

**The Hofmann Elimination of Dimethiodide V with Lithium Diethylamide as the Base.**—Diethylamine (6 ml.) was distilled from potassium into a dry 100-ml. flask swept with dry oxygen-free nitrogen. The dimethiodide V (4.75 g., 8.2 mmoles), dried 3 hr. at 85° and 0.01 mm., was added and the flask was evacuated at the oil pump while being cooled in a Dry Ice-acetone bath. Dry oxygen-free nitrogen was admitted and a solution of 32.5 mmoles of butyllithium in 50 ml. of ether was added quickly. The solution, now at 0°, turned a dark red color. Stirring at 0° under N<sub>2</sub> was continued for 22 hr., at which time the solution was black in color. Methanol (30 ml.) was added and the solution was reduced to dryness at 20° at the water pump. The residue was extracted with several portions of benzene totaling 300 ml. and the benzene solution was extracted with dilute HCl, then washed with water. The dried benzene solution, which contained 1.45 g. of a reddish oil, was evaporated onto 10 g. of alumina and this material was added to the top of a column of 100 g. of alumina in hexane. Elution was carried out with pentane containing increasing amounts of ether. The cyclooctadienes were eluted with mixtures containing 1.5 to 5% ether. The fractions were placed in the deep freeze at -20°, and after 1 day the supernatants were decanted from the white heavy needles of tricyclooctadiene X which had formed (290 mg.). The mother liquids were evaporated to dryness at 20° and the residues were dissolved in a minimum of chloroform. Ethanol (95%) was added and the solutions were cooled to give second crops of compound X. The total recovery of tricyclooctadiene X was 345 mg. (0.845 mmole, 20.6%), m.p. 183-185° (the melting points varied with the rate of heating).

*Anal.* Calcd. for C<sub>32</sub>H<sub>24</sub>: C, 94.08; H, 5.92. Found: C, 93.87; H, 5.98.

Concentration of the mother liquids then yielded (with more difficulty) tricyclooctadiene XI (140 mg., 0.343 mmole, 8.4%) in the form of white crystals, m.p. 124-128° dec.

*Anal.* Calcd. for C<sub>32</sub>H<sub>24</sub>: C, 94.08; H, 5.92. Found: C, 93.69; H, 5.89.

In addition, runs carried out in furan yielded up to 22% of tricyclooctadiene X. The reaction of potassium *t*-butoxide with dimethiodide V at room temperature also yielded the tricyclooctadienes, but the yields were lower.

The cyclooctadienes isomerized cleanly to the corresponding cyclooctatetraenes in both liquid and solid phases. Dispersed in KBr, the half-life at room temperature for the conversion of X to VIII was less than 1 week, whereas the half-life for XI → IX was about 10 weeks. The rates in solution were considerably faster; the half-life for the isomerization of X in methylene chloride at 25° was about 12 hr. These changes could be followed easily in the infrared. In addition, powder patterns of the four compounds proved to be quite different, and the rate could be followed by this method as well.

Attempts to react the tricyclooctadienes (X and XI) with phenyl azide at 25° were unsuccessful. In each case, the corresponding cyclooctatetraene was isolated.

**The Reaction of Dimethiodide V with Lithium Diethylamide in Furan.**—Butyllithium (15 ml. of an ether solution, 14 mmoles) was added to a solution of diethylamine (2.96 g., 40 mmoles, distilled from potassium) in 35 ml. of furan (distilled from potassium). The mixture was added to 0.7 g. (1.22 mmoles) of the dimethiodide V under nitrogen, and the mixture, which became very dark in color, was stirred at -5° for 1 day and then at 25° for 40 min. A mixture of D<sub>2</sub>O and ether was added and the product was quickly worked up at 0° as outlined above to give 0.22 g. of a red oil plus some crystalline material. The total product was chromatographed on alumina. The 1% ether eluate yielded an oil which crystallized slowly in the refrigerator. It was sublimed at 50° and 0.01 mm. and recrystallized from 95% alcohol to give needles, m.p. 89-92°, which decomposed on standing at room temperature. The ultraviolet spectrum showed two maxima: 314 mμ (log ε 4.60) and 334 mμ (log ε 4.41).

*Anal.* Calcd. for C<sub>15</sub>H<sub>14</sub>: C, 93.16; H, 6.84. Found: C, 93.40; H, 6.55.

The remaining fractions yielded only the tricyclooctadienes X (22% yield) and XI, although in one case, a 3% yield of 1,3,5-triphenylbenzene was isolated in addition.<sup>29</sup> The infrared spectrum of compound X was superimposable on that of an authentic sample; *i.e.*, the compound did not contain deuterium. No evidence was obtained for a furan adduct.

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## Ring Inversion in Cycloheptatriene

By F. A. L. ANET

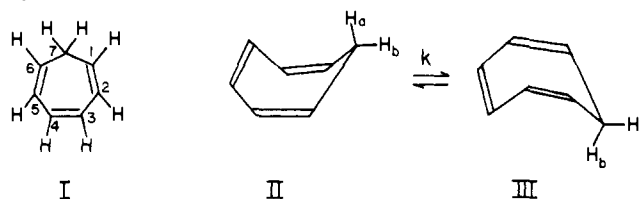
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The n.m.r. spectrum of tropilidene is temperature dependent below about -120°. At -150°, the methylene protons give rise to two chemically shifted bands and thus the molecule is nonplanar. The activation energy for the inversion process is 6.3 kcal./mole.

### Introduction

Although tropilidene is known<sup>1</sup> to have the 1,3,5-cycloheptatriene (I) rather than the norcaradiene structure, the planarity or nonplanarity of the seven-membered ring has been in dispute. A planar structure with appreciable aromatic character was suggested<sup>2</sup> as a result of theoretical speculations. Infrared and Raman spectral measurements<sup>3</sup> were interpreted on the basis of the planar structure, but these did not rule out completely the possibility of C-7 being slightly out of plane of the remaining carbon atoms. A recent X-ray determination<sup>4</sup> of the structure of the *p*-bromophenacyl ester of 7,7-dimethylcycloheptatriene-3-carboxylic acid showed that the seven-membered ring exists, in this compound at least, in a boat conformation, with C-7 and C-3-C-4 at distances of 0.63 and 0.48 Å., respectively, from the plane of C-1-C-2-C-5-C-6. The boat structure has also received support from the

observation<sup>5</sup> of 1,5-transannular hydrogen shift in cycloheptatriene.



The n.m.r. spectrum of tropilidene can be interpreted on the basis either of a planar structure or of a rapidly inverting nonplanar structure. In either case, the two methylene protons would appear equivalent, as is indeed observed.<sup>1,6</sup>

In a very recent paper, which appeared after completion of our own work, Conrow, *et al.*,<sup>7</sup> made the interesting observation that the 7,7-dimethyl groups of 2-*t*-butyl-3,7,7-trimethyltropilidene (Ia) were non-equivalent at low temperatures (*e.g.*, -100°). This

(1) E. J. Corey, H. J. Burke, and W. A. Remers, *J. Am. Chem. Soc.*, **77**, 4941 (1955).

(2) W. von E. Doering and I. M. Knox, *ibid.*, **76**, 3203 (1954).

(3) M. V. Evans and R. C. Lord, *ibid.*, **82**, 1876 (1960). However, the infrared spectrum of 7-deuteriocycloheptatriene shows that the carbon skeleton must be nonplanar; C. Lalau and H. de Ruyter, unpublished results, quoted in ref. 5.

(4) A. Tulinsky and R. F. Davis, *Tetrahedron Letters*, 839 (1962).

(5) A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962).

(6) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1961.

(7) K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, **85**, 1929 (1963).

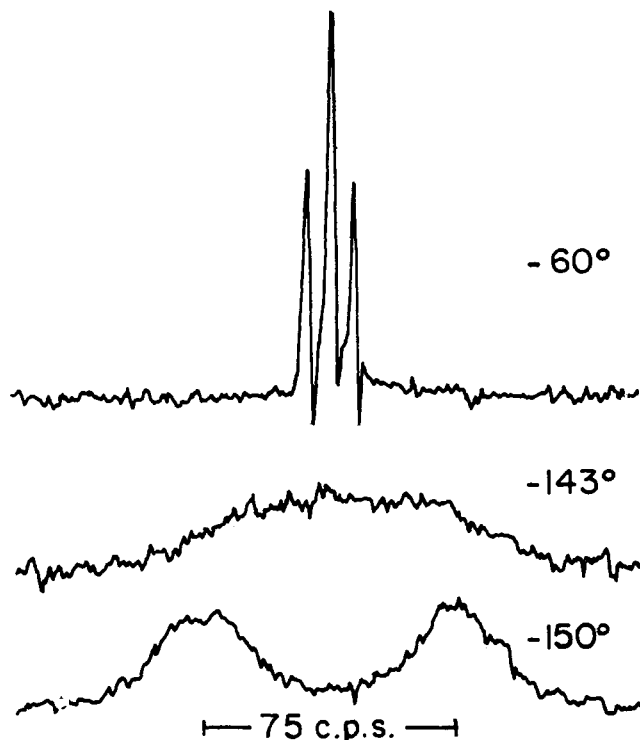


Fig. 1.—N.m.r. spectra (60 Mc./sec.) of methylene protons of tropilidene in dichlorodifluoromethane at various temperatures. The top spectrum is at a lower amplitude than the other two.

was not found in other compounds in which the 2-*t*-butyl group was replaced by a smaller alkyl group. Compound Ia must therefore be nonplanar and its higher barrier to inversion, compared to simpler derivatives of I, was ascribed to steric compression between the 2- and 3-substituents in the transition state for inversion. However, this evidence still allows the simple derivatives to have planar rings, although arguments were advanced to show that nonplanarity is likely to be general in the cycloheptatriene series.

### Results and Discussion

We have found that the n.m.r. spectrum of tropilidene at very low temperatures shows conclusively that the molecule is nonplanar, and also provides information on the barrier to inversion of the seven-membered ring.

Below  $-143^\circ$ , the methylene protons give rise to two distinct bands. At  $-150^\circ$ , the lowest temperature reached, the separation between the bands (Fig. 1) is 76 c.p.s., but is still increasing. The true chemical shift is estimated to be about 80 c.p.s. The mean chemical shift of the methylene protons is 132 c.p.s. (7.8  $\tau$ ) from tetramethylsilane, almost unchanged<sup>6</sup> from that observed at higher temperatures (Fig. 1). Although the low-field band is slightly broader than the upfield one, no fine structure can be seen. This is not surprising, as the interconversion rate is still appreciable and, in any case, the resolution is limited at these very low temperatures. Thus, the line width at half-height of tetramethylsilane at  $-150^\circ$  is about 6 c.p.s.

The only change which can be observed in the olefinic proton band is that due to the viscosity broadening just mentioned.

From the above results, the rate ( $k$ ) of ring inversion (II  $\rightleftharpoons$  III) at  $-143^\circ$  is calculated<sup>8</sup> to be about 180 sec.<sup>-1</sup>,

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

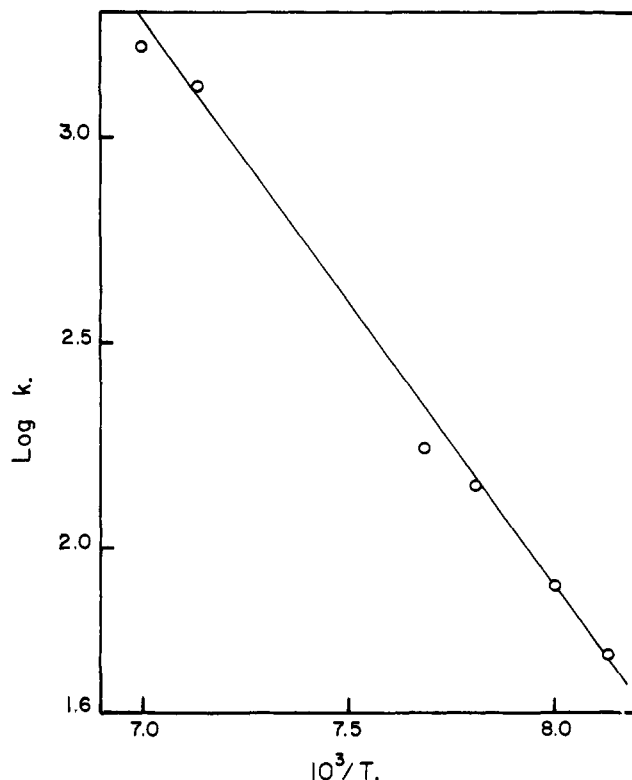


Fig. 2.—Plot of  $\log k$  against  $10^3/T$  for ring inversion of tropilidene.

which corresponds<sup>9</sup> to a free energy of activation ( $\Delta F^\ddagger$ ) of 6.1 kcal./mole.

The rate constant of 180 sec.<sup>-1</sup> at  $-143^\circ$  should<sup>10</sup> be reasonably accurate, even though it is deduced from the expression,  $k = \pi\nu/\sqrt{2}$ , which applies strictly only to the case of two sharp lines of relative chemical shift  $\nu$ , c.p.s., changing ultimately to a single sharp line.

In order to obtain the activation energy for the inversion process, it is necessary to measure the rate at more than one temperature. The use of peak separation<sup>8</sup> at temperatures below coalescence, while simple and often used, is not very suitable for tropilidene because of the unfavorable signal-to-noise ratio of the dilute solutions employed at very low temperatures. Furthermore, this method requires an accurate value of the chemical shift in the absence of exchange, if rates are needed at temperatures appreciably lower (say  $10^\circ$ ) than the coalescence temperature. In any case, the temperature range at which measurements can be made in the present instance is severely limited by other factors.

Fortunately, rates well above the coalescence temperature can be obtained<sup>8</sup> by measuring line widths. Since at high temperatures the methylene protons form a triplet (Fig. 1) and not a single line, the line-width measurements were made under conditions that these protons were decoupled from the adjacent protons on C-1 and C-6. No difficulty was experienced in collapsing the triplet by double-irradiation (see Experimental).

By combining the line width and peak separation data,  $k$  was obtained over a range of  $20^\circ$  (Table I). A plot of  $\log k$  against  $10^3/T$  is shown in Fig. 2. From the slope of the line, the activation energy is calculated to be  $6.3 \pm 0.5$  kcal./mole. Thus the entropy of activation is virtually zero.

(9) Calculated from the absolute rate theory, with the transmission coefficient equal to unity.

(10) K. G. Untch and R. J. Kurland, *J. Am. Chem. Soc.*, **85**, 346 (1963).

TABLE I  
RATES OF INVERSION ( $k$ ) OF TROPILIDENE AT VARIOUS TEMPERATURES

Temp., °C.	Peak sepn., c.p.s.	Corr. line width, <sup>a</sup> c.p.s.	$k$ , sec. <sup>-1</sup>
-150	76.0		55
-148	71.0		82
-145	49		140
-143	0		180
-133		7.8	1300
-130		6.2	1650

<sup>a</sup> Full line width at half-height of decoupled methylene protons minus line width of tetramethylsilane at the same temperature.

Molecular models show that the transition state for ring inversion is very likely to be the planar form. Since this has only slight angle distortion,<sup>11</sup> the low barrier to inversion of tropilidene is understandable. From the published<sup>7</sup> spectra of 2-*t*-butyl-3,7,7-trimethyltropilidene, it can be calculated that the free energy of inversion at -87° is about 9.2 kcal./mole., some 3 kcal./mole greater than in tropilidene itself. Although the former compound is probably strained because of overcrowding of the alkyl groups, this strain is greatly increased if the molecule becomes planar in the transition state for inversion. It must be pointed out, however, that factors other than steric strain may be important. In particular, the degree of overlap<sup>3,4</sup> between the p-orbitals on C-1 and C-6 may change appreciably during the inversion process.

It is interesting that the difference in chemical shifts between the methylene protons of tropilidene is very close to that found between the somewhat similar methylene protons of 1,4,7-cyclonatriene.<sup>10,12</sup> Different chemical shifts for the methylene protons are

(11) On the other hand, the suggestion<sup>10</sup> that 1,4,7-cyclonatriene inverts *via* a planar transition state appears unlikely in view of the very large angle distortions required in that case.

(12) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963).

found in the metal carbonyl complexes<sup>13</sup> of tropilidene, but these cannot readily be compared with those of the parent compound at low temperatures.

From a consideration of the magnetic anisotropy of the double bond,<sup>14</sup> the quasi-axial proton of the methylene group should occur at higher field than the quasi-equatorial one, at least in tropilidene.

### Experimental

Tropilidene (98% min.) was obtained from the Columbia Organic Chemicals Co., and gave an n.m.r. spectrum at room temperature identical with those previously<sup>1,6</sup> published.

Spectra were measured on a Varian 60-Mc. HR60 high-resolution spectrometer. The low-temperature probe assembly was a modification of one designed at the California Institute of Technology. Details of the design were kindly furnished by Dr. P. R. Shafer. The dichlorodifluoromethane (Freon 12), m.p. -160°, b.p. -28°, was condensed directly into an n.m.r. tube cooled by Dry Ice. The tube, after addition of the sample, was loosely stoppered and transferred to the precooled probe. The decoupling experiments were carried out by the method of Freeman and Whiffen.<sup>16</sup> The audiophase detector of the Varian integrator was employed in the way suggested by L. F. Johnson.<sup>16</sup> The frequency and the amplitude of the decoupling side band was adjusted by watching the ringing of the peak being observed on the oscilloscope. With the Varian integrator, it was necessary to set the function switch on "spectrum" and the frequency response switch to 20 c.p.s. The frequency response of the "scope" position is so high that an intense beat pattern of the two modulation frequencies obscures the signal.

In the fast exchange approximation, the expression for  $k$  is<sup>8</sup>  $k = \pi\nu^2/2(\nu_2 - \nu_1)$ , where  $\nu$  is the relative chemical shift (in c.p.s.) in the absence of exchange, and  $\nu_2$  and  $\nu_1$  are full line widths at half-height in the presence and absence of exchange, respectively. The value of  $\nu_1$  was taken to be approximately equal to the line width of tetramethylsilane at the temperature where  $\nu_2$  was being measured. At -130° and -133°,  $\nu_1$  was equal to 2.1 and 2.3 c.p.s., respectively.

(13) M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 129.

(15) R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 321 (1961).

(16) Varian Technical Information Bulletin.

[CONTRIBUTION FROM YERKES RESEARCH & DEVELOPMENT LABORATORY, FILM DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC., BUFFALO, N. Y.]

## Structure of Vinyl Fluoride-Trifluoromethyl Iodide Telomers

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Products resulting from both "normal" addition (*i.e.*, to CH<sub>2</sub>) and "abnormal" addition (to CHF) have been identified among the reaction products of vinyl fluoride and trifluoromethyl iodide. Addition by CF<sub>3</sub> radical is highly specific with  $k_{\text{CH}_2}/k_{\text{CHF}} \approx 11$ , while for propagating radicals this ratio is only about 2.

With the advent of vapor phase chromatography (v.p.c.), many reactions earlier thought to be relatively simple have been shown to lead to varying amounts of isomeric and/or side products. Several examples are found in the general area of olefin addition reactions. For example, the addition of iodine monochloride to chlorotrifluoroethylene reported to give exclusively CF<sub>2</sub>ClCFClI<sup>1</sup> has been shown recently by v.p.c. techniques to yield also 20-30% of the isomeric iodide CFCl<sub>2</sub>CF<sub>2</sub>I.<sup>2</sup> Similarly, the thermal telomerizations of perfluoropropene with CF<sub>3</sub>I and with *n*-C<sub>3</sub>F<sub>7</sub>I have been found to yield products resulting from addition to both positions of the double bond<sup>2</sup> and not exclusively those in which the attacking radical becomes attached to the CF<sub>2</sub> group as originally reported.<sup>3</sup>

(1) R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

(2) M. Hauptschein, M. Braid, and A. H. Fainberg, *J. Am. Chem. Soc.*, **83**, 2495 (1961).

(3) M. Hauptschein, M. Braid, and F. E. Lewis, *ibid.*, **79**, 2549 (1957).

The free radical additions of alkyl polyhalides to halo olefins have been extensively studied. In most cases with olefins of the type R<sub>1</sub>R<sub>2</sub>C = CH<sub>2</sub> (R = halogen or hydrogen) radical addition has been found to occur exclusively at the methylene group.<sup>4</sup> Vinyl fluoride is reported to be no exception. Thus the benzoyl peroxide-initiated addition of CF<sub>2</sub>Br<sub>2</sub>,<sup>5</sup> CF<sub>2</sub>BrCFClBr,<sup>6</sup> and the photochemical-initiated addition of CF<sub>2</sub>=CFI<sup>7</sup> and CF<sub>3</sub>I<sup>8</sup> to this olefin have all been reported to yield only products of the type RCH<sub>2</sub>-CHFX. We now report that in the benzoyl peroxide-induced telomerization of vinyl fluoride (VF) with trifluoromethyl iodide CF<sub>3</sub>I radical addition is highly specific

(4) See for example, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 247-252.

(5) P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Am. Chem. Soc.*, **77**, 2783 (1955).

(6) P. Tarrant and M. R. Lilyquist, *ibid.*, **77**, 3640 (1955).

(7) J. D. Park, R. F. Seffl, and J. R. Lacher, *ibid.*, **78**, 59 (1956).

(8) R. N. Haszeldine, *J. Chem. Soc.*, 1199 (1953).