tubes were open to the atmosphere (as during the cleaning and sealing operations) the Grignard reagent solutions were probably adequately protected by the 10-cm. column of ether vapor above the solution in the n.m.r. tube.

Dialkylmagnesium solutions were prepared from the corresponding Grignard reagents by opening the n.m.r. tube, adding 100 μl. of dry dioxane and then capping and shaking the tube. The dioxane addition resulted in immediate production of a voluminous white precipitate in such quantity that the sample frequently became almost solid.

The neck of the tube was cleaned with pipe cleaner and sealed in the usual manner. After sealing, the solution was allowed to stand in contact with the precipitate for 10–12 hr. with frequent shaking and then centrifuged in the manner described previously. Centrifugation at 1600 r.p.m. (3 to 4 hr.) were frequently required to compact completely the voluminous precipitate of magnesium halide dioxanate. The volume of the compacted precipitate was usually approximately one-third that of the original Grignard reagent solution. This precipitate was usually removed from dialkylmagnesium samples to be examined at high temperature by cutting off the part of the tube containing the precipitate and immediately sealing the tube again.

Yields of Grignard reagent in diethyl ether solution were estimated to be 85–95%, by comparison with the ^{13}C satellite of ether.

Analyses of n.m.r. spectra were performed using an iterative program.[32] The solution for 3,3-dimethylbutyl chloride (and by inference for bis(3,3-dimethylbutyl)magnesium) is not unique; an equally close fit between observed and calculated spectra could be obtained using all positive signs for the coupling constants. In the latter solution, the magnitudes J_{12} and J_{34} were different than those reported in Table I; the magnitudes of the vicinal coupling constants were the same.

(32) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, 37, 21 (1962).

Nuclear Magnetic Resonance Spectroscopy. Temperature Dependence of the Spectrum of Fluorocyclooctatetraene[1]

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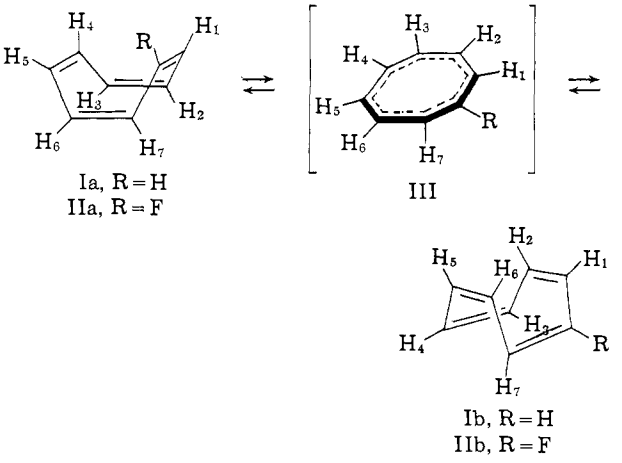
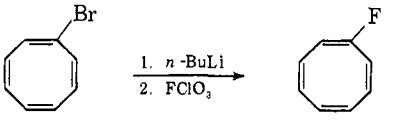
Contribution No. 3184 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. *Received March 5, 1965*

The fluorine n.m.r. spectrum of fluorocyclooctatetraene has been shown to be temperature dependent between 30 and −65°. This is attributed to changes in the rate of an inversion-bond-shift process which is slow on the n.m.r. time scale at low temperatures. The free energy of activation for inversion is approximately 12 kcal./mole at −33°.



Cyclooctatetraene and some of its derivatives appear to undergo inversion with or without accompanying bond shifts (most likely through considerably strained planar intermediates or transition states). The activation energy required for this kind of dynamic process is of considerable theoretical interest.[2] Anet and coworkers[2a,b] and Whitesides[3] have shown that the rate of establishment of the equilibrium represented by Ia ⇄ Ib can be studied by n.m.r. spectroscopy. In a further investigation of this phenomenon, we have investigated the temperature dependence of the fluorine n.m.r. spectrum of fluorocyclooctatetraene (II).

Fluorocyclooctatetraene was prepared for this study in 10% yield by reaction of perchloryl fluoride with an ethereal solution of cyclooctatetraenyllithium at −75°. The product was purified by preparative gas chromatography and the structure was confirmed by spectroscopic evidence. The proton n.m.r. spectrum of II showed a main signal at 345 with much weaker peaks at 329



II

and 322 c.p.s. This spectrum is compatible with a structure possessing only olefinic hydrogens. The ultraviolet spectrum of II with strong end absorption at 220 mμ and a broad λ_{max} at 285.5 mμ (ϵ 225) very

(1) Supported in part by the Office of Naval Research.

(2) (a) F. A. L. Anet, *J. Am. Chem. Soc.*, 84, 671 (1962); (b) F. A. L. Anet, A. J. R. Brown, and Y. S. Lin, *ibid.*, 86, 3576 (1964); (c) K. Mislow and H. D. Perlmutter, *ibid.*, 84, 3591 (1962); (d) N. L. Allinger, *J. Org. Chem.*, 27, 443 (1962).

(3) G. M. Whitesides and J. D. Roberts, unpublished results, California Institute of Technology; *cf.* J. D. Roberts, *J. Vsuesnoe Chem.* (USSR), 7, 367 (1962).

closely resembles the spectra of cyclooctatetraene and its bromo and chloro derivatives.[4]

The temperature dependence of the fluorine n.m.r. spectrum of fluorocyclooctatetraene is shown in Figure 1. The complex fluorine signal which is observed at 29° is seen to broaden as the temperature is lowered and then coalesce at about −33°. As the temperature is lowered further, a doublet with considerable second-order splitting appears and remains unchanged below −65°. Surprisingly, the proton signal of II showed essentially no change over the same temperature range other than what could be attributed to viscous broadening at the low temperatures.

Rapid equilibration of IIa and IIb at room temperature should result in the averaging of these two forms such that the n.m.r. picture of fluorocyclooctatetraene at 29° will have the symmetry of the planar structure III but not (except accidentally) have the coupling constants or chemical shifts expected for III. The protons H_1 and H_7 will be equivalent with respect to their spin–spin coupling interactions with the fluorine atom, and the magnitude of this interaction, $J_{H_{1(7)}F}$, will be the average of $J_{H_1F} + J_{H_7F}$ for either IIa or IIb. The same kind of thing will be true for the proton pairs H_2–H_6 and H_3–H_5, each of which can enter into long-range coupling with the fluorine atom.[5] Furthermore, at least some long-range coupling between proton H_4 and the fluorine atom might be expected on the basis of reported[5a,b] six-bond H–F couplings. These interactions could well lead to a very complex fluorine resonance in accord with the observed room-temperature fluorine signal.[6]

The doublet in the fluorine spectrum at −65° where inversion is slow must arise from a primary coupling between the fluorine atom and proton H_1 (IIa) or H_7 (IIb) which is situated *cis* with respect to the fluorine atom on the double bond. The separation of the two centers of the doublet is about 20 c.p.s. which agrees well with the *cis* H–F coupling constant range (13–19 c.p.s.) predicted by Karplus[7] in a study of the angular dependence of spin–spin coupling constants. On the other hand, coupling between the fluorine and adjacent proton H_7 of IIa or H_1 of IIb should be small since the dihedral angle in this case is about 80–85°, a minimum on the Karplus[7] scale. Possibly a weak coupling between the fluorine and this proton is responsible in part for the additional small splittings of the doublet although more than likely this is the result of long-range H–F coupling involving the other protons of the ring.

The complexity of the spectra of II precluded determination of the activation parameters for the cyclooctatetraene inversion bond-shift process. At the point where the principal doublet coalesces, −33°, the approximate reaction rate[8] is on the order of 44 sec.$^{-1}$ from which the free energy of activation can be calculated to be about 12 kcal./mole by the Eyring rate equation.

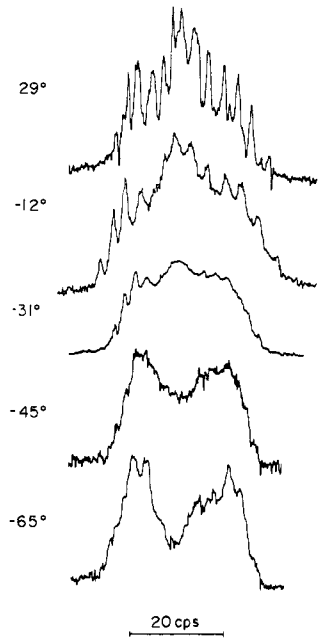


Figure 1. Temperature-dependent spectrum of fluorocyclooctatetraene in carbon disulfide solution. The field strength increases from left to right.

The present results parallel those obtained in studies of the temperature dependence of the ^{13}C satellites of cyclooctatetraene[2a,3] where the proton attached to the ^{13}C of the cyclooctatetraene ring serves as the X portion of the spectrum and experiences similar changes in spin–spin interactions of the other ring protons with changes in temperature as does the fluorine atom of fluorocyclooctatetraene. Thus, the ^{13}C satellite at room temperature is broad and complex and on cooling changes into a doublet with some second-order splitting. The free energy of activation for ring interconversion of cyclooctatetraene itself was found to be approximately 13.7 kcal./mole which is reasonably close to the value determined for fluorocyclooctatetraene.

Experimental

Fluorocyclooctatetraene. An ethereal solution of cyclooctatetraenyllithium[9] was obtained from the reaction of 11.46 g. (0.0625 mole) of bromocyclooctatetraene with a *n*-butyllithium solution prepared from 11.0 g. (0.08 mole) of *n*-butyl bromide and 1.4 g. (0.20 mole) of lithium wire. Perchloryl fluoride (~2 g., 0.2 mole), was then bubbled into the cyclooctatetraenyllithium solution during 1 hr. while the temperature was maintained at −75°. The reaction was stirred for an additional hour at −75° and slowly allowed to warm. When the temperature reached −30°, the reaction mixture was poured into 400 ml. of water and extracted with ether. The dried ethereal extract was fractionally distilled at a bath temperature of 45°, and the desired fluorocyclooctatetraene was separated from the mixture of other products by pre-

(4) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, 74, 168 (1952).

(5) For examples of long-range H–F coupling see: (a) A. H. Lewin, *ibid.*, **86**, 2303 (1964); (b) A. D. Cross and P. W. Landis, *ibid.*, **84**, 1736 (1962); (c) A. D. Cross and P. W. Landis, *ibid.*, **84**, 3784 (1962); (d) M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962); (e) D. R. Davis, R. P. Lutz, and J. D. Roberts, *ibid.*, **83**, 246 (1961).

(6) Some confirmation of the suggested long-range H–F couplings were obtained from attempts to duplicate the room-temperature spectrum by computer procedures. A number of sample calculations indicated that the fluorine spectrum could not be reproduced even approximately by assuming that only two (or four) protons are in effect coupled to the fluorine.

(7) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(8) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).

(9) A. C. Cope. M. Burg, and S. W. Fenton, *J. Am. Chem. Soc.*, **74**, 173 (1952).

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 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.

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

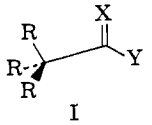
Structural Studies by Nuclear Magnetic Resonance. X. Conformations of Aliphatic Aldehydes

Gerasimos J. Karabatsos[1] and Nelson Hsi[2]

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 ⇌ 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 ⇌ 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 ⇌ 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.

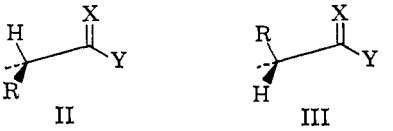
Several investigations have showed that the stable conformation of a tetrahedral carbon bonded to a trigonal carbon is I, whereby a single bond (C–R)



I

eclipses the C=X double bond. These include Raman 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

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

(3) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa, and N. Shido, *J. Chem. Phys.*, 21, 815 (1953).
(4) I. Nakagawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *ibid.*, **20**, 1720 (1952).
(5) A. Miyake, I. Nakagawa, T. Miyazawa, I. Ichishima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **13**, 161 (1958).
(6) S. Mizushima, T. Shimanouchi, I. Ichishima, T. Miyazawa, I. Nakagawa, and T. Araki, *J. Am. Chem. Soc.*, **78**, 2038 (1956). The infrared spectra of α-halogenated carbonyl compounds [L. J. Bellamy, R. C. Thomas, and R. L. Williams, *J. Chem. Soc.*, 3704 (1956); L. J. Bellamy and R. L. Williams, *ibid.*, 4294 (1957)] and phenacyl ethers [P. Yates, S. Lipinsky, and D. Vossius, *Can. J. Chem.*, **39**, 1977 (1961)] have also been interpreted in terms of eclipsing conformations.
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(8) S. S. Butcher and E. B. Wilson, Jr., *ibid.*, **40**, 1671 (1964).
(9) K. M. Sinnott, *ibid.*, **34**, 851 (1961).
(10) D. R. Herschbach and L. C. Krishner, *ibid.*, **28**, 728 (1958).
(11) C. Romers and J. E. G. Creutzberg, *Rec. trav. chim.*, **75**, 331 (1956).
(12) L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Letters*, **13**, 705 (1964).
(13) R. J. Abraham and J. A. Pople, *Mol. Phys.*, **3**, 609 (1960).
(14) E. B. Whipple, J. H. Goldstein, and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960).
(15) E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961).
(16) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).
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(18) A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, **34**, 127 (1962).