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STRUCTURAL STUDIES BY NUCLEAR MAGNETIC RESONANCE. XIII.
ROTATIONAL ISOMERISM ABOUT THE ALKYL-OXYGEN BOND OF ACETATES.

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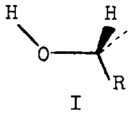
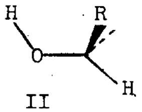
Although I and II have been detected by infrared studies

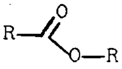


I

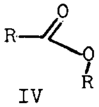


II

of various alcohols (1), quantitative studies of rotational isomerism about carbon-oxygen bonds involving distinguishable rotamers have been confined mainly to the acyl-oxygen bond (2). For example, $\Delta H^\circ_{III \rightarrow IV}$ is higher than +2.0 Kcal/mole for



III



IV

formic acid (2a), +2.5 Kcal/mole for ethyl formate (2b), and +3.7 Kcal/mole for isopropyl formate (2c). Failure to detect

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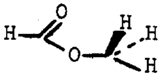
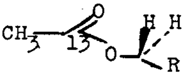
*Fellow of the Alfred P. Sloan Foundation the s-*trans* rotamer (IV) of methyl formate (2d-f), acetate (2e, 2f) and chloroformate (2e) suggests that the s-*cis* rotamer (III) of these compounds is also favored by at least 2 Kcal/mole. The stable rotamer of methyl formate, whose rotational barrier about the methyl-oxygen bond is 1.2 Kcal/mole (2d), is shown in V.

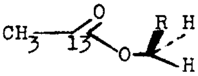


V

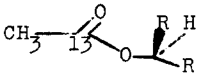
The considerably higher stability of III over IV and the adequate barriers about the alkyl-oxygen bonds of esters allow, at least in principle, evaluation of $\Delta H^{\circ}_{VI \rightarrow VII(VIII \rightarrow IX)}$ from nmr studies of carbonyl -^{13}C labeled acetates.



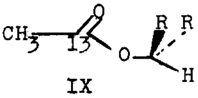
VI



VII



VIII



IX

In the accompanying Table we have summarized the pertinent nmr information for six 30% excess ^{13}C carbonyl enriched acetates. The data, except those of *di*-*t*-butylcarbinyl acetate, are interpretable in terms of VI - IX. The identity of the three rotamers of methyl acetate explains the temperature independence of its $J_{^{13}COCH}$. By making the reasonable assumption that *trans* $J_{^{13}COCH}$ is larger than

TABLE

$CH_3{}^{13}CO_2CHR_1R_2$		$J_{^{13}COCH}$(cps.)[a]						
R_1	R_2	-45°	-30°	-15°	0°	+20°	+40°	+60°
H	H	4.00	3.95	4.00	3.95		3.95	
H	CH_3	2.80	2.85	2.95	3.05	3.15	3.25	
H	C_6H_5	2.85	3.00	3.05	3.20	3.30	3.40	3.40
H	$C(CH_3)_3$	2.30	2.35	2.45	2.55	2.65	2.70	2.70
CH_3	CH_3	2.60	2.65	2.70	2.80	2.80	2.90	2.95
$C(CH_3)_3$	$C(CH_3)_3$		4.55[b]	4.60[b]	4.60[b]		4.60	4.55[c]

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[a] All values were obtained from first order spectral analysis. They are accurate to about ±0.07 cps.

[b] Values from 50% carbon tetrachloride solutions.

[c] Values of 4.55, 4.55, and 4.60 cps. were obtained at 80°, 100° and 140°, respectively.

gauche (3), $\Delta H^\circ_{VI \rightarrow VII(VIII \rightarrow IX)}$ must be positive.

ΔH° may be qualitatively estimated as follows:

$$J_{obs.} = pJ_g + (1-p)(J_t + J_g)/2 \qquad 1$$

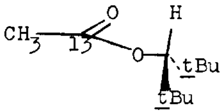
$$J_{obs.} = pJ_g + (1-p)J_t \qquad 2$$

$$4.0 = 1/3(J_t + 2J_g) \qquad 3$$

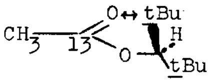
Equation 1 relates the fractional populations p and (1-p) of VI and VII to the observed proton-^{13}C coupling of monosubstituted carbinyl acetates. The corresponding quantities of the disubstituted compounds are related by equation 2. From equation 3, which is obtained from the data of methyl acetate, and the lowest $J_{obs.}$ value (2.3 cps. of *t*-butylcarbinyl acetate), J_g must be smaller than 2.3 cps.

and J_t larger than 7.4 cps. $\Delta H^\circ_{VI \rightarrow VII}$ for R = methyl varies, therefore, from +600 to +1,400 cal/mole, as J_g is varied from zero to 2.3 cps. and J_t, correspondingly, from 12.0 to 7.4 cps. Similar values are obtained for the other compounds.

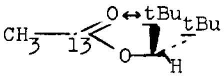
The unexpected temperature independence of $J_{^{13}COCH}$ of *di-t*-butylcarbinyl acetate over a 170° range necessitates the following conclusions: 1. Contributions to the *vicinal* proton-^{13}C coupling from torsional oscillations and excited vibrational states must be small. 2. The compound is effectively locked into a single conformation. From the intermediate between J_g and J_t value of $J_{obs.}$ the proton and ^{13}C are probably closer to a *cis* than either a *trans* or a *gauche* relationship. We propose a conformation closely related to X, as repulsive interactions in XI and XII might conceivably force carbonyl and C-H into virtual coplanarity.



X



XI



XII

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