parative gas chromatography.[10] In this manner 0.520 g. (~10% based on recovered *n*-butyl bromide) of pale yellow fluorocyclooctatetraene was obtained.

Anal. Calcd. for C_8H_7F: C, 78.66; H, 5.78. Found: C, 78.89; H, 5.81.

The infrared spectrum showed absorption at 3000 (olefinic H), 1685, 1675 (sh.), and 1640 (C=C), and

(10) A Beckman Megachrome preparative gas chromatograph was employed with a column of 35% Carbowax 20M on firebrick.

1125 cm.$^{-1}$ (v.s.; C—F). The ultraviolet spectrum in 95% ethanol showed very strong end absorption at 220 mμ with a broad maximum at 285.5 mμ (ϵ 225). The proton n.m.r. spectrum showed a strong signal at 345 with much weaker peaks at 329 and 322 c.p.s.

The spectra shown in Figure 1 were obtained with a Varian high-resolution n.m.r. spectrometer Model V-5400 D having a 12-in. magnet equipped with Super Stabilizer operating at 56.4 Mc.

Structural Studies by Nuclear Magnetic Resonance. X. Conformations of Aliphatic Aldehydes

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Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan. Received February 2, 1965

The spin–spin coupling constants between the aldehydic and α-protons of 18 substituted acetaldehydes were studied as functions of temperature and solvent. Interpretation of the data in terms of rotamers II and III, whereby a single bond eclipses the carbonyl group, leads to the following conclusions. (1) Monosubstituted acetaldehydes: In the absence of solvent when R is methyl, ethyl, n-propyl, n-amyl, isopropyl, or phenyl, ΔH° for II $\rightleftharpoons$ III is -800, -700, -600, -500, and about -300 cal./mole, respectively. When R is t-butyl, II is more stable by 250 cal./mole. The ratio II/III increases with increase in solvent polarity, except for phenylacetaldehyde where it decreases. In the nonpolar solvents carbon tetrachloride and cyclohexane, II and III of phenylacetaldehyde are energetically equivalent. (2) Disubstituted acetaldehydes: In the absence of solvent when both substituents are methyls, ΔH° for II $\rightleftharpoons$ III is -500 cal./mole; when they are ethyl or t-butyl groups it is $+250$ and $+1100$ cal./mole, respectively. When only one of the substituents is methyl, the more stable rotamer has the methyl eclipsing the carbonyl; when neither substituent is methyl, II is the more stable rotamer. The ratio II/III increases with increase in solvent polarity. (3) Cycloalkylcarboxaldehydes: When the ring is cyclohexyl, ΔH° for II $\rightleftharpoons$ III is -400 cal./mole; when it is cyclopentyl, II is slightly more stable than III; when it is cyclobutyl, III is more stable by about 150 cal./mole; and when it is cyclopropyl II is favored by about 1500 cal./mole. Again the ratio II/III increases with increase in solvent polarity.

Several investigations have showed that the stable conformation of a tetrahedral carbon bonded to a trigonal carbon is I, whereby a single bond (C–R)

I
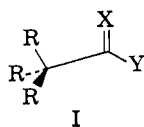
eclipses the C=X double bond. These include Raman

(1) Fellow of the Alfred P. Sloan Foundation.
(2) Lubrizol Fellow, 1964–1965.

and infrared studies on chloroacetone,[3] haloacetyl halides,[4,5] and *N*-methylchloroacetamide[6]; microwave studies on acetaldehyde,[7] propionaldehyde,[8] acetyl chloride,[9] and propene[10]; electron diffraction studies on aliphatic ketones[11] and aldehydes[12]; and n.m.r. studies on propionaldehyde[13] and olefins.[14–18]

Some of our investigations have been directed toward elucidation of the relative stabilities of rotamers II and III as functions of X, Y, and R. In this paper we shall

discuss the conformations of aliphatic aldehydes.

Results

Table I summarizes the coupling constants between the aldehydic proton and the α-protons of several

(3) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa, and N. Shido, *J. Chem. Phys.*, 21, 815 (1953).
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(7) R. W. Kolb, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, 26, 1695 (1957).
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(17) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *ibid.*, 84, 2748 (1962).
(18) A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, 34, 127 (1962).

aliphatic aldehydes. All values are averages of several measurements with a precision of ±0.03 c.p.s. To ensure accuracy and internal consistency values were always checked against the coupling of acetaldehyde, 2.85, 288, and 2.90 c.p.s. at 36, 0, and −30°, respectively.[19]

Table I. Spin–Spin Coupling Constants[a] of Aldehydes

|		J_{CHCHO}		
Aldehyde	−30°	0°	36°	70°
CH_3CHO	2.90	2.88	2.85	
$MeCH_2CHO$	1.06	1.22	1.31	
$EtCH_2CHO$	1.42	1.53	1.69[e]	1.80
$n\text{-}PrCH_2CHO$	1.51	1.60	1.75	1.80
$n\text{-}AmCH_2CHO$	1.48[b]	1.56	1.73	1.78
$i\text{-}PrCH_2CHO$	1.81	1.88	1.92	2.05
$t\text{-}BuCH_2CHO$	2.95	2.94	2.92	2.84
$C_6H_5CH_2CHO$			2.18	2.20, 2.24[c]
	2.40[b]	2.40[b]	(2.40)[b]	(2.43)[b]
$(Me)_2CHCHO$	1.01	1.12	1.17	1.35[d]
$(Et)_2CHCHO$	2.52	2.35	2.36	2.25
$(t\text{-}Bu)_2CHCHO$	6.20[b]		6.00[b]	5.75[b]
$Me(Et)CHCHO$	1.56	1.60	1.67	1.70
$Me(n\text{-}Pr)CHCHO$	1.45	1.59	1.76	1.75
$Me(C_6H_5)CHCHO$	1.07	1.25	1.31	1.45
$Et(n\text{-}Bu)CHCHO$	2.70[b]	2.55	2.52	2.35
▷–CHO	6.14	5.95	5.75	5.35
◇–CHO	1.72		1.82	
▢–CHO	2.11	2.12	2.12	2.05
⬡–CHO	0.92	1.03	1.14	1.15

[a] Unless otherwise denoted all coupling constants are those of neat solutions; values in c.p.s. [b] About 10% solution in carbon tetrachloride. [c] Value at 90°. [d] Value at 60°. [e] Value at 50°.

The coupling constants of monosubstituted acetaldehydes are smaller than that of acetaldehyde and increase with increase in temperature. Notable exceptions are t-butylacetaldehyde, whose coupling is larger than that of acetaldehyde and decreases with increase in temperature, and phenylacetaldehyde, whose coupling (in carbon tetrachloride) is independent of temperature. The couplings of disubstituted acetaldehydes vary extensively. When one of the substituents is methyl, the couplings increase with increase in temperature; when neither group is methyl they decrease. Cycloalkylcarboxaldehydes, except cyclopropylcarboxaldehyde, have small couplings. Those of cyclobutyl and cyclohexyl increase with increase in temperature; that of cyclopropyl decreases; and that of cyclopentyl is almost temperature independent.

Table II summarizes the effect of solvent on the coupling constants of several aldehydes. Increase in solvent polarity increases the coupling, except for phenylacetaldehyde, whose coupling decreases with increase in solvent polarity, and acetaldehyde, whose coupling shows only small variations.

The relative stabilities of the various rotamers of a substituted acetaldehyde can be qualitatively assessed from the dependence of its coupling on temperature. Assuming $J_t > J_g$, where J_t is the *trans* coupling (dihedral

(19) These values are consistent with those reported in ref. 13 and by J. G. Powels and J. H. Strange, *Mol. Phys.*, 5, 329 (1962).

Table II. Solvent Effects on J_{CHCHO} of Aldehydes

	J_{HH}, c.p.s.[a]		
Aldehyde	Cyclohexane	Nitrobenzene	Acetonitrile
CH_3CHO	2.79	2.83	2.87
$MeCH_2CHO$	1.25	1.30	1.33
$t\text{-}BuCH_2CHO$	2.80	2.93	3.05
$(Et)_2CHCHO$	2.25	2.40	2.55
$Me(Et)CHCHO$	1.63	1.70	1.78
$Et(n\text{-}Bu)CHCHO$	2.40	2.60	2.70
▷–CHO	5.05	5.60	5.80
▢–CHO	1.97	2.15	2.30
⬡–CHO	1.00	1.15	1.20
$C_6H_5CH_2CHO$	2.40	2.18	2.00

[a] All values are at 36°.

angle 180°) and J_g the *gauche* (dihedral angle 60°), the coupling should be temperature independent if IV_a, IV_b, and V are energetically equivalent. If V is more stable
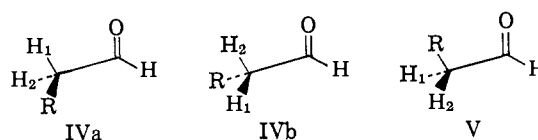
than IV_a, the coupling should increase with increase in temperature; and if less stable, it should decrease. Similarly, for disubstituted and cycloalkylcarboxaldehydes the coupling should be temperature independent if VI, VIIa, and VIIb (also VIII, IXa, and IXb) are energetically equivalent. If VIIa ($R_1 = R_2$) is more stable than VI (also IXa more stable than VIII), the coupling should increase with increase in temperature; and if less stable, it should decrease.
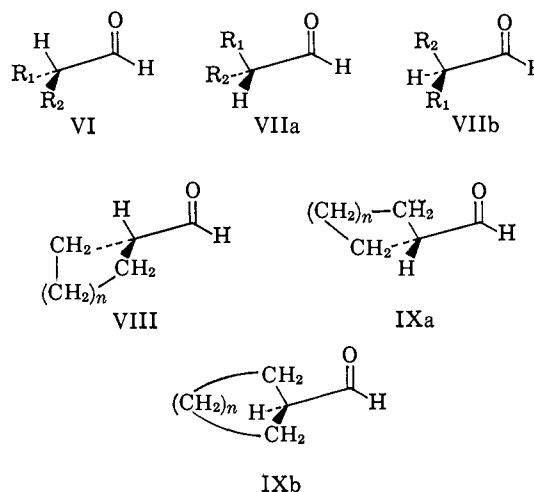

Table III summarizes per cent populations of the various rotamers of substituted acetaldehydes. Table IV shows their dependence on solvent. Values for monosubstituted acetaldehydes were calculated from eq. 1

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

where y is the fractional population of IV and $(1 - y)$ that of V; values for disubstituted acetaldehydes were calculated from eq. 2, where y is the fractional population

$$J_{obsd} = yJ_t + (1 - y)J_g \qquad (2)$$

Figure 1. 1, Et(n-Bu)CHCHO; 2, (Et)₂CHCHO; 3, C₅H₉CHO; 4, Me(Et)CHCHO; 5, Me(C₆H₅)CHCHO; and 6, (Me)₂CHCHO.

Table III. Relative Population of Aldehydic Rotamers[a]

Aldehyde	−30°	0°	36°	70°
MeCH₂CHO	23	31	34	
EtCH₂CHO	37	40	45	48
n-PrCH₂CHO	39	42	46	48
n-AmCH₂CHO	39[c]	41	46	47
i-PrCH₂CHO	48	50	51	55
t-BuCH₂CHO	80	79	79	77
C₆H₅CH₂CHO	65[c]	65[c]	65[c] (58)	66[c] (60)
(Me)₂CHCHO	19	20	21	23[d]
(Et)₂CHCHO	40	37	37	36
(t-Bu)₂CHCHO	92[c]		89[c]	85[c]
Me(Et)CHCHO	26	27	28	
Me(n-Pr)CHCHO	25	27	29	
Me(C₆H₅)CHCHO	19	22	23	25
Et(n-Bu)CHCHO	42[c]	40	40	37
▷—CHO	91	88	85	80
◇—CHO	28		30	
☐—CHO	34	34	34	33
⬡—CHO	17	19	20	21

[a] Unless otherwise indicated these values are those of neat solutions. [b] The remaining per cent corresponds to the rotamer having the R group eclipsing the carbonyl. [c] About 10% solution in carbon tetrachloride. [d] Value from 60°.

Table IV. Solvent Effect on the Relative Populations of Aldehydic Rotamers

Aldehyde	Cyclohexane, 36°	Acetonitrile, 36°
MeCH₂CHO	33	35
t-BuCH₂CHO	78	83
(Et)₂CHCHO	36	40
Me(Et)CHCHO	27	29
Et(n-Bu)CHCHO	38	42
▷—CHO	76	86
☐—CHO	32	37
⬡—CHO	19	21
C₆H₅CH₂CHO	65	53

tion of VI (also VIII) and (1 − y) that of VII (also X).

Calculation of these values required knowledge of J_t and J_g. Evaluation of J_t and J_g could be achieved as follows. Equation 3 expresses the coupling of acetal-

$$J_{obsd} = \frac{1}{3}(J_t + 2J_g) \qquad (3)$$

dehyde and also of substituted acetaldehydes at very high temperatures (approach to free rotation), or at ordinary temperatures if it so happens that the various rotamers are energetically equivalent. If we assumed that t-butylacetaldehyde exists exclusively in IV, then eq. 4 expresses its coupling. A combination of eq. 3 (using

$$J_{obsd} = \frac{1}{2}(J_t + J_g) \qquad (4)$$

the value of acetaldehyde) and eq. 4 gives $J_t = 3.1$ and $J_g = 2.7$ c.p.s. These values are obviously incorrect, since the coupling of di-t-butylacetaldehyde is 6.2 c.p.s. If we assumed that di-t-butylacetaldehyde exists exclusively in VI, then J_t would have a value of 6.2 c.p.s. and J_g would have a value of 1.2 c.p.s. These values (6.2 and 1.2 c.p.s.) are lower and upper limits, respectively.

A serious error arises from the assumption that J_t and J_g will be the same for acetaldehyde, monosubstituted acetaldehydes, and disubstituted acetaldehydes. There is ample evidence in the literature that substitution of an alkyl group for a hydrogen decreases the coupling. For example, whereas the coupling of ethane[20] is 8.0 c.p.s., that of propane[21] and isobutane[22] is 7.3 and 6.8 c.p.s. From electronegativity considerations[23] substitution of an alkyl group for a hydrogen should decrease the coupling by about 0.3 c.p.s. We can show that in aliphatic aldehydes each alkyl (also phenyl) substituent decreases the average coupling (eq. 3) by about 0.4–0.5 c.p.s. For example, whereas the coupling of acetaldehyde is 2.85 c.p.s., that of phenylacetaldehyde (temperature independent) is only 2.40 c.p.s.; and that of cyclopentylcarboxaldehyde (again

temperature independent) is about 2.1 c.p.s. When the couplings of various disubstituted acetaldehydes are plotted against temperature, Figure 1, the lines converge (for simplicity we have drawn straight lines) at high temperatures around 2.0 rather than 2.8 c.p.s.

A more direct approach involves the simultaneous evaluation of J_t, J_g, and $\Delta H°$ for each substituted acetaldehyde. For monosubstituted acetaldehydes these quantities could be evaluated from eq. 6 and for disubstituted acetaldehydes from eq. 8. This approach
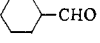
$$K_{eq}(\text{monosubstituted}) = 2(1 − y)/y \qquad (5)$$

$$\Delta H° = −RT \ln (J_t − J_g − 2J_{obsd})/(J_{obsd} − J_g) \qquad (6)$$

$$K_{eq}(\text{disubstituted}) = (1 − y)/2y \qquad (7)$$

$$\Delta H° = RT \ln \frac{1}{2}(J_t − J_{obsd})/(J_{obsd} − J_g) \qquad (8)$$

(20) R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc. (London), A269, 385 (1962).
(21) D. R. Whitman, L. Onsager, M. Saunders, and H. E. Dubb, J. Chem. Phys., 32, 67 (1960).
(22) J. S. Waugh and F. W. Dobbs, ibid., 31, 1235 (1959).
(23) R. J. Abraham and K. G. R. Pachler, Mol. Phys., 7, 165 (1963–1964). See also R. Glick and A. A. Bothner-By, J. Chem. Phys., 25, 362 (1956).

Table V

Aldehyde	ΔH°, cal./mole[a]
MeCH$_2$CHO	-800
EtCH$_2$CHO	-700
n-PrCH$_2$CHO	-600
n-AmCH$_2$CHO	-500
i-PrCH$_2$CHO	-400
t-BuCH$_2$CHO	$+250$
C$_6$H$_5$CH$_2$CHO	-300 (0[b])
(Me)$_2$CHCHO	-500
(Et)$_2$CHCHO	$+250$
(t-Bu)$_2$CHCHO	$+1,100$[b]
Me(Et)CHCHO	-200[c]
Me(n-Pr)CHCHO	-200[c]
Me(C$_6$H$_5$)CHCHO	-400[c]
Et(n-Bu)CHCHO	$+300$[c]
▷–CHO	$+1,500$
◇–CHO	-150[d]
▢–CHO	~ 0
⬡–CHO	-400

[a] Unless otherwise denoted these are values of neat solutions. [b] From about 10% solution in carbon tetrachloride. [c] These values were calculated as if R$_1$ = R$_2$. See text. [d] Calculated from only two temperatures.

Table VI. ΔF_{36}° as Function of Solvent

Aldehyde	ΔF_{36}° cal./mole[a] Cyclo-hexane	Aceto-nitrile
MeCH$_2$CHO	-880	-820
t-BuCH$_2$CHO	$+330$	$+550$
(Et)$_2$CHCHO	$+70$	$+180$
Me(Et)CHCHO	-180	-120
Et(n-Bu)CHCHO	$+130$	$+230$
▷–CHO	$+1,100$	$+1,500$
▢–CHO	-30	$+90$
⬡–CHO	-480	-380
C$_6$H$_5$CH$_2$CHO	-50	-340

[a] ΔF° rather than ΔH° is used because we did not study the temperature dependence of coupling in these solvents.

R$_2$, ΔH° and ΔF° values were calculated as if VIIa and VIIb were equivalent. Although such values have no physical significance they will be helpful in some later comparisons.

The accuracy of the ΔH° values depends on the values chosen for J_t, J_g, and substituent effect. To get an estimate of this accuracy we have calculated them as functions of J_t, J_g, and substituent effect. With substituent corrections of 0.3 and 0.5 c.p.s. they increase and decrease by about 5%. By changing J_t from 7.2 to 8.0 c.p.s. they vary by about ±10%. An error of ±30% therefore seems reasonable, if we were to account for experimental errors and changes in the dielectric constants of the liquids with temperature.

Discussion

Monosubstituted Acetaldehydes. When R is methyl, ethyl, n-propyl, n-amyl, or isopropyl, V (alkyl eclipsing the carbonyl) is more stable than IVa or IVb (hydrogen eclipsing the carbonyl). The 800-cal./mole enthalpy difference between IVa and V when R is methyl is comparable to the 900-cal./mole difference obtained by microwave.[8] As anticipated, the enthalpy difference decreases as R increases in size, and becomes positive when R is t-butyl (IVa more stable than V).

The relative populations of V and IVa are solvent dependent. Increase in solvent polarity decreases the population of V, e.g., when R is t-butyl the population of V is 23 (cyclohexane) and 17% (acetonitrile). In terms of free energy, the ΔF° between IVa and V becomes more positive (Table VI) in going from cyclohexane to acetonitrile. Such changes with solvent polarity are certainly reasonable, in view of the expected higher dipole moment of IV over V, as shown in X and XI. We want to point out, however, that the increase in J cannot be due solely to changes in the

X   XI

relative populations of IVa and V, as the coupling of acetaldehyde also increases (but only by about 2–3%) in going from cyclohexane to acetonitrile.[25]
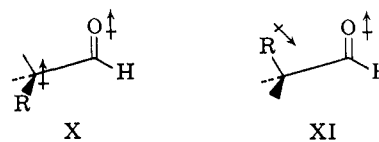
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requires that ΔS° = 0 for the equilibrium between rotamers. Although this assumption may be true if the substituent is halogen or perhaps methyl, it would hardly be true if the substituent were a larger alkyl group; e.g., rotation of a t-butyl group should be much more hindered in V than in IV.

The difficulties associated with the exact solution of eq. 6 and 8 for each substituted acetaldehyde have led us to use a simpler approach to the problem. If J_t and J_g of acetaldehyde were known, one could use these values for all alkyl- or aryl-substituted acetaldehydes (eq. 1 and 2) by correcting J_{obsd} for the effect of a substituent (0.4 c.p.s. for each substituent). The values that give us the most consistent results are J_t = 7.6 and J_g (calculated from the coupling of acetaldehyde) = 0.5 c.p.s. A J_t of 7.6 c.p.s. for acetaldehyde is certainly reasonable. For example, a lower limit of 7.0 c.p.s. (6.2 + 0.8) can be set from the highest coupling value di-t-butylacetaldehyde; an 8.3-c.p.s. value was calculated from detailed temperature studies of the coupling of propionaldehyde[13]; and a 7.7-c.p.s. coupling is observed with α,β-unsaturated aldehydes,[24] which presumably exist in the s-trans conformation. The data in Tables III and IV were calculated from these values after correcting the observed coupling constants by 0.4 c.p.s. for each alkyl or aryl substituent.

Table V summarizes the enthalpy differences, calculated from plots of log K vs. $1/T$, between individual rotamers, e.g., V vs. IVa, VI vs. VIIa, and VIII vs. IXa. Table VI shows the effect of solvent on the free energy difference, at 36°, between such individual rotamer. For disubstituted acetaldehydes where R $\neq$

(24) J. A. Pople and T. Schaefer, *Mol. Phys.*, 3, 547 (1960); also A. A. Bothner-By, private communication.

Phenylacetaldehyde presents a sharp contrast to the alkyl-monosubstituted acetaldehydes. Whereas in the nonpolar solvents, carbon tetrachloride and cyclohexane, IVa and V are energetically equivalent, V rather than IVa becomes more stable in the more polar solvents (in acetonitrile V is more stable than IVa by about 350 cal./mole). It seems reasonable that V should have a higher dipole moment than IVa (sp^2 carbon more electronegative than sp^3 carbon), as shown in XII and XIII. The greater effect of solvent


XII   XIII
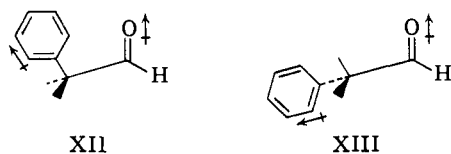
polarity on the ratio IV/V when R is phenyl than alkyl agrees with the greater contribution of phenyl over alkyl to the dipole moment of the aldehydic rotamers.

Disubstituted Acetaldehydes. Examining first the cases where $R_1 = R_2$ we conclude that, when the alkyl groups are methyl, VIIa is more stable than VI by 500 cal./mole; and when they are ethyl or *t*-butyl groups, VI is more stable than VIIa by 250 and 1100 cal./mole. The interesting observation that VI (hydrogen eclipsing the carbonyl) is more stable than VIIa (ethyl eclipsing the carbonyl), whereas V (ethyl eclipsing) is more stable than IVa (hydrogen eclipsing) merits some comment. This apparent inconsistency can be readily explained as follows. The most stable conformation of the ethyl groups when the hydrogen eclipses the carbonyl VI is XIV, whereby the alkyl chain is all *trans* and completely staggered. If the alkyl chain

XIV   XV   XVa

XVb
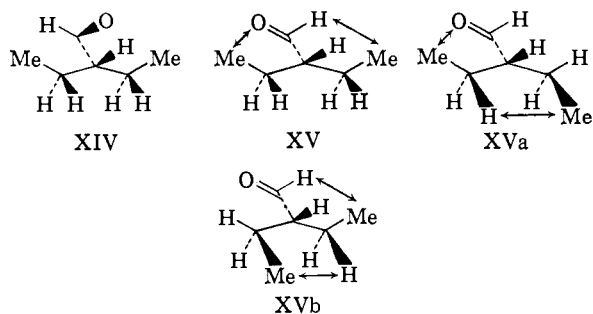
were to be kept all *trans* staggered in VII, a 1,3-eclipsing methyl–proton interaction, and a less severe methyl–carbonyl interaction (XV), would result. Rotating to avoid these interactions leads to conformations XVa and XVb, which suffer from similar interactions. Consequently VI becomes more stable than VIIa. In ethylacetaldehyde the isomer having the carbonyl eclipsing the ethyl group does not suffer from such interactions, as shown in XVI.

Of the two interactions shown in XV the 1,3-eclipsing methyl–proton interaction is probably the more severe and the one responsible for making VIIa less stable

XVI   XVII   XVIII
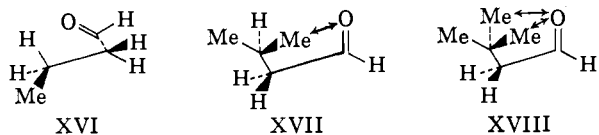
(25) A detailed discussion of coupling constant dependence on solvent will appear elsewhere.

than VI. That the methyl–carbonyl interaction cannot be the significant one is attested by the fact that when R is isopropyl, V is more stable than IVa, although in V, as shown in XVII, such an interaction exists. Apparently two such interactions, as in *t*-butylacetaldehyde (XVIII), are sufficient to reverse the relative stability of the rotamers.

When $R_1 \neq R_2$, the data afford the following firm conclusions. If R_1 = methyl and R_2 = ethyl or any alkyl, VIIa (methyl eclipsing) is the most stable rotamer. VI (proton eclipsing) and VIIb (ethyl or other alkyl eclipsing) are practically energetically equivalent. The latter conclusion is drawn from the observation that $\Delta H°$ for these compounds, if R_1 is treated as equivalent to R_2, is about half that for dimethylacetaldehyde. If R_1 and R_2 are neither hydrogen nor methyl, then the most stable rotamer is VI, apparently for the same reasons given for diethylacetaldehyde.

As with monosubstituted acetaldehydes the solvent effects are in accord with the proposed conformations, e.g., the ratio VI/VII increases with increase in solvent polarity, as VI should have a higher dipole moment than VII.

Cycloalkylcarboxaldehydes. The relative stabilities of VIII and IXa are very sensitive to ring size. Whereas IXa is more stable than VIII by 400 cal./mole when $n = 3$ (cyclohexyl), it is only slightly less stable when $n = 2$ (cyclopentyl), more stable by about 150 cal./mole when $n = 1$ (cyclobutyl), and finally less stable by about 1.5 kcal./mole when $n = 0$ (cyclopropyl).

A. Cyclohexylcarboxaldehyde. The finding that IXa (alkyl eclipsing the carbonyl) is more stable than VIII by about 400 cal./mole is as expected and supports the arguments advanced in the case of diethylacetaldehyde. In either conformation XIX or XX, the alkyl chain is all *gauche* staggered and the differences in

XIX   XX
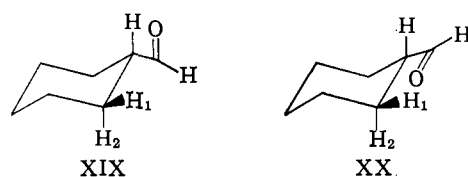
interactions between XIV and XV are absent. Since in conformation XX the carbonyl is bisecting the H_1CH_2 angle, it is no surprise that cyclohexylcarboxaldehyde shows the same behavior as dimethylacetaldehyde.

B. Cyclopentyl- and Cyclobutylcarboxaldehyde. The sharp contrast between cyclohexylcarboxaldehyde and either cyclobutyl- or cyclopentylcarboxaldehyde can be rationalized as follows. The ring puckering in cyclopentyl and cyclobutylcarboxaldehyde is certainly less than it is in cyclohexylcarboxaldehyde. Using the envelope form[26] for cyclopentylcarboxaldehyde, it can be seen that in the isomer where the carbonyl is eclipsed by the carbon–carbon bond, the carbonyl is

XXI   XXII
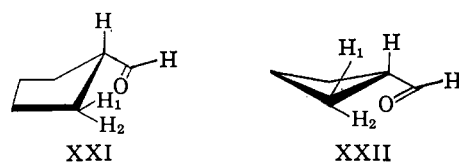
(26) F. V. Brutcher, Jr., T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

closer to H_2 (XXI) instead of bisecting the angle H_1CH_2 as in cyclohexylcarboxaldehyde. Apparently this proximity is sufficiently large to destabilize IXa to the extent that it is slightly less stable than VIII. The same argument can be applied to cyclobutylcarboxaldehyde (XXII).[27]

C. Cyclopropylcarboxaldehyde. The complete reversal in cyclopropylcarboxaldehyde, VIII being more stable than IXa by about 1.5 kcal./mole, can be explained as follows. Extending the arguments used for cyclopentyl- and cyclobutylcarboxaldehyde it is evident that in IXa the carbonyl group eclipses H_2 (XXIII). This interaction apparently destabilizes IXa to such an

XXIII
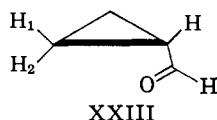
extent that VIII becomes energetically favored. In addition, whatever factors force α,β-unsaturated aldehydes to assume the *s-trans* conformation[24] may be responsible for the greater stability of VIII over IXa. We have certain reservations, however, regarding the magnitude of $\Delta H°$. In deriving this value we have assumed that J_t and J_g for cyclopropylcarboxaldehyde are the same as they are in other disubstituted acetaldehydes. Because of changes in angles and carbon hybridization in the cyclopropane ring this assumption is probably incorrect, and if J_t is larger than the value that we have used, then a more reasonable value for $\Delta H°$ may be 1 kcal./mole rather than 1.5 kcal./mole.

It is suggested[12] that in the gas phase cyclopropylcarboxaldehyde exists 50% in VIII and 50% in XXIV (carbonyl bisecting the cyclopropyl ring) rather than
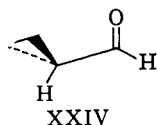
XXIV

VIII and IX. Although our data do not permit an unequivocal choice between the two possibilities, on the basis of the following arguments VIII and IX rather than VIII and XXIV seem more reasonable in the liquid phase.

Assuming VIII and XXIV as the only rotamers, the coupling constant is expressed by eq. 9, where y is the population of VIII and $(1 - y)$ the population of

$$J_{obsd} = yJ_t + (1 - y)J_c \qquad (9)$$

XXIV. From the strong dependence of J on temperature we draw the firm conclusion that in the liquid phase VIII and XXIV cannot be energetically equivalent. If J_t and J_c are comparable in magnitude (with J_t larger than J_c), then it is evident that VIII is more stable than XXIV. The large coupling constant of cyclopropylcarboxaldehyde is in agreement with VIII and XXIV, as both J_t and J_c should be large. This interpretation, however, requires J_c to be quite small (judging from the large variation of coupling with temperature). Although we cannot exclude this possibility (especially in the absence of an accurate J_t for cyclopropylcarboxaldehyde and of the change of di-

(27) It is reasonable to assume that the ring of cyclobutylcarboxaldehyde is puckered. For puckering of cyclobutyl rings see J. B. Lambert and J. D. Roberts, *ibid.*, **85**, 3710 (1963), and references cited therein. Although in these arguments we have used the aldehydic group in the equatorial or pseudo-equatorial positions, analogous conclusions can be drawn from the conformations where the aldehydic group is axial.

electric constant of the aldehyde with temperature) we consider it rather unlikely. Further experimentation is in progress.

The variation of coupling constant with solvent polarity is again in accord with the higher dipole moment of VIII over IX.

Consideration of Other Confirmations. As we have showed, our data are in good accord with eclipsed conformations. We wish to consider now bisecting conformations, XXV and XXVI for monosubstituted acetaldehydes, and XXVII and XXVIII for disubstituted acetaldehydes. Equations 1, 2, and 3 become 10, 11, and 12, respectively, where J_c is the *cis* coupling

XXVa   XXVb   XXVI

XXVII   XXVIIIa   XXVIIIb
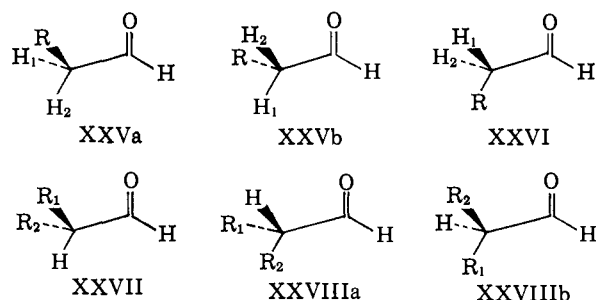
and J_{120} the coupling when the dihedral angle is 120°.

$$J_{obsd}(\text{monosubstituted}) = y(J_c + J_{120})/2 + (1 - y)J_{120} \qquad (10)$$

$$J_{obsd}(\text{disubstituted}) = yJ_c + (1 - y)J_{120} \qquad (11)$$

$$J_{obsd} = \frac{1}{3}(J_c + 2J_{120}) \qquad (12)$$

Since J_c should be comparable to J_t, and J_{120} comparable to J_g, the data could be interpreted in terms of bisecting conformations. We can, however, exclude these conformations on the basis of the following arguments.

(a) As mentioned, microwave and electron diffraction studies have showed that in the gas phase the stable conformations are eclipsing rather than bisecting. We see no good reason why in solution a reversal should occur.

(b) Since XXV and XXVII have higher coupling constants than XXVI and XXVIII one must conclude that increase in the size of R shifts the equilibrium in favor of XXV and XXVII. In terms of steric repulsions such a conclusion is highly improbable; *e.g.*, models show that XXVII of di-*t*-butylacetaldehyde is much more crowded than XXVIII.

(c) Since XXVI should have a higher dipole moment than XXV, and XXVIII higher than XXVII, increase in solvent polarity should decrease the coupling. Experimentally, however, the coupling increases with increase of solvent polarity.

Although we have interpreted our data in terms of eclipsing conformations, *i.e.*, with the dihedral angle ϕ as zero (XXIX), we want to emphasize that small

XXIX
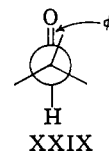
variations in ϕ would not alter the interpretation of the results. This is a limitation of current understanding of spin–spin coupling and our results should not be construed as proof that the dihedral angle is zero.

For accurate dihedral angle measurements one must rely on methods more accurate than n.m.r.

The causes responsible for making V more stable than IVa, even when R is isopropyl, are not well understood. Although the more favorable dipole–dipole interactions in V over IVa and the possibility of hydrogen bonding in V are plausible explanations, they cannot be the sole factors responsible for the greater stability of V, as witnessed by the case of phenylacetaldehyde. Very likely here are good examples of two interacting groups whose distance is in the attractive portion of the van der Waals curve.

Experimental

Except for *t*-butylacetaldehyde, di-*t*-butylacetaldehyde, cyclopropyl-, cyclobutyl-, and cyclopentylcarboxaldehydes, all aldehydes used were freshly distilled samples of commercially available materials.

Di-*t*-butylacetaldehyde was prepared from di-*t*-butyl ketone.[28] Cyclopropylcarboxaldehyde was prepared from cyclopropylnitrile.[29] *t*-Butylacetaldehyde, cyclobutylcarboxaldehyde, and cyclopentylcarboxaldehyde were prepared from the corresponding acids.[30]

N.m.r. spectra were determined at 60 Mc. on a Model A-60 spectrometer.

(28) M. S. Newman, A. Arkell, and T. Fukunaga, *J. Am. Chem. Soc.*, **82**, 2498 (1960).
(29) H. C. Brown and C. P. Garg, *ibid.*, **86**, 1085 (1964).
(30) H. C. Brown and A. Tsukamoto, *ibid.*, **86**, 1089 (1964).

Bridged Polycyclic Compounds. XXIX. Some Rearrangements of Dibenzobicyclo[2.2.2]octadienes to Dibenzobicyclo[3.2.1]octadienes[1]

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Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado. Received February 19, 1965

Addition of bromine in acetic acid and of iodine and silver acetate to dibenzobicyclo[2.2.2]octatriene (I) led to syn-8-bromo- (II) and syn-8-iododibenzobicyclo[3.2.1]octadien-exo-2-ol acetate (III), respectively. Solvolysis of three 7-dibenzobicyclo[2.2.2]octyl pairs (dichlorides V and VI, chloro p-toluenesulfonates X and XI, and chloro acetates XII and XIII) gave rearranged [3.2.1] derivatives with a high degree of stereoselectivity. These results are discussed in light of various carbonium ion intermediates and seem best to be interpreted by classical benzylic cationic intermediates.

Previous work on Wagner–Meerwein rearrangements of dibenzobicyclo[2.2.2]octadienes to dibenzobicyclo[3.2.1]octadienes has indicated the high degree of stereospecificity of bond migration in rearrangements accompanying both addition and solvolysis.[2-4] It was desirable to test the generality of these findings further in order to elucidate the mechanistic details involved. Examination of both addition rearrangement and solvolysis rearrangement reactions was undertaken.

Addition of the elements of acetyl hypobromite to dibenzobicyclo[2.2.2]octatriene (I) *via* bromine in acetic acid led to only one product, *syn*-8-bromodi-

benzobicyclo[3.2.1]octadien-*exo*-2-ol acetate (II). In an analogous manner, the product of the treatment of I with iodine and silver acetate was exclusively the *syn-exo* iodo acetate III. When the Prévost reaction was carried out in acetic acid rather than in benzene and with excess silver acetate, the known[3] *exo-syn* diacetate IV was formed.

I

II

III

IV
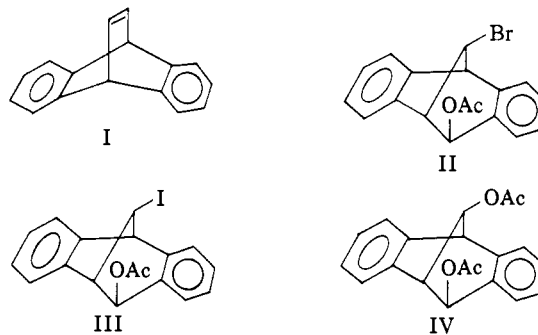
Solvolysis rearrangements of three epimeric pairs of disubstituted dibenzobicyclo[2.2.2]octadienes were also investigated. The *cis-* V and *trans*-dichloride VI reported earlier[5] were solvolyzed in acetic acid assisted by silver acetate. Acetolysis of V led to two known[4,6] products: *syn-exo* chloro acetate VII and *syn-endo* chloro acetate VIII. The relative proportions of VII and VIII changed with reaction time, VIII increasing with longer times. The acid-catalyzed rearrangement of VII to VIII has been reported earlier.[6]

(1) Previous paper in series: S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, 30, 1956 (1965). This work was reported at the 19th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 1963.
(2) W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.*, 80, 1956 (1958).
(3) S. J. Cristol and R. K. Bly, *ibid.*, 82, 6155 (1960).
(4) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, 28, 1374 (1963).
(5) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, 74, 2193 (1952).
(6) S. J. Cristol and D. D. Tanner, *ibid.*, 86, 3122 (1964).