates the temperature dependence of the vicinal coupling constants of the five aldehydes. In all solvents, those of phenoxyacetaldehyde and methoxyacetaldehyde increase with increasing temperature. This observation leads to the conclusion that rotamer II is more stable than I_a. From the data summarized in Table II, and from plots of these coupling constants *vs.* temperature, it appears that about 1.6 and 1.5 cps are the values where the coupling constant of phenoxyacetaldehyde and methoxyacetaldehyde, respectively, become temperature independent.

In contrast to the two coupling constants just discussed, those of the other three compounds decrease with increasing temperature. Hence, rotamer II of methylmercaptoacetaldehyde is less, not more, stable than I_a; and III and VI are the most stable rotamers of cyclopropanecarboxaldehyde and glycidaldehyde, respectively. The coupling constant of methylmercaptoacetaldehyde, when plotted against temperature, appears to level off at about 3.0 cps.

The qualitative conclusions that we have reached up to this point regarding the relative stabilities of the various rotamers are based on the assumption that J_t, the *trans* coupling, is larger than J_c, the *cis* coupling, or J_g, the *gauche* coupling.

Semiquantitative Treatment of Data. Leaving glycidaldehyde and cyclopropanecarboxaldehyde for later discussion, we can treat the data from the other three aldehydes so as to yield rotamer populations, free energies, and enthalpies. As previously discussed,[1] rotamer populations and free energies can be calculated from eq 1 and 2, respectively, where p is the fractional popula-

$$J_{\text{obsd}} = p(J_t + J_g)/2 + (1 - p)J_g \qquad (1)$$

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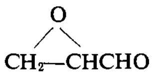
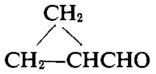
(5) (a) J. A. Pople and T. Schaefer, *Mol. Phys.*, 3, 547 (1960); (b) A. A. Bothner-By and R. K. Harris, *J. Org. Chem.*, 30, 254 (1965).

Table II. Temperature Dependence of the Vicinal Spin-Spin Coupling Constants of Some Substituted Acetaldehydes

Solvent[a]	J_{CH-CHO}, cps										
	−30°	−15°	0°	15°	36°	50°	70°	90°	100°	110°	130°
					$C_6H_5OCH_2CHO$						
Cyclohexane			1.44		1.46	1.53	1.52	1.52[b]			
trans-Decalin	1.30[c]		1.38		1.45		1.51		1.53		1.54 (1.53)[d]
$C_6H_5CH_3$	0.79		1.08		1.21		1.32			1.40	
C_6H_5Cl	0.78		.07		1.16		1.31			1.36	
Neat					0.73	0.80	0.88		0.97		1.05
$(CH_3)_2NCHO$					0.48	0.54	0.61	0.70		0.78	
					CH_3OCH_2CHO						
Cyclohexane			1.19		1.29	1.32	1.39	1.39[b]			
trans-Decalin			1.20		1.31		1.34		1.38		1.39
$C_6H_5CH_3$			0.83		0.99		1.18		1.23		
$(CH_3)_2NCHO$					0.57		0.75		0.80		
					CH_3SCH_2CHO						
trans-Decalin	3.82		3.77		3.63		3.60			3.47	
$C_6H_5CH_3$	3.74		3.68		3.52		3.50			3.43	
C_6H_5Cl	3.69		3.61		3.49		3.43			3.34	
$(CH_3)_2NCHO$	3.46		3.38		3.25		3.25			3.20	
H_2NCHO			3.32	3.20	3.16		3.02[e]	3.05[b]	3.03		
											
trans-Decalin		6.51	6.44	6.40	6.28	6.27	6.18	6.20		6.12	
$(CH_3)_2NCHO$	6.20	6.15	6.12	6.09	5.88	5.86	5.83	5.78		5.64	
											
trans-Decalin	5.39	5.14	5.11	4.95	4.74	4.70	4.60	4.56		4.53	

[a] 5% solutions. [b] Value at 80°. [c] Value at −20°. [d] Value at 160°. [e] Value at 60°.

$$\Delta G^\circ = -RT \ln (J_t + J_g - 2J_{obsd})/(J_{obsd} - J_g) \quad (2)$$

tion of I, and $(1 - p)$ that of II. Enthalpies can be calculated from plots of log K_{eq} *vs.* $1/T$, where K_{eq} is given by eq 3. The parameters J_t and J_g needed to

$$K_{eq} = 2(1 - p)/p \quad (3)$$

$$J_{av} = {}^1/_3(J_t + 2J_g) \quad (4)$$

solve eq 1 and 2 can be estimated from the experimental data and eq 4, which relates the experimental coupling constant to J_t and J_g, either when the three rotamers I_a, I_b, and II are equally populated, or at the state of free rotation—usually at very high temperatures—about the carbon–carbon bond. The values of phenoxyacetaldehyde, methoxyacetaldehyde, and methylmercaptoacetaldehyde that satisfy eq 4 are, respectively, about 1.6, 1.5, and 3.0 cps. Let us now proceed to set limits for J_t and J_g.

Since the lowest experimentally measured vicinal coupling constant of phenoxyacetaldehyde is 0.5 cps, J_g must be equal to or smaller (in absolute magnitude) than 0.5 cps. If J_t and J_g have the same sign, then eq 4 yields: $J_g \leqslant 0.5$ cps and $J_t \geqslant 3.8$ cps. If they have opposite signs, then $J_g \leqslant 0.5$ cps and $J_t \geqslant 5.8$ cps. Similar treatment of the data of methoxyacetaldehyde yields: $J_g \leqslant 0.4$ cps and $J_t \geqslant 3.7$ cps, if the signs are the same; and $J_g \leqslant 0.4$ cps and $J_t \geqslant 5.3$ cps, if the signs are opposite.

Because the coupling constant of methylmercaptoacetaldehyde does not vary extensively with solvent polarity, it is difficult to set any reasonable limits on J_t and J_g. Judging from the similarity among the values of J_{av} of acetaldehyde (2.85 cps), bromoacetaldehyde (2.75 cps), and methylmercaptoacetaldehyde (3.0 cps), we have chosen 0.6 and 7.8 cps as reasonable values, respectively, for J_g and J_t of methylmercaptoacetaldehyde.

Table III. Solvent Dependence of Rotamer Populations[a] of Phenoxyacetaldehyde, Methoxyacetaldehyde, and Methylmercaptoacetaldehyde

Solvent[b]	% II				
	$C_6H_5OCH_2CHO$		CH_3OCH_2CHO		CH_3SCH_2-CHO
	A[c]	B[d]	A′[e]	B′[f]	E[g]
$CH_3(CH_2)_3CH_3$	38	36	46	38	16
Cyclohexane	40	37	48	39	16
trans-Decalin	42	38	51	41	16
CCl_4	41	37	52	41	16
$CHCl_3$	60	47	78	58	18
CH_2Br_2	67	52	79	59	19
CH_2Cl_2	73	54	80	50	21
CH_3COCH_3	86	61	80	59	24
$(CH_3)_2NCHO$	>99	69	96	70	26
CH_3CN	>99	70	>99	72	26
H_2NCHO					31
C_6H_6	61	48	67	51	19
$C_6H_5CH_3$	56	45	67	51	19
C_6H_5Cl	61	48	71	54	20
C_6H_5CN	87	62	84	62	24
$C_6H_5NO_2$	87	62	90	65	23
Neat	89	62			

[a] All values calculated for 36°. [b] 5% solutions. [c] Coupling constants used: $J_t = +3.8$ cps and $J_g = +0.5$ cps. [d] Coupling constants used: $J_t = +5.8$ cps and $J_g = -0.5$ cps. [e] Coupling constants used: $J_t = +3.7$ cps and $J_g = +0.4$ cps. [f] Coupling constants used: $J_t = +5.3$ cps and $J_g = -0.4$ cps. [g] Coupling constants used: $J_t = +7.8$ cps and $J_g = +0.6$ cps.

In Tables III, IV, and V are summarized the rotamer populations, free energies, and enthalpies, respectively,

Table IV. Solvent Dependence of the Free Energy Difference,[a] ΔG°, between Rotamers of Phenoxyacetaldehyde, Methoxyacetaldehyde, and Methylmercaptoacetaldehyde

	ΔG°, cal/mol, for $I_a \rightleftharpoons II$				
	$C_6H_5OCH_2CHO$		CH_3OCH_2CHO		CH_3SCH_2CHO
Solvent[b]	*A*	*B*	*A'*	*B'*	*C*
$CH_3(CH_2)_3CH_3$	−130	−70	−340	−120	+600
Cyclohexane	−180	−90	−380	−150	+600
trans-Decalin	−240	−130	−440	−200	+600
CCl_4	−200	−100	−470	−200	+600
$CHCl_3$	−700	−360	−1200	−620	+500
CH_2Br_2	−860	−470	−1200	−640	+450
CH_2Cl_2	−960	−530	−1200	−650	+400
CH_3COCH_3	−1500	−700	−1300	−660	+300
$(CH_3)_2NCHO$		−900	−2400	−930	+200
CH_3CN		−950	−3600	−1000	+200
H_2NCHO					+80
C_6H_6	−700	−370	−870	−460	+500
$C_6H_5CH_3$	−600	−300	−870	−460	+500
C_6H_5Cl	−700	−380	−1000	−540	+400
C_6H_5CN	−1600	−700	−1400	−700	+300
$C_6H_5NO_2$	−1600	−700	−1700	−800	+330
Neat	−1700	−700			

[a] Calculated for 36° from data of Table III. To identify the coupling constants used in calculating values under *A*, *B*, etc., see Table III. [b] 5% solutions.

Table V. Enthalpy Differences,[a] ΔH°, between Rotamers of Phenoxyacetaldehyde, Methoxyacetaldehyde, and Methylmercaptoacetaldehyde

	ΔH°, cal/mol, for $I \rightleftharpoons II$				
	$C_6H_5OCH_2CHO$		CH_3OCH_2CHO		CH_3SCH_2CHO
Solvent	*A*	*B*	*A'*	*B'*	*C*
Cyclohexane			−1400	−600	
trans-Decalin	−1200	−500	−1400	−600	+1000
$C_6H_5CH_3$	−1700	−700	−2200	−800	+900
C_6H_5Cl	−1700	−900			+900
$(CH_3)_2NCHO$		−1300	−2600	−1200	+500
H_2NCHO					+300
Neat	−3600	−1200			

[a] To identify the coupling constants used for *A*, *B*, etc., see Table III.

that have been calculated according to the procedure just outlined.

The most stable rotamer of phenoxyacetaldehyde and methoxyacetaldehyde is II, its stability increasing rapidly with increase of the dielectric constant of the solvent. In contrast, II is the least stable rotamer of methylmercaptoacetaldehyde. The stability of II of the first two compounds is again greater, as was that of the analogous rotamer of haloacetaldehydes,[1,2] in the aromatic solvents benzene and toluene than warranted from their dielectric constants (ϵ of 2.3 and 2.4 for benzene and toluene, respectively). The type of solute–solvent stereospecific association suggested for the haloacetaldehydes[2] probably accounts for this effect.

Particularly obvious are the large discrepancies between free energies (Table IV) and enthalpies (Table V), especially between those of phenoxyacetaldehyde and methoxyacetaldehyde, in the low dielectric constant solvents. Although entropy differences between rotamers might be partly responsible for these discrepancies, we feel that the choice of J_t and J_g constitutes the major source of them. These parameters were calculated on the basis that J_{av} satisfying eq 4 is 1.6 cps for phenoxyacetaldehyde and 1.5 cps for methoxyacetaldehyde. These values are, however, considerably lower than those of acetaldehyde (2.85 cps), bromoacetaldehyde (2.75 cps), and chloroacetaldehyde (2.5 cps). From electronegativity considerations,[6] they ought to be between 2.0 and 2.5 cps. To show how the use of J_{av} of 2.0 and 2.5 cps would affect rotamer populations, free energies, and enthalpies, we have summarized those in low dielectric constant solvents in Tables VI and VII. The much better correspondence between free energies and enthalpies suggests that these values are more reliable than those summarized in Tables III–V.

The relative stabilities of I_a and II are shown below as a function of X. The rough order indicated is based on present and previous[1–3] results, and is valid only in

$$X = CH_3 > CH_2CH_3 \sim C_6H_5O \sim CH_3O >$$

$$CH(CH_3)_2 > C_6H_5 \sim Cl > Br > C(CH_3)_3 > CH_3S$$

$$\text{increased stability of II} \longleftrightarrow \text{decreased stability of II}$$

solvents of low dielectric constant, such as carbon tetrachloride and saturated hydrocarbons. In solvents of high dielectric constant, the methoxy, phenoxy, chloro, and bromo groups move ahead of the methyl group in the order. For groups preceding bromine in the indicated order, ΔH° for $I \rightleftharpoons II$ is negative, and for those following it, it is positive. The position of the more polarizable methylmercapto group with respect to that of the less polarizable methoxy, as well as that of bromine with respect to that of chlorine, reinforces

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(6) (a) S. Ebersole, S. M. Castellano, and A. A. Bothner-By, *J. Phys. Chem.*, **68**, 3430 (1964); (b) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, 7, 165 (1963).

Table VI. Rotamer Populations[a] of Phenoxyacetaldehyde and Methoxyacetaldehyde

Solvent[b]	% II			
	$C_6H_5OCH_2CHO$		CH_3OCH_2CHO	
	A[c]	*B*[d]	*A'*[e]	*B'*[f]
$J_{av} = {}^1/_3(J_t + 2J_g) = 2.0$ cps				
n-Pentane	55	46	53	47
Cyclohexane	56	47	55	48
trans-Decalin	58	48	56	49
$J_{av} = {}^1/_3(J_t + 2J_g) = 2.5$ cps				
n-Pentane	66	55	64	56
Cyclohexane	67	56	65	57
trans-Decalin	68	57	67	57

[a] All values calculated for 36°. [b] 5% solutions. [c] Coupling constants used: $J_t = +5.0$ cps and $J_g = +0.5$ cps for $J_{av} = 2.0$ cps, and $J_t = +6.5$ cps and $J_g = +0.5$ cps for $J_{av} = 2.5$ cps. [d] Coupling constants used: $J_t = +7.0$ cps and $J_g = -0.5$ cps for $J_{av} = 2.0$ cps, and $J_t = +8.5$ cps and $J_g = -0.5$ cps for $J_{av} = 2.5$ cps. [e] Coupling constants are: $J_t = +5.2$ cps and $J_g = +0.4$ cps for $J_{av} = 2.0$ cps, and $J_t = +6.7$ cps and $J_g = +0.4$ cps for $J_{av} = 2.5$ cps. [f] Coupling constants used: $J_t = +6.8$ cps and $J_g = -0.4$ cps for $J_{av} = 2.0$ cps, and $J_t = +8.3$ cps and $J_g = -0.4$ cps for $J_{av} = 2.5$ cps.

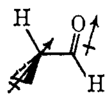
Table VII. Free Energy Difference,[a] $\Delta G°$, between Rotamers of Phenoxyacetaldehyde and Methoxyacetaldehyde

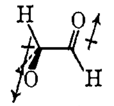
Solvent	$\Delta G°$, cal/mol, for $I_a \rightleftharpoons II$			
	$C_6H_5OCH_2CHO$		CH_3OCH_2CHO	
	A	*B*	*A'*	*B'*
$J_{av} = {}^1/_3(J_t + 2J_g) = 2.0$ cps				
n-Pentane	−540	−320	−510	−350
Cyclohexane	−570	−350	−540	−370
trans-Decalin	−620	−380	−580	−400
$J_{av} = {}^1/_3(J_t + 2J_g) = 2.5$ cps				
n-Pentane	−830	−550	−780	−570
Cyclohexane	−880	−570	−810	−590
trans-Decalin	−900	−580	−850	−610
$\Delta H°$, cal/mol, for $I \rightleftharpoons II$				
Cyclohexane ($J_{av} = 2.0$ cps)			−800	−500
Cyclohexane ($J_{av} = 2.5$ cps)			−800	−500
trans-Decalin ($J_{av} = 2.0$ cps)	−600	−400	−600	−400
trans-Decalin ($J_{av} = 2.5$ cps)	−500	−300	−500	−300

[a] Calculated for 36° from data of Table VI. To identify the coupling constants used to calculate the values under *A, B*, etc., use Table VI.

the conclusion[1] that dipole-induced dipole interactions play minor roles in determining the relative stabilities of I and II. Nonbonded repulsions are partly responsible for the position of the bulky *t*-butyl and methylmercato groups. Their relative positions, however, again reinforce the conclusion[1,3] that nonbonded replusions are not the overriding factor controlling the relative stabilities of I and II. What this factor is, still remains to be determined.[1]

Glycidaldehyde and Cyclopropanecarboxaldehyde. The large vicinal coupling constants of glycidaldehyde and cyclopropanecarboxaldehyde, and their decrease with increasing temperature, mean that III and VI are the most stable rotamers of these compounds in solution. From the dependence of these coupling constants on solvent dielectric constant, the firm conclusion can be drawn that, whereas the cyclopropane ring donates electronic charge (III'), the oxirane ring withdraws it (VI'). From the per cent changes of two coupling constants with solvent polarity, it appears that the two effects (donation and withdrawal of charge) are of the same magnitude. If the per cent decrease (*ca.* 10%) of the coupling constant of glycidaldehyde in going from the least polar solvents to the most polar solvents is compared to those of dichloroacetaldehyde[2] (*ca.* 75%), dibromoacetaldehyde[2] (*ca.* 60%), methoxyacetaldehyde (*ca.* 70%), phenoxyacetaldehyde (*ca.* 70%), chloroacetaldehyde[1] (*ca.* 60%), and bromoacetaldehyde[1] (*ca.* 35%), it becomes evident that the oxirane ring acts as a much weaker electron-withdrawing group than expected from an alkoxy group. In this sense, it acts much more like a cyclopropyl than like an alkoxy group.


III'


VI'

We turn our attention now to the question of what is the nature of the less stable rotamer of cyclopropanecarboxaldehyde in solution, *i.e.*, whether it is IV (twofold barrier to rotation) or V (threefold barrier to rotation). If the barrier to rotation is twofold, then eq 4 becomes eq 5. From the available experimental data we can only estimate J_{av}, J_t, and J_c.

$$J_{av} = {}^1/_2(J_t + J_c) \qquad (5)$$

The lowest experimentally measured vicinal coupling constant of this aldehyde is 4.5 cps (Table II), in *trans*-decalin, at 110°. Let us assume that rotamers III and IV are equally populated at this temperature, in which case J_{av} becomes 4.53 cps. Since this assumption is incorrect, *i.e.*, there is still more III than IV present at this temperature, the 4.53-cps value is an upper limit of J_{av}. The largest experimentally measured coupling constant of cyclopropanecarboxaldehyde is 6.20 cps (Table I), in formamide, at 36°. Let us now assume that at this state there is 100% III. If so, 6.2 cps would represent J_t. Again, this assumption is incorrect, and 6.2 cps represents a lower limit of J_t. From these two quantities and eq 5, J_c is calculated to be equal to or smaller than 2.84 cps. From the J_t values of aliphatic aldehydes[3] and α,β-unsaturated aldehydes,[5] the J_t of cyclopropanecarboxaldehyde may be estimated to be between 7.0 and 7.7 cps. If so, J_c must be between 1 and 2 cps. As pointed out in the previous paper,[2] the decision of whether such relative values of J_t and J_c are reasonable or not is a difficult one to make and rests more on personal taste than on sound scientific deduction. Since the more accurate and reliable microwave and electron diffraction techniques have shown that cyclopropanecarboxaldehyde,[4] cyclopropyl methyl ketone,[7] cyclopropanecarboxylic acid chloride,[7] and cyclopropanecarboxylic acid fluoride[4b] exhibit twofold barriers to rotation in the gas phase, it is reasonable to assume that the same will be true for cyclopropanecarboxaldehyde in solution. The weak-

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(7) L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

ness of the nmr technique to be used as a tool from which to decide such questions,[2] is further illustrated by the opposite conclusions drawn regarding the nature of the barrier to rotation, twofold[8] *vs.* threefold[9,10] about the analogous bond of vinylcyclopropane.

From the similarity between the vicinal coupling constants of cyclopropanecarboxaldehyde and glycidaldehyde, and on the basis of the microwave and electron diffraction results just mentioned, it may be concluded that glycidaldehyde also exhibits a twofold barrier to rotation.

Experimental Section

Phenoxyacetaldehyde,[11] methylmercaptoacetaldehyde,[12] and cyclopropanecarboxaldehyde[13] were prepared according to published procedures. Methoxyacetaldehyde (Jefferson Chemical Co.) and glycidaldehyde (Aldrich Chemical Co.) were commercially available. All compounds were purified either by fractional distillation or by gas chromatography prior to use.

All nmr spectra were determined at 60 Mc on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.) equipped with a variable-temperature probe and a V-6040 variable-temperature controller.

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Internal Hydrogen Rearrangement as a Function of Ion Lifetime in the Mass Spectra of Aliphatic Ketones

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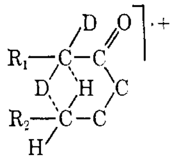
Abstract: From a study of various specifically deuterated aliphatic ketones, it has been shown that internal hydrogen rearrangement (H/D scrambling) occurs at a rate which is slow on the time scale of the mass spectrometer. Single-bond cleavage processes show little evidence of H/D scrambling at 70 eV because the rate of fragmentation is much faster than that of the scrambling processes. On the other hand, fragmentation processes accompanied by rearrangement show signs of H/D scrambling prior to the formation of the fragment ions at 70 eV because such processes occur with *k vs. E* curves that are comparable to those of the scrambling processes. Ions of relatively long lifetimes, such as those decomposing in the first and second field-free regions of the MS-9 double focussing mass spectrometer show extensive H/D scrambling prior to all the various decompositions. The relationship between lifetime and the extent of H/D scrambling requires that great care must be exercised in the interpretation of deuterium-labeling data, particularly when rearrangement processes are implicated.

A recent study[1] of the low electron voltage spectra of deuterated octan-3-one showed that H/D scrambling occurs in the alkyl chain prior to loss of an ethyl radical by α cleavage. The observation that such scrambling is evident only at low electron voltages indicates that the scrambling processes (or process) must be slow relative to the fragmentation processes at 70 eV, but proceed at a comparable (or faster) rate at about 10 eV. This suggests that the scrambling processes have relatively low activation energies (E_0) and low-frequency factors (ν).[2] Any mechanism proposed for such scrambling processes must therefore be consistent with these two factors. Relatively low activation energies are frequently associated with processes in which cyclic transition states, with concerted making and breaking of bonds, are operative. Low-frequency factors are also often associated with rearrangement processes, with transition states in which certain spatial orientations must be attained. These reactions usually have a low probability which is reflected by the low-frequency factor. A transition state of the type **1** might satisfy both the conditions (low E_0, low ν) for the scrambling processes; obviously, various ring sizes for the transition states may be visualized.



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From consideration of the quasi-equilibrium theory of mass spectra in its original and simplest from,[3] the rate constant, k, of any process occurring in an ion with internal energy E is given to a first approximation, by the equation

$$k = \nu\left(\frac{E - E_0}{E}\right)^{s-1} \qquad (1)$$

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