The Proton Magnetic Resonance Spectra of Olefins. II. Internal Rotation in Alkylethylenes

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Parameters obtained from the analysis of proton magnetic resonance spectra of several alkylethylenes are reported. From these values and others previously reported, it may be deduced that: (1) the spin–spin coupling constant between protons on adjacent trigonal and tetrahedral carbons depends on the rotational conformation, having a value near 11.5 c.p.s. when the protons are *trans* oriented and near 3.7 c.p.s. when they are *gauche* oriented; (2) the long-range allylic coupling constants also depend on the rotational conformation, having the smallest absolute value when the allylic proton and the $=CH_2$ group are eclipsed; (3) in the compounds $RCH_2CH=CH_2$ and $R_2CH—CH=CH_2$, the rotational conformers are about equally populated when $R = CH_3$, but as R is increased in size, the conformation with R and $=CH_2$ eclipsed becomes less favored.

Introduction.—Over the past twenty-five years there has accumulated considerable evidence for the existence of distinct rotational conformers in open-chain organic compounds containing a single bond between a tetrahedral and a trigonal carbon atom. Such conformers are sufficiently short-lived that physical separation has not been feasible; information about them has been obtained indirectly by physical measurements on mixtures.

Thus infrared and Raman spectroscopy have been applied to the problem and strongly indicate the existence of rotational conformers in liquid allyl halides,[1] allyl alcohol,[1] allylamine,[1] chloroacetone,[2] chloroacetyl chloride,[3] bromoacetyl chloride,[3] bromoacetyl bromide,[3] N-methylchloroacetamide,[4] dichloroacetyl chloride[5] and 1,2,3,3-tetrachloro-1-propene.[6] In a number of cases[2-5] the proportions in which the conformers occur could be shown to differ for samples in the gaseous, liquid or solid state. A change in the proportions of conformers could often be brought about by changing the dielectric constant of the medium in which the sample was dissolved. From a consideration of the vibrational frequencies, Mizushima and co-workers[2-5] have suggested that for carbonyl-containing compounds, one of the stable conformations is that in which the carbonyl oxygen is eclipsed with a substituent on the tetrahedral carbon, while the other is obtained from it by rotation through ∼ 90 or ∼ 150°.

Microwave spectroscopy has been applied in order to ascertain the structures in the cases of acetaldehyde[7] and propene.[8] While the symmetry of the methyl group precludes the existence of distinguishable rotational conformers in this case, the most stable conformation is confirmed as that in which one of the substituents on tetrahedral carbon is eclipsed with the carbonyl oxygen or the vinyl methylene.

Nuclear magnetic resonance has been applied in

a study of 2,3-disubstituted propenes. In discussing this work, Whipple, Goldstein and McClure[9,10] suggest that the observed solvent dependence of long-range proton–proton spin coupling in 2,3-dihalopropenes is a result of a change in the proportion of rotamers, and deduce that this coupling decreases in magnitude as the protons on tetrahedral carbon spend a greater proportion of time in the conformation in which they are eclipsed with the vinyl methylene.[11] Abraham and Pople[12] have studied the n.m.r. spectra of acetaldehyde and propionaldehyde, and have found for propionaldehyde a dependence of J_{HH} (aldehyde proton to methylene proton) on temperature. This is interpreted in terms of a temperature dependence of rotamer population, and leads to the conclusion that the preferred conformation in liquid propionaldehyde is that in which the methyl group is eclipsed with the carbonyl. They deduce that in propionaldehyde J_{HH} has a value of *ca.* 8.3 c.p.s. when the protons are oriented *trans* and *ca.* 0.1 c.p.s. when they are *gauche*.

In the case of the hydrocarbon 1-butene, there is mild disagreement[13-17] as to whether two conformers coexist in the liquid, and if so in what proportion. In a previous study,[18] bearing on this problem, it was noted that the vicinal proton–proton coupling constants for protons on the $C_{III}–C_{IV}$ bond were within experimental error the same for propene, 1-butene and 1-hexene. If 1-butene can exist in

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(2) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, J. Chem. Phys., **21**, 815 (1953).

(3) I. Nakagawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi and S. Mizushima, ibid., **20**, 1720 (1952).

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(5) A. Miyake, 1. Nakagawa, T. Miyazawa, I. Ichishima, T. Shimanouchi and S. Mizushima, Spectrochim. Acta, **13**, 161 (1958).

(6) H. Gerding and H. G. Haring, Rec. trav. chim., **74**, 957 (1955).

(7) R. W. Kilb, C. C. Lin and E. B. Wilson, J. Chem. Phys., **26**, 1695 (1957).

(8) D. R. Herschbach and L. C. Krisher, ibid., **28**, 728 (1958).

(9) E. B. Whipple, J. H. Goldstein and G. R. McClure, J. Am. Chem. Soc., **82**, 3811 (1960).

(10) E. B. Whipple, J. Chem. Phys., **35**, 1039 (1961).

(11) Actually the stable conformation suggested by Whipple, et al.,[9,10] differs from the conformation suggested here by a 30° rotation, which has the effect of allowing the halogen substituent to retreat to the maximum distance from both the vinylmethylene and the halogen on trigonal carbon. This assignment is based on measurements of long-range coupling in 2-halo- and 2,3-dihalopropenes. It is not clear that the relation between coupling constant and dihedral angle assumed in interpreting their data holds sufficiently exactly (cf. ref. 9, footnote 8) to permit an unequivocal choice between the two conformations. In the compounds examined in the present work there are no bulky and/or polar groups on carbon-2, so that one of the factors favoring the Whipple conformation is absent. We therefore slightly prefer the conformations as described in the present paper.

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(13) J. G. Aston, G. Szasz, H. W. Woolley and F. G. Brickwedde, J. Chem. Phys., **14**, 67 (1946).

(14) J. E. Kilpatrick and K. S. Pitzer, J. Res. Natl. Bur. Stand., **37**, 163 (1946).

(15) R. S. Rasmussen and R. R. Brattain, J. Chem. Phys., **15**, 120 (1947).

(16) N. Sheppard, J. Chem. Phys., **17**, 74 (1949).

(17) L. A. Harrah and D. W. Mayo, ibid., **33**, 298 (1960).

(18) A. A. Bothner-By and C. Naar-Colin, J. Am. Chem. Soc., **83**, 231 (1961).

distinguishable conformers, the observations are consistent with two sets of *a priori* postulates: either (1), 1-butene and 1-hexene exist predominantly as one of the conformers, and the coupling constant in the H–C_{III}–C_{IV}–H system is independent of the H–C–C–H dihedral angle; or (2), the coupling constant depends on the value of the dihedral angle, but the conformers of 1-butene and of 1-hexene are about equally populated. Either alternative is somewhat surprising, but on the basis of measurements of the H–C_{III}–C_{IV}–H couplings in compounds of known geometry, *e.g.*, cyclohexane, it was felt[18] that alternative 2 was preferable. The evidence was sufficiently tenuous, however, that further confirmation appeared necessary, and the present work was undertaken in order to provide information useful in settling the question.

The approach was simple: if the methyl group of 1-butene is not large enough to interfere sterically with the methylene when eclipsed with it, an effect might be noticed if the group were enlarged. Therefore spectra were obtained and interpreted on the compounds 3-isopropylpropene-1,[19] 3-*t*-butylpropene-1, 3,3-dimethylpropene-1 and 3,3-di-*tert*-butylpropene-1. In addition the spectrum of 1,1-dimethyl-3,3-di-*tert*-butylpropene-1 was examined, with the hope that substitution of methyls on the terminal methylene might further restrict rotation of the (*tert*-C_4H_9)$_2$CH–group about the C_{III}–C_{IV} bond.

Experimental

4-Methylpentene-1 (3-Isopropylpropene-1).—A commercial sample (Phillip 66 pure grade, 99 mole % minimum) was used as received.

4,4-Dimethylpentene-1 (3-*tert*-Butylpropene).—The reaction of *tert*-butyl Grignard reagent with allyl bromide was carried out as described by Whitmore and Homeyer.[20] The hydrocarbon was purified by conversion to the dibromide and regeneration with zinc dust. The product distilled completely at 71° (740 mm.). The reported boiling point is 71.8° (760 mm.). Vapor phase chromatography revealed no impurities exceeding 0.5%.

3-Methylbutene-1 (3,3-Dimethylpropene-1).—A commercial sample (Phillip 66 pure grade, 99 mole % minimum) was used as received.

4,4-Dimethyl-3-*tert*-butylpentene-1 (3,3-Di-*tert*-butylpropene-1).—In a dry Schlenk-tube, filled with dry, oxygen-free nitrogen, a suspension of 17.86 g. (50 mmoles) of methyltriphenylphosphonium bromide in 100 ml. of anhydrous tetrahydrofuran was stirred and 50 mmoles of phenyllithium in ether was added dropwise.[21] The mixture was stirred for 2 hours, then 5.7 g. (36.2 mmoles) of 1,1-di-*tert*-butylacetaldehyde,[22] dissolved in 50 ml. of tetrahydrofuran, was added slowly. The mixture was allowed to stand overnight, then washed twice with saturated ammonium chloride solution and dried over potassium carbonate. The solvent was evaporated and the residue extracted with petroleum ether, b.p. 30–60°, for 2 hours. After filtration the precipitate was washed with petroleum ether and dried; yield of triphenylphosphine oxide, m.p. 145–151°, 7.3 g. (26.3 mmoles), or 73% based on the aldehyde.

The petroleum ether fraction was distilled and yielded 4.45 g. of a cut, boiling range 163–168°. V.P.C. demon-

strated that it contained 76% of an olefin, whose n.m.r. spectrum was consistent with that of the desired product.

The hydrocarbon was purified by distillation using a spinning band column. The best sample obtained was 98% pure by V.P.C. and had the physical characteristics b.p. 164° (745 mm.), n^{24}D 1.4398.

Anal.[23] Calcd. for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.73; H, 14.48.

2,5,5-Trimethyl-4-*tert*-butylhexene-2 (1,1-Dimethyl-3,3-di - *tert* - butyl - propene - 1).—Isopropylidenetriphenylphosphine[24] was prepared as above from 17.28 g. (40 mmoles) of isopropyltriphenylphosphonium iodide,[24] and allowed to react with 5.2 g. (33 mmoles) of di-*tert*-butylacetaldehyde.[22] After work-up essentially as above, a crude distilled fraction, boiling range 190–199°, was obtained. V.P.C. indicated that it contained 3.87 g. (21.2 mmoles, 64% based on aldehyde) of a hydrocarbon whose n.m.r. spectrum was consistent with the proposed structure.

The best fraction obtained by distillation through a spinning band column was 99.2% pure by V.P.C.; b.p. 191° (760 mm.), $n^{25.5}$D 1.4479.

Anal.[25] Calcd. for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.65, 85.75; H, 14.22, 14.27.

Preparation of Samples.—Samples of the above materials, neat or at 10% (v./v.) in CCl_4 with 1% tetramethylsilane added, were degassed on the vacuum line and sealed in 5 mm. o.d. Pyrex tubes.

Spectra.—Spectra were obtained with a Varian model V4302 and/or A-60 spectrometer. Calibration in either case was by means of interpolation between side-bands produced by audio modulation. Line positions when completely resolved were measured with a probable error of ±0.05 c.p.s.

Interpretation of Spectra.—Parameters estimated by first-order considerations were used to calculate predicted spectra. The calculations were performed on an IBM 704 computer using a modification of a previously described[18] program. The modification causes the computer to calculate a predicted spectrum from a set of estimated parameters and additional spectra varying selected members of this set. The computer then forms the group of partial derivatives $\delta\nu_i/\delta p_j$; giving the linear dependence of the frequency of line i on the jth parameter (a single parametric variation may affect several pieces of input data, *e.g.*, coupling to all protons of a methyl group, etc.). The observed spectral frequencies are then matched with the appropriate calculated frequencies by the operator. The computer forms the set of i equations

$$\sum_j \frac{\delta\nu_i}{\delta p_j} \Delta p_j = \nu_{ix} - \nu_{ic}$$

where ν_{ix} is the experimentally observed frequency of line i and ν_{ic} the calculated frequency of the corresponding line in the original calculation. This usually over-determined set of equations is then solved for the corrections, Δp_j, to be applied to the original set of estimated parameters. The least squares solution is obtained by solving the set of equations

$$\mathbf{D}^T\mathbf{D}\,\vec{p} = \mathbf{D}^T\vec{\nu}$$

where $\mathbf{D}^T$ is the transpose of the matrix $\mathbf{D}$ of partial differentials, and $\vec{p}$ and $\vec{\nu}$ are the column vectors of Δp_i and $(\nu_{ix} - \nu_{ic})$, respectively. With a reasonably good choice of initial parameters (errors of 1 c.p.s. or so), one computation cycle is usually sufficient to reduce mean absolute deviation of the line positions to the range 0.05 to 0.10 c.p.s. Refinement of the fit by iteration of the procedure may be conveniently performed if required.[26]

Results

The values for the chemical shifts and coupling constants obtained are given in Table I. The 40-mc. spectrum of 3,3-dimethylpropene-1 has recently been analyzed and reported by Banwell

(19) For the purposes of this paper, the hydrocarbons studied will be, named as derivatives of propene, *e.g.*, 3-methylpropene (1-butene) 3,3-dimethylpropene (3-methylbutene-1), 3-*tert*-butylpropene (4,4-dimethylpentene-1). This nomenclature is admittedly poor usage, but greatly simplifies the presentation of the reasoning.

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(21) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

(22) M. S. Newman, A. Arkell and T. Fukunaga, *J. Am. Chem. Soc.*, **82**, 2501 (1960).

(23) Microanalytical Laboratory, Mellon Institute.

(24) G. Wittig and D. Wittenberg, *Ann.*, **606**, 18 (1957).

(25) Illini Microanalytical Laboratory, Urbana, Ill.

(26) Listings and punched cards for this FORTRAN program are available upon request.

Table I

Chemical Shifts and Coupling Constants for Several Olefins

$$R_3 \diagdown \overset{\displaystyle H(4)\quad R_4'}{\diagup}$$

Substn. on olefin				State[a]	Chemical shifts[b]				Coupling constants					
R_2	R_3	R_4	R_4'		$\nu(1)$	$\nu(2)$	$\nu(3)$	$\nu(4)$	$J(1,2)$	$J(1,3)$	$J(1,4)$	$J(2,3)$	$J(2,4)$	$J(3,4)$
H	H	CH_3	CH_3	N	256.27	311.18	305.29	(490)[c]	10.37	17.22	6.41	1.74	−1.17	−1.43
				S	256.57	311.15	306.13	(490)[c]						
H	H	H	$i\text{-}C_3H_7$	N	256.79	304.48	303.48	(480)[c]	10.13	17.02	7.00	2.05	−1.15	−1.43
				S	257.70	304.42	303.84	(480)[c]						
H	H	H	$t\text{-}C_4H_9$	N	253.36	301.93	303.30	484.90	10.02	17.10	7.46	2.37	−0.94	−1.32
				S	253.87	302.16	303.68	484.50						
H	H	$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	N	255.59	300.75	312.88	506.02	9.97	17.01	10.65	2.63	−0.10	−0.63
				S	255.71	301.17	313.27	506.10						
CH_3	CH_3	$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	N	286.50	(506.55, 496.74)[d]		486.42	−1.25[e]	−1.25[e]	11.37	..[f]	...[f]	...[f]
				S	287.50	(506.25, 496.55)[d]		487.51						

[a] N = neat, S = 10% (v./v.) in CCl_4. [b] On a frequency scale with $\nu SiMe_4$ = +600.00 c.p.s.; the scale numbers increase with increasing applied field; spectrometer frequency = 60.00 mc./sec. [c] Assumed, not analyzed. [d] Assignment not certain. [e] $J(H\text{-}CH_3)$. [f] Not resolved, probably less than 0.2 c.p.s.

and Sheppard.[27] Their values for the coupling constants and internal chemical shifts and those reported here agree well. There is a small discrepancy in the values of the chemical shifts relative to tetramethylsilane reported in the two studies.

Discussion

In propene itself, the three most stable rotational conformations are energetically indistinguishable. The observed coupling constant for protons on adjacent trigonal and tetrahedral carbon, $J_{1,4}{}^0$, may be related to the coupling constants for such protons when they are *trans* oriented, J_t, and when they are *gauche* oriented, J_g, by the expression[18]

$$J_{1,4}{}^0 = \frac{J_t + 2J_g}{3} \qquad (1)$$

Probable stable conformations for 3-monoalkyl-propenes (I_a, I_b, I_c) and for 3,3-dialkylpropenes (II_a, II_b, II_c) are illustrated in Fig. 1. If the rota-
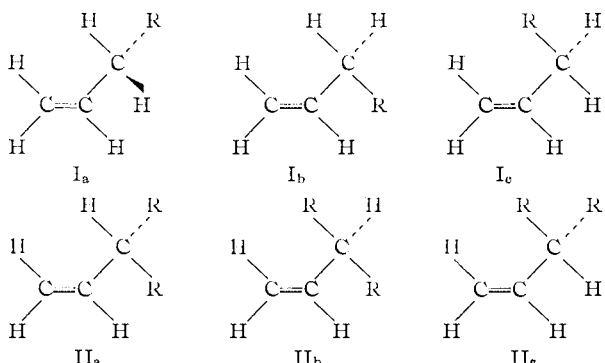

Fig. 1.—Probable stable conformations for $RCH_2CH{=}CH_2$ (I_a, I_b, I_c) and $R_2CHCH{=}CH_2$ (II_a, II_b, II_c).

mers I_a, I_b, and I_c are present in the proportion $x:x:1$, the observed coupling $J_{1,4}{}^I$, may be related to J_g and J_t by the expression

$$J_{1,4}{}^I = \frac{xJ_t + (1 + x)J_g}{1 + 2x} \qquad (2)$$

Similarly, if the rotamers II_a, II_b and II_c are present in the proportions $y:1:1$, the observed average coupling $J_{1,4}{}^{II}$ will be given by

(27) C. N. Bunwell and N. Sheppard, *Proc. Roy. Soc. (London)*, **263A**, 136 (1961).
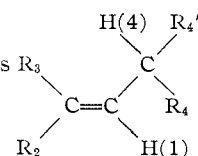
$$J_{1,4}{}^{II} = \frac{yJ_t + 2J_g}{y + 2} \qquad (3)$$

In the case of the monosubstituted propenes (I), if the introduction of bulkier alkyl groups increases the populations of forms I_a and I_b at the expense of I_c, $J_{1,4}{}^I$ will tend toward the limit $1/2(J_t + J_g)$. In the monosubstituted series, $J_{1,4}{}^I$ does increase from 6.22 to 7.46 c.p.s. as R is changed from methyl through isopropyl to *tert*-butyl. This observation strongly supports the suggestions that J_t is larger than J_g, that 1-butene exists essentially as a 1:1:1 mixture of forms I_a, I_b and I_c, and that bulkier substituents favor forms I_a and I_b. Further, by setting $1/3(J_t + 2J_g)$ equal to 6.3 c.p.s. (within experimental error of both 1-butene and 1-propene) and $1/2(J_t + J_g)$ equal to 7.5 c.p.s. a *lower limit* for J_t of 11.1 c.p.s. and an *upper limit* for J_g of 3.9 c.p.s. is obtained. If the mono-*tert*-butyl compound is less than 100% in forms I_a and I_b it follows that J_t must be greater than 11.1 c.p.s. (equation 2).

For corresponding mono- and disubstituted compounds with the same alkyl substituents (e.g., butene-1 and 3-methylbutene-1), it may be predicted that $J_{1,4}{}^I$ and $J_{1,4}{}^{II}$ can be calcuated from eq. 2 and 3 setting x equal to y. The justification for this procedure comes from a consideration of first-order repulsive interactions between groups on C_{III} and C_{IV}.

Considering form I_a, it is noted that there is one eclipsed methylene–H repulsion, one *gauche* H–H repulsion and one *gauche* H–R repulsion. Symbolizing the energies of these interactions by $E(CH_2\text{–}H)$ $G(H\text{–}H)$ and $G(R\text{–}H)$, respectively, and noting that form I_c has repulsive interactions of energies $E(CH_2\text{–}R)$ and $2G(H\text{–}H)$, one derives for the energy difference between forms I_a and I_c

$$\Delta E_I = (E(CH_2\text{–}R) + 2G(H\text{–}H)) - (E(CH_2\text{–}H) + G(H\text{–}H) + G(R\text{–}H))$$

$$= E(CH_2\text{–}R) + G(H\text{–}H) - E(CH_2\text{–}H) - G(R\text{–}H)$$

Similarly

$$\Delta E_{II} = (E(CH_2\text{–}R) + G(R\text{–}H) + G(H\text{–}H)) - (E(CH_2\text{–}H) + 2G(R\text{–}H))$$

$$= E(CH_2\text{–}R) + G(H\text{–}H) - E(CH_2\text{–}H) - G(R\text{–}H)$$

So that

$$\Delta E_I = \Delta E_{II}$$

Further since

$$x = \exp (\Delta E_{\mathrm{I}}/RT)$$
$$y = \exp (\Delta E_{\mathrm{II}}/RT)$$

the relation $x = y$ is indicated. This derivation ignores second-order effects such as bond deformation would introduce, and must be regarded as approximate only. Also the calculation of $J_{1,4}{}^{\mathrm{I}}$ and $J_{1,4}{}^{\mathrm{II}}$ from eq. 2 and 3 with $x = y$ is made with the implicit assumption that J_{g} and J_{t} are constant in a series of hydrocarbons and this may introduce further error.

Nevertheless, on this basis it is predicted that since $x = 1$ for butene, $y = 1$ for 3-methylbutene, and this compound should also be characterized by a $J_{1,4}$ essentially equal to that of propene. Such is indeed the case.

In the case of the mono- and di-*tert*-butyl derivatives, it is possible to estimate J_{g}, J_{t}, and x, all from the experimental data using eq. 1, 2, and 3, together with the additional relation $x = y$.

The relations obtained by solving eq. 1, 2, and 3 for x and J_{g} are

$$x = 2(J_{1,4}{}^{\mathrm{I}} - J_{1,4}{}^{\mathrm{II}})/(3J_{1,4}{}^{0} - 4J_{1,4}{}^{\mathrm{I}} + J_{1,4}{}^{\mathrm{II}})$$
$$J_{\mathrm{g}} = (2J_{1,4}{}^{0}J_{1,4}{}^{\mathrm{II}} - J_{1,4}{}^{\mathrm{I}}(J_{1,4}{}^{0} + J_{1,4}{}^{\mathrm{II}}))/ \\ (J_{1,4}{}^{0} + J_{1,4}{}^{\mathrm{II}} - 2J_{1,4}{}^{\mathrm{I}}) \quad (6)$$

The value for J_{t} may then be found by substituting in the relation

$$J_{\mathrm{t}} = 3J_{1,4}{}^{0} - 2J_{\mathrm{g}}$$

For the *tert*-butyl series, the value of x obtained by substitution in these relations is quite sensitive to the observed values of $J_{1,4}{}^{0}$, $J_{1,4}{}^{\mathrm{I}}$ and $J_{1,4}{}^{\mathrm{II}}$ used, varying from 10 to ∞ with changes in the second decimal place of these values. The derived values of J_{g} and J_{t} are quite constant, however. Using the approximate values 6.3, 7.5 and 10.7 for $J_{1,4}{}^{0}$ $J_{1,4}{}^{\mathrm{I}}$ and $J_{1,4}{}^{\mathrm{II}}$, respectively, one obtains the results $x = 16$, $J_{\mathrm{g}} = 3.7$, $J_{\mathrm{t}} = 11.6$. These values reinforce earlier conclusions concerning J_{g} and J_{t}. The value of x obtained implies that the mono-*tert*-butyl compound is largely in forms $\mathrm{I_a}$ and $\mathrm{I_b}$,

and the di-*tert*-butyl compound is predominantly in form $\mathrm{II_a}$.

Finally, $J_{1,4}$ in the compound 1,1-dimethyl-3,3-di-*tert*-butylpropene-1 has the value 11.37 c.p.s., which must very nearly represent J_{t}. Models indicate a very high energy for conformers of this molecule with *tert*-butyl and isopropylidene groups eclipsed.

The data also confirm in a very satisfactory manner the suggestion of Whipple, Goldstein and Mc-Clure[9] that the allylic couplings $J_{2,4}$ and $J_{3,4}$ vary with rotational conformer population and are smallest in magnitude in the conformer with eclipsed methylene and allylic proton. The effect of conformer population on these coupling constants (as well as on $J_{1,4}$) is most strikingly displayed in the data obtained for 3,3-di-*tert*-butylpropene-1 (Table I).

Di-*tert*-butylacetaldehyde was prepared in the course of the synthesis of di-*tert*-butylpropylene, and, in view of the findings of Abraham and Pople,[12] it also appeared of interest to investigate the coupling constants in this case. The coupling constant between the aldehyde proton and the proton on the adjacent carbon had the value 5.0 c.p.s.; *i.e.*, considerably larger than for acetaldehyde (2.8 c.p.s.). This suggests that steric interference between the *tert*-butyl group and the carbonyl when they are eclipsed is large, so that the conformer with the carbonyl and proton eclipsed (analogous to $\mathrm{II_a}$) is favored. The explanation for the preferred conformation of propionaldehyde (analogous to $\mathrm{I_c}$), is probably the same as that advanced by Szasz[28] for the preferred *gauche* conformation of *n*-propyl chloride.

(28) G. J. Szasz, *J. Chem. Phys.*, **23**, 2449 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

The Action of Elementary Fluorine Upon Organic Compounds. XXV. The Direct Fluorination of Cyanuric Fluoride[1]

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Cyanuric fluoride has been fluorinated in both the jet and T-reactors under a variety of operating conditions. There were formed in considerable yields heptafluoro-1,3,5-triazacyclohexene (tetrafluoride adduct), perfluoro-1,3,5-triazacyclohexane (perfluoro-*s*-triazine) and perfluoro-1,3-diazacyclopentane (perfluoroimidazolidine), the last involving a ring contraction. Fragmentation also occurred with the formation in small amounts of the linear products $CF_3NFCF_2NFCF_2NF_2$, $CF_3NFCF_2NFCF_3$ and several others whose structures have been assigned on the basis of spectroscopic evidence. The physical properties of these new compounds have been presented, and a mechanistic interpretation of this reaction has been proposed.

Cyanuric fluoride, $(FCN)_3$, which may be regarded either as the acid fluoride of cyanuric acid

or as the cyclic trimer of cyanogen fluoride, was reported first from this laboratory by Maxwell.[3]