BIBLIOGRAPHY

[1] *B. Waegell & G. Ourisson*, Bull. Soc. chim. France *1961*, 2443; *G. A. Bottomley & P. R. Jefferies*, Austral. J. Chemistry *14*, 657 (1961); *J. B. Hendrickson*, J. Amer. chem. Soc. *83*, 4537 (1961); *85*, 4059 (1963); *B. Waegell, P. Pouzet & G. Ourisson*, Bull. Soc. chim. France *1963*, 1821; *R. Bucourt, ibid. 1964*, 2080; *R. Bucourt & D. Hainaut, ibid. 1965*, 1366; *C. Altona & M. Sundaralingam*, Tetrahedron *26*, 925 (1970).

[2] *C. Romers, C. Altona, H. R. Buys & E. Havinga* in 'Topics in Stereochemistry', Vol. 4, p. 39, Ed. *E. L. Eliel & N. L. Allinger*, Wiley-Interscience, New York 1969; *L. C. Goaman & D. F. Grant*, Tetrahedron *19*, 1531 (1963); *A. Baretta, C. W. Jefford & B. Waegell*, unpublished results; *A. Baretta*, thèse de 3° cycle, Marseille, June 17, 1969; *J. B. Lambert, R. E. Carhart & P. W. R. Corfield*, J. Amer. chem. Soc. *91*, 3567 (1969); *R. J. Abraham, F. H. Bottom, M. A. Cooper & J. R. Salmon*, Org. mag. Res. *1*, 51 (1969).

[3] *M. Davis & O. Hassel*, Acta chem. scand. *17*, 1181 (1963).

[4] *B. Waegell & G. Ourisson*, Bull. Soc. chim. France *1963*, 495, 496, 503.

[5] *B. Waegell & C. W. Jefford*, Bull. Soc. chim. France *1964*, 844; *J. G. Durocher & H. Favre*, Canad. J. Chemistry *42*, 260 (1964).

[6] *P. Teisseire, A. Galfré, M. Plattier & B. Corbier*, Recherches *15*, 52 (1966).

[7] *J. Fournier & B. Waegell*, Tetrahedron 1970, in the press; *J. Fournier*, thèse de 3° cycle, Marseille, January 29, 1970.

[8] *M. Karplus*, J. Amer. chem. Soc. *85*, 2870 (1963).

[9] *C. W. Jefford, J. Gunsher & B. Waegell*, Tetrahedron Letters 2333 (1965); *C. W. Jefford, D. T. Hill & J. Gunsher*, J. Amer. chem. Soc. *89*, 6881 (1967).

[10] *F. A. L. Anet*, J. Amer. chem. Soc. *84*, 1053 (1962).

[11] *C. W. Jefford, S. N. Mahajan, J. Waslyn & B. Waegell*, J. Amer. chem. Soc. *87*, 2183 (1965).

[12] *N. A. Le Bel & R. J. Maxwell*, J. Amer. chem. Soc. *91*, 2307 (1969).

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137. Fluorine NMR. Spectra of Conformationally Constrained *Gem*-Difluorocyclohexanes

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(15. V. 70)

Summary. The ^{19}F chemical shifts and geminal coupling constants have been measured for 3,3-dimethyl- (I), 3,3,5-trimethyl- (II) and 3,3,5,5-tetramethyl-1,1-difluorocyclohexane (III) and 3,3-difluorobicyclo[3.2.1]octane (IV). The *Eyring* parameters for the ring inversion were obtained for I and III. Representative values for the *Arrhenius* activation energy (*Ea*), $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ are: 11.0, 9.4, 10.4 kcal/mole and 4.5 e.u. for I, and 10.0, 8.3, 9.7 kcal/mole and 8.3 e.u. for III. It appears that the *syn*-axial methyl-fluorine interaction has a negligible effect on the inversion process. However, the *syn*-axial methyl-methyl interaction, as found in III, significantly increases the rate of inversion. Substituent effects on the ^{19}F shifts are marked. Introduction of methyl at C-3 in an equatorial position leads to shielding of the equatorial and axial fluorines (+1.8 and +1.3 ppm). Substitution in the axial C-3 position causes deshielding of the equatorial and axial fluorines (–5.9 and –4.9 ppm).

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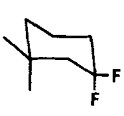
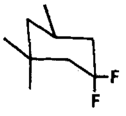
Introduction. – As part of a programme devoted to flexional effects and in particular reflex effects [1] [2] we have examined four sterically constrained derivatives of 1,1-difluorocyclohexane. By treatment of the corresponding ketones with sulfur tetrafluoride, the 3,3-dimethyl- (I), 3,3,5-trimethyl- (II) and the 3,3,5,5-tetramethyl-1,1-difluorocyclohexanes (III) and also 3,3-difluorobicyclo[3.2.1]octane (IV) were prepared. The original idea was to explore the usefulness of the *gem*-difluoro grouping as a conformational probe [3] [4] in a series of compounds where conformational effects had been evaluated by other methods. Moreover, compounds I–IV present an additional interest in that they complement a series already studied [5].

Results. – The ^{19}F spectra of compounds I–IV were determined in a solution of trichlorofluoromethane at 94.1 MHz (geminal coupling constants and chemical shifts of the frozen conformations, see Table 1). For the two conformationally mobile compounds (I and III) measurements were taken at various temperatures to yield the thermodynamic parameters for the ring inversion process (Table 1).

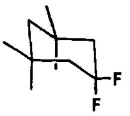
At ambient temperature the fluorine resonances of 3,3-difluorobicyclo[3.2.1]-octane (IV) showed as a pair of doublets further split by vicinal fluorine-proton coupling into multiplets. The downfield signal consisted of a doublet of quintuplets from which the coupling constants between the equatorial fluorine and the vicinal protons were found to be about 10.0 Hz, ($^3J_{\mathrm{F_{eq}H_{ax}}} \sim {}^3J_{\mathrm{F_{eq}H_{eq}}} = 10.0$ Hz), whereas the upfield signal showed as a doublet of triplets of triplets. Inspection gave the following constants for the axial fluorine: $^3J_{\mathrm{F_{ax}H_{ax}}} = 50.0$ Hz and $^3J_{\mathrm{F_{ax}H_{eq}}} = 20.0$ Hz.



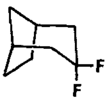
I



II



III



IV

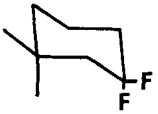
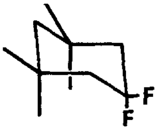
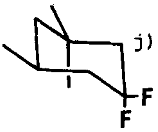
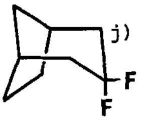
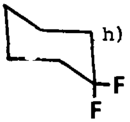
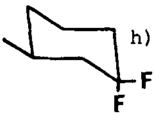
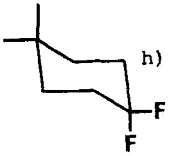
1,1-Difluoro-3,3,5-trimethylcyclohexane (II) exhibited a ^{19}F spectrum similar to that of IV. By inspection, the vicinal fluorine-proton couplings were obtained; $^3J_{\mathrm{F_{eq}H_{ax}}} \sim {}^3J_{\mathrm{F_{eq}H_{eq}}} \sim 5$–7 Hz, $^3J_{\mathrm{F_{ax}H_{ax}}} = 37.0$ Hz and $^3J_{\mathrm{F_{ax}H_{eq}}} = 13.0$ Hz.

These results are characteristic of static cyclohexane chairs, which for conformational reasons, are expected of II and IV [6]. However, both 3,3-dimethyl- and 3,3,5,5-tetramethyl-1,1-difluorocyclohexanes (I and III), on account of their conformational mobility, gave a time averaged ^{19}F signal at ambient temperature. Typically, I displayed a quintuplet ($^3J_{\mathrm{FH}} \sim 13.5$ Hz) which, as the temperature was lowered, resolved itself at the coalescence temperature into two sets of signals arising from the separate identities on the time scale of the equatorial and axial fluorines.

At 186 K, the appearance of the spectrum consisted of an *AB* quartet similar to those displayed by II and IV. The upfield multiplets were appreciably wider than those downfield because of the greater values of the vicinal coupling constants.

This temperature dependent behaviour is characteristic of signals which are due to nuclei which are exchanging between two different sites. The mean lifetime of the nucleus in one of the sites (τ) was calculated by the total line shape method [4] using the corrected line width at half height ($W^1/_2$) modification [7]. Thus a suitable set of values of τ and hence rates of conformational isomerization (k) at various

Table 1. *^{19}F Chemical Shifts, Geminal Coupling Constants, Coalescence Temperatures and Kinetic Parameters for some Constrained 1,1-Difluorocyclohexanes (I–VII)*

		Chemical Shift ^{19}F[a])		$\Delta\delta$	$\lvert {}^2J_{FF} \rvert$	Coal. Temp.	Ea	$\Delta G^{\neq}$ [d])	$\Delta H^{\neq}$	$\Delta S^{\neq}$
		δ_{eq}	δ_{ax}	$\delta_{ax}-\delta_{eq}$	Hz	K	kcal	kcal	kcal	e.u.
I		83.0	94.2	11.2[b])	240	223	11.0[e])	9.4 (218 K)	10.4[e])	+4.5[g])
III		78.9	90.6	11.7[c])	243	175	10.0[f])	8.3 (173 K)	9.7[f])	+8.3[g])
II	 j)	84.8	95.5	10.7	251	–	–	–	–	–
IV	 j)	77.1	82.5	5.4	251	–	–	–	–	–
V	 h)	87.4	103.0	15.6[i])	237	227	10.9	9.7	10.4	+3.0
VII	 h)	90.2	102.0	11.8[i])	239	–	–	–	–	–
VI	 h)	–	–	–	235	234	9.4	10.18	8.87	– 5.4

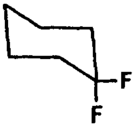
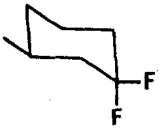
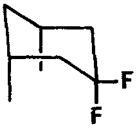
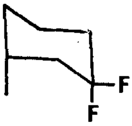
[a]) Expressed as ppm upfield from $CFCl_3$ (used as reference and solvent).
[b]) Average of 4 separate runs at 193 K.
[c]) Average of 4 runs at 167 K.
[d]) Calculated for the average temperature of the range which is shown in parentheses.
[e]) Based on 8 points between 191–248 K. Standard error in Ea and $\Delta H^{\neq}$ is ± 0.3.
[f]) Based on 7 points between 168–205 K. Standard error in Ea and $\Delta H^{\neq}$ is ± 0.5.
[g]) We feel that systematic errors are most likely in $\Delta S^{\neq}$ (ref. [20]). We suggest an error of ± 3 e.u.
[h]) Data obtained from ref. [5].
[i]) Private communication from *J. D. Roberts*.
[j]) Data obtained at 303 K.

temperatures (T) were obtained (as $k = 1/2\,\tau$). First of all $\ln k$ was plotted against $1/T$ by computer using a least squares analysis to yield Ea, the *Arrhenius* activation energy. Next, $\ln(k/T)$ was plotted against $1/T$ to yield the *Eyring* parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ [4]. The free energy of activation $\Delta G^{\ddagger}$ was calculated for the average temperature. The ^{19}F spectrum of 1,1-difluoro-3,3,5,5-tetramethyl-cyclohexane (III) was also temperature-dependent and the experimental and derived data, together with that of I, are assembled in Table 1.

Discussion. – *Chemical Shifts.* Comparison of the chemical shifts of the methyl derivatives I–III reveals that the configuration of the substitution of a methyl group at C-3 has a decisive effect on the fluorine resonance (Table 1). Equatorial substitution causes shielding of the equatorial and axial fluorines by about the same amount (+1.8 and +1.3 ppm), whereas axial placement causes net deshielding, but with a significantly greater effect on the non-contiguous equatorial fluorine (−5.9 compared to −4.9 ppm). The same trend is seen in 3,3-difluorobicyclo[3.2.1]octane where the *syn*-axially disposed ethane bridge behaves rather like two axial methyl groups.

At this point the question arises;—are these substituent shifts additive and can they therefore be used to predict ^{19}F shifts for other 1,1-difluoro-3-methyl-cyclohexanes? For the hypothetical conformationally frozen structure diaxial-1,1-difluoro-3,6-dimethyl-cyclohexane (VIII), the predicted shifts are qualitatively in the right direction as those found for the analogous structure IV (Table 2). Comparison of the predicted values for 1,1-difluorocyclohexane (V) and its 3-methyl derivative VII with

Table 2. *Predicted ^{19}F Chemical Shifts*[a] *for 1,1-Difluorocyclohexane (V) and some C-3 Methyl Derivatives* (real and imaginary)

		δ_{eq}	δ_{ax}	$\delta_{ax}-\delta_{eq}$
V		87.1	97.8	10.7
VII		88.9	99.1	10.2
VIII		75.3	88.9	13.6
IX		81.2	92.9	11.7

[a] In ppm upfield from $CFCl_3$.

those observed (Tables 1 and 2) shows that agreement is reasonably close for the equatorial fluorine, but poor for the axial fluorine.

A model for the hypothetical *syn*-axial fluorine-methyl arrangement, exemplified by IX, is found in 2,2-difluoro-*endo*-6-methyl-norbornane. In the latter compound the introduction of the methyl group has produced deshieldings of – 11.0 and – 6.6 ppm for the *exo* and *endo* fluorines [8]. Although the effect is much greater than that anticipated for IX, the direction and order of magnitude of the shifts is the same. It is difficult from the present evidence to attribute an origin to these shifts. Certainly, substitution on the cyclohexane chair produces flattening, however, proton NMR. evidence and calculation shows that the valence angle at C-1 in cyclohexanes substituted at C-3 and C-5 maintains a fairly constant value of 113° [2]. Indeed, the values of the geminal fluorine-fluorine coupling constants, despite small variations, seem to indicate that whatever substitution does, it does not change the hybridization at C-1. Undoubtedly substitution and the resultant ring deformation are responsible for these differential shielding-deshielding effects, but probably indirectly through the associated changes in the overall diamagnetic anisotropy of the molecule. Steric compressional effects have also been cited to explain similar deshieldings [9], however the odd result in the present case is that substitution *syn*-axial to fluorine brings about the greater deshielding on its equatorial twin.

Coupling Constants. The coupling constants will be discussed elsewhere in a broader context [10]. However, it will suffice to remark that in the trimethyl structure II of fixed conformation, the gauche ^{19}F-H coupling constants for equatorial fluorine (5–7 Hz) compare favourably with the value of 5.6 Hz found in the structurally related 1-fluoroadamantane [10]. Configuration clearly has an effect, since the gauche coupling for the axial fluorine, like the analogous proton coupling [11], is about twice as large ($^3J_{F_{ax}F_{eq}} = 13.0$ Hz). The trans coupling ($^3J_{F_{ax}H_{ax}} = 37$ Hz) is characteristically large. In fact the values for II closely parallel those reported for 1,1-difluorocyclohexane [12]. All the values found for IV are larger than those usually found, but they fall within the range already reported [13]. Long range coupling over four and five sigma bonds was distinctly observed in compounds I and III. The time averaged signal due to the methyl protons of the dimethyl and tetramethyl compounds showed as a triplet with a splitting of 1.0 Hz. The protons responsible for this multiplicity are most likely those on the axial methyl group, as they alone satisfy the geometric requirements for such coupling [14].

Activation Parameters for Ring Inversion. The data in Table 1 are calculated on the basis of a transmission coefficient of unity and for exchange between sites of equal populations. The model assumed for the inversion process is that in which the cyclohexane chair undergoes deformation to an unstable cyclohexene-like transition state which collapses to a metastable state, consisting of an assembly of rapid interconverting boat conformations. Departure from the metastable state then occurs with equal probability to either one of the enantiomeric sets of cyclohexene-like transition states which lead back to the chair [15].

The essential difference between compounds I and III is that the substitution of the second pair of geminal dimethyls has increased the rate of conformational inversion. Thus the tetramethyl derivative III has a coalescence temperature 48° lower than I. Moreover, the values for *Ea* and $\Delta G^{\neq}$ are plainly about a kilocalorie lower. Interestingly enough, differences of similar magnitude have been reported for the pair of unfluorinated derivatives, 1,1-dimethyl- and 1,1,3,3-tetramethylcyclohexane; $\Delta G^{\neq}$ being 10.6 and 9.6 kcal/mole respectively [16]. The lower values (by about 1.3 kcal) of $\Delta G^{\neq}$ for the fluoro analogues might be rationalized in terms of elevated ground state energies due to *syn*-axial fluorine-methyl interactions in I and III, together with the additional *syn*-axial methyl-methyl interaction in III [17]. However, the contribution to such ground state elevation by the *syn*-axial fluorine-methyl interaction is apparently negligible as revealed by comparison of the dimethyl compound I with the parent compound V. Both sets of thermodynamic parameters display no real differences. Similarly, 4,4-dimethyl-1,1-difluorocyclohexane (VI) demonstrates conformational behaviour essentially indistinguishable from that of I and V [5].

Entropy values are notoriously unreliable, not only in themselves, but as guides to inversion behaviour. The present cases are probably no exception and consequently care has to be exercised in interpretation. However an encouraging sign is that the values are unmistakeably positive for I and III. On the basis of symmetry considerations alone, positive entropies are predicted, but with I expected to have a larger value than III. For example, 3,3,5,5-tetramethyl-1,1-difluoro-cyclohexane (III) in the chair form, can convert itself into two enantiomeric sets of *three* cyclohexene-like transition states, therefore $\Delta S^{\neq} = R\ln 3 = 2.2$ e.u. (Fig. 1). On the other hand, 3,3-dimethyl-1,1-difluorocyclohexane (I), as it can attain *six* cyclohexene-like transition states has $\Delta S^{\neq} = R\ln 6 = 3.8$ e.u.

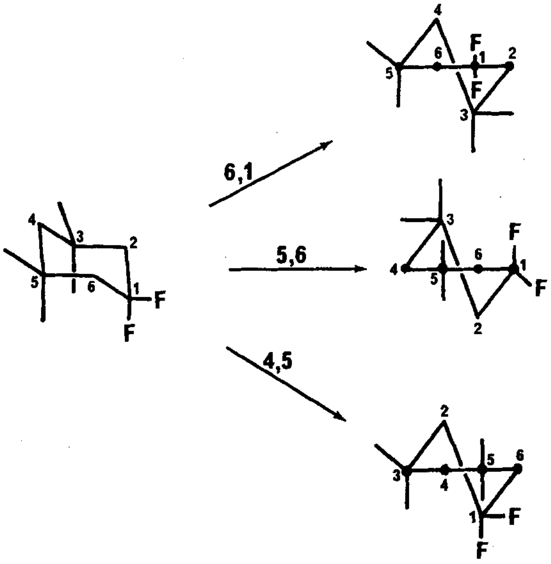


Fig. 1. *One enantiomeric set of three cyclohexene-like transition states which can be attained by the partial flattening of 3,3,5,5-tetramethyl-1,1-difluorocyclohexane (III) at the C6-C1, C5-C6, and C4-C5 pairs of atoms*

For simple rings such as cyclohexane itself [18], perfluorocyclohexene and 1,2-dichloro-octafluoro-cyclohexene [19] agreement between calculated and observed entropies has been good. In the present case the observed entropies are somewhat higher than those calculated. However it is better to attach no mechanistic importance to the difference and to be content with the positiveness of the entropy rather than with its magnitude. Nevertheless these results do suggest that the negative entropies cited for 1,1,2,2-tetrafluorocyclohexane, 4-methyl-4-ethyl-1,1-difluorocyclohexane, perfluorocyclohexane, difluorocyclohexane and its 4,4-dimethyl derivative are suspect and that they need to be re-investigated [5] [12] [20].

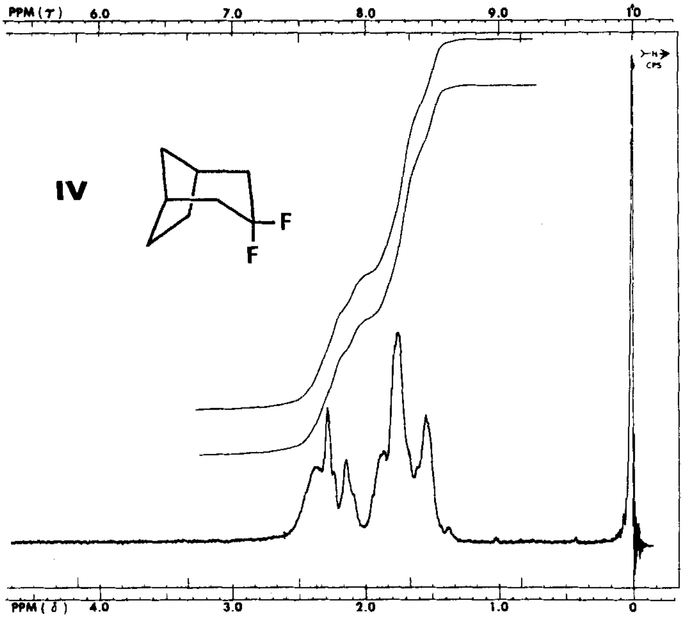


Fig. 2. *Proton NMR. spectrum of 3,3-Difluorobicyclo[3.2.1]octane (IV) in $CDCl_3$*

Experimental

Melting and boiling points are uncorrected. Microanalyses were performed by Dr. *G. Robertson*, Florham Park, New Jersey, and by *Microanalysis, Inc.*, Wilmington, Delaware.

Infrared spectra were determined on a *Beckman* Model IR-5A (NaCl optics) spectrophotometer. The spectra were taken as films on NaCl plates. Spectra were calibrated by superpositioning the band at 1603 cm^{-1} of a polystyrene film onto the spectra. Maxima (max.) are described as very strong (*vs*), strong (*s*), medium (*m*) and weak (*w*).

Indices of refraction were measured by a *Bausch and Lomb Abbé* refractometer. Melting points were determined by means of a *Thomas-Hoover* capillary melting point apparatus.

Proton magnetic resonance spectra (PMR.) were determined at 60 MHz on a model A-60A spectrometer (*Varian Associates*, Palo Alto, Calif.) between 37° and 40° using deuterochloroform as solvent (except as noted) and tetramethylsilane as internal standard, ($\delta = 0.00$ ppm).

^{19}F spectra were obtained on a model HA-100 instrument (*Varian*) converted to 94.1 MHz. Trichlorofluoromethane was employed as both solvent and internal standard. ^{19}F chemical shifts are expressed in ppm and were calibrated by the usual side band technique.

The temperature dependence of the spectra was studied using a *Varian 4343* temperature controller calibrated with methanol at 100 MHz for a given gas flow rate following the specifications of the manufacturer who claims an accuracy of ± 2.0°. After calibration the spectrometer was changed to 94.1 MHz and spectra were recorded at least four times. The calibration was then rechecked within 24 hrs at 100 MHz. The temperatures were reproducible to ± 0.5° at the temperature extremes of 193K and 313K.

The inversion rates ($k = {}^1/_2\tau$) were obtained by a modification of the total line shape method [7]. The experimental values of $W^1/_2$ were matched with linewidths calculated as a function of the chemical shifts of the axial and equatorial fluorines, the geminal ^{19}F coupling constant, an assumed[2]) transverse relaxation time ($T_2{}^{\circ}$) of 25 s and arbitrary values of τ. Calculation was carried out on an IBM 360/50 computer using the *Quabex* programme [4]. Two typical sets of corrected values of $W^1/_2$ and the corresponding values of τ so obtained are shown in Table 3.

Table 3. *Width at half-height* ($W^1/_2$) *of* ^{19}F *signals at various temperatures and associated mean lifetimes* (τ)

3,3-Dimethyl-1,1-difluorocyclohexane (I)

T	Corrected $W^1/_2$ in Hz		τ in s
243 K	39		0.000021
238	50		0.000029
233	64		0.000036
228	101		0.000060
223	160		0.000090
218	222		0.000120
199	141	138	0.0026
195	63	62	0.0048
190	28	31	0.0090
186	12	13	0.0120

For the range 218–243 K; experimental $W^1/_2$ was corrected by 40 Hz. From 186–199 K lines 2 and 3 were corrected by 24 and 66 Hz respectively.

3,3,5,5-tetramethyl-1,1-difluorocyclohexane (III)

T	Corrected $W^1/_2$ in Hz		τ in s
196	18		0.00001
192	33		0.00002
188	53		0.00003
184	84		0.00005
180	187		0.0001
160	63	48	0.005
156	24	25	0.01

The exptl. $W^1/_2$ was corrected by 34 Hz for the range 180–196 K and lines 2 and 3 were corrected by 25 and 78 Hz for the range 156–160 K.

Materials. Sulfur tetrafluoride was purchased in small bottles ('lecture' size) from the *Matheson Company, Inc.*, East Rutherford, N.J. 07073, and from *Columbia Organic Chemicals Co., Inc.*, Columbia, S.C. 29209.

Bicyclo[3.2.1]octan-3-one and 3,3,5,5-tetramethylcyclohexanone were prepared according to previously published procedures [1] [21]. 3,3,5-Trimethylcyclohexanone was prepared by the reduction of isophorone [22]. 3,3-Dimethylcyclohexanone was prepared by modification of a published procedure which is outlined below [23].

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[2]) Based on the value found for cyclohexane [18].

3,3-Dimethylcyclohexanone. Methyl iodide (30.0 g, 0.21 mole) was added dropwise to magnesium turnings (5.0 g, 0.205 mole) in anhydrous ether (60 ml) under a nitrogen atmosphere. Upon completion of the reaction, the solution was cooled to room temperature and 200 ml of tetrahydrofuran (dried over lithium aluminium hydride) was added dropwise (caution: exothermic reaction). The resulting mixture was distilled, with stirring, until the temperature of the distilland reached 50°. On cooling, cuprous chloride (1.0 g, 0.01 mole; dried overnight at 124 °C) was added with stirring, heat was generated and a black precipitate formed. 3-Methyl-2-cyclohexene-1-one (obtained from the *Aldrich Chemical Co.*, 10.0 g, 0.091 mole) was then added dropwise and the mixture was heated under reflux for 3 hours. The mixture was poured onto ice (200 g) and ammonium chloride (20 g). The aqueous phase was extracted with ether (3 × 50 ml), the ether extracts were dried over anhydrous magnesium sulfate, filtered and the solvent evaporated on a steam bath. Distillation of the residual oil, employing a foam trap, gave, after a small forerun, 8.0 g (70%) of 3,3-dimethylcyclohexanone: b.p. 64–66°/12 Torr.

General Procedure for Reactions with Sulfur tetrafluoride. All reactions were carried out in a stainless steel autoclave (*Aminco* Cat. No. 406-358 × 3, capacity 110 ml) fitted with a *Hoke* all brass needle valve, model 309. Teflon tape was employed as a sealer between the valve and autoclave. The autoclave was connected to the pre-weighed lecture bottle of sulfur tetrafluoride by means of copper tubing. Sulfur tetrafluoride was transferred from lecture bottle to autoclave in the way described by *Hasek* [24]. The reactions were carried out following the procedure of *Hasek* and *Roberts* with some modification [25]. A typical reaction is as follows.

A mixture of ketone ($\sim$ 5 g), methylene chloride (25 ml) and water (3 ml) is placed in the autoclave which is flushed with nitrogen and cooled in a bath of acetone-solid carbon dioxide. After standing for 45 min, the autoclave is evacuated to a pressure of about 1 Torr and sulfur tetrafluoride (about 40–60 g) is introduced. The autoclave is removed from the cooling bath and rocked for 24 h at about 20°. (All the above operations are carried out in a well-ventilated hood.) After reaction, the autoclave is vented through a train comprised of two one-litre suction flasks each equipped with magnetic stirrers and rubber stoppers and filled with 700 ml of nearly saturated potassium hydroxide solution. The contents of the autoclave are poured into water (100 ml). The resultant mixture is neutralized to litmus with saturated aqueous K_2CO_3 solution. After separation of the layers the aqueous phase is extracted with ether (2 × 50 ml), the combined organic layers are dried ($MgSO_4$), filtered, and solvent is removed by distillation on a steam bath. The residue is then either distilled (using a foam trap), or sublimed.

1,1-Difluoro-3,3-dimethyl-cyclohexane (*I*). The corresponding ketone (5.0 g, 0.04 mole) and sulfur tetrafluoride (67 g, 0.62), gave an orange coloured oil, distillation of which gave 1.31 g (24%) of a colourless liquid: b.p. 50°/39 Torr, n_d^{25} = 1.4010. IR. (neat); max.: 1459 (*m*), 1359 (*s*), 1324 (*m*), 1269 (*m*), 1249 (*s*), 1189 (*m*), 1169 (*m*), 1084 (*vs*), 1024 (*m*), 979 (*m*) and 946 (*s*) cm^{-1}. PMR.: Characteristic resonances: at 0.98 ppm (triplet, 6H, $^4J_{HH} \sim {}^5J_{HF} = 1.0$ Hz, methyls), and at 1.69 ppm (triplet, $^3J_{HF} = 15.0$ Hz, CH_2–CF_2).

$C_8H_{14}F_2$ Calc. C 64.83 H 9.52 F 25.64% Found C 64.93 H 9.44 F 25.75%

1,1-Difluoro-3,3,5-trimethyl-cyclohexane (*II*). The ketone (5.5 g, 0.039 mole) and sulfur tetrafluoride (65 g, 0.60 mole) gave a dark oil. Distillation yielded (after a small forerun) 2.41 g (38%) of a colourless liquid: b.p. 60–61°/36 Torr, n_d^{25} = 1.4042. IR. (neat); max.: 1460 (*s*), 1431 (*w*), 1393 (*w*), 1370 (*s*), 1359 (*s*), 1321 (*m*), 1302 (*w*), 1290 (*s*), 1250 (*s*), 1206 (*s*), 1190 (*w*), 1153 (*vs*), 1104 (*vs*), 1067 (*w*), 1045 (*vs*), 1024 (*m*), 990 (*vs*), 959 (*m*), 934 (*m*) and 923 (*w*) cm^{-1}. PMR. Resonances: at 1.00 ppm (singlet, 9H, methyls), diffuse signals between 1.0 and 2.0 ppm (methylene protons). PMR. in benzene: doublet at 0.88 ppm (3H, $^5J_{HF}$ or $^4J_{HH} = 1.5$ Hz, axial methyl); singlet at 0.73 ppm (C-3 equatorial methyl); doublet at 0.67 ppm ($^3J_{HH} = 6.0$ Hz, C-5 equatorial methyl).

$C_9H_{15}F_2$ Calc. C 66.63 H 9.94 F 23.42% Found C 66.55 H 9.72 F 23.53%

1,1-Difluoro-3,3,5,5-tetramethyl-cyclohexane (*III*). The crude oil obtained from reaction of the ketone (5.0 g, 0.032 mole) and sulfur tetrafluoride (57 g, 0.53 mole) distilled to give 0.66 g (12%) of colourless liquid: b.p. 56–58°/15 Torr, n_d^{25} = 1.4155. IR. (neat); max.: 1460, 1357 (*s*), 1315 (*m*), 1255 (*m*), 1217 (*m*), 1205 (*m*), 1080 (*vs*), 1048 (*s*), 1003 (*m*), 987 (*s*), 932 (*m*), 877 (*m*) and 812 (*m*) cm^{-1}. NMR.: triplet at 1.03 ppm (12 H, $^4J_{HH} \sim {}^5J_{HF} = 1.0$ Hz methyls); singlet at

1.28 ppm (2H, C-4 methylene) and a triplet at 1.70 ppm (4H, $^3J_{HF}$ = 15 Hz, C-2 and C-6 methylenes). $C_{10}H_{18}F_2$ Calc. C 68.15 H 10.29% Found C 67.89 H 10.36%

3,3-Difluorobicyclo[3.2.1]octane (IV). This compound was not as readily obtainable as were the previous three *gem*-difluorides. The reaction of bicyclo[3.2.1]octan-3-one (4.7 g, 0.038 mole) and sulfur tetrafluoride (41 g, 0.38 mole) afforded a yellow solid (8.5 g). Thin layer chromatography (silica gel G, pentane, H_2SO_4) indicated the presence of at least four substances. Trituration with ether and cooling yielded a yellow insoluble precipitate (presumed to be sulfur) which was filtered off. Lithium aluminium hydride, (2.0 g, 0.053 mole) was added to the mixture when a gas evolved. The mixture was stirred for 14 hours and then treated with saturated aqueous sodium sulfate. Drying ($MgSO_4$) and removal of solvent left a white solid (7.0 g) which sublimed on a steam bath at atmospheric pressure to give 4.5 g of product. This product was analysed on a *Wilkens* Aerograph Model A-90-P3 gas chromatograph [stainless steel column (1.5 m long and 6.5 mm calibre) packed with carbowax (15%) on Chrom P; He flow rate: 30 ml/min; column temperature: 70°; injector: 222°; detector: 262°; collector: 233°]. Five major and three minor peaks were observed. The desired difluoro compound (retention time: 7.7 min) comprised 17% of this mixture (15% yield based on ketone) as determined by weighing the various peak areas. Preparative gas liquid chromatography yielded IV as white, extremely volatile, wax. It proved impossible to obtain an acceptable elemental analysis; however, its identity was secured by its spectral properties. IR. (neat solid cast on a salt plate); max.: 1458 (*m*), 1437 (*w*), 1374 (*s*), 1323 (*m*), 1279 (*m*), 1247 (*m*), 1217 (*m*), 1178 (*m*), 1124 (*vs*), 1088 (*vs*), 1024 (*s*), 996 (*m*), 974 (*s*), and 910 (*s*) cm^{-1}. The PMR. spectrum (Fig. 2) and the ^{19}F spectrum characterized the structure.

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BIBLIOGRAPHY

[1] *C. Sandris & G. Ourisson*, Bull. Soc. chim. France *1958*, 1524; *B. Waegell & G. Ourisson, ibid. 1963*, 496, 503; *B. Waegell & C. W. Jefford, ibid. 1964*, 844; *B. Waegell, ibid. 1964*, 855.

[2] *C. W. Jefford, A. Baretta, J. Fournier & B. Waegell*, Helv. *53*, 1180 (1970).

[3] *J. D. Roberts*, Chemistry Brit. *1966*, 524.

[4] *G. Binsch* in 'Topics in Stereochemistry', Vol. 3, Chap. 2, Ed. *E. L. Eliel & N. L. Allinger*, Interscience, New York 1968.

[5] *S. L. Spassov, D. L. Griffiths, E. S. Glazer, K. Nagarajan & J. D. Roberts*, J. Amer. chem. Soc. *89*, 88 (1967).

[6] *C. W. Jefford, D. T. Hill & J. Gunsher*, J. Amer. chem. Soc. *89*, 6881 (1967); *A. Baretta, J. P. Zahra, B. Waegell & C. W. Jefford*, Tetrahedron *26*, 15 (1970).

[7] *K. C. Ramey, D. J. Louick, P. W. Whitehurst, W. B. Wise, S. Mukherjee & R. M. Moriarty*, to be submitted.

[8] *J. B. Dence & J. D. Roberts*, J. Amer. chem. Soc. *91*, 1542 (1969).

[9] *B. V. Cheney*, J. Amer. chem. Soc. *90*, 5386 (1968); *L. M. Jackman*, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry', 2nd Impression, Chap. 7, Pergamon Press, 1962; *A. Segre & J. I. Musher*, J. Amer. chem. Soc. *89*, 706 (1967).

[10] *C. W. Jefford, D. T. Hill, K. C. Ramey, R. Gleiter & P. v. R. Schleyer*, in preparation.

[11] *D. H. Williams & N. S. Bhacca*, J. Amer. chem. Soc. *86*, 2742 (1964).

[12] *J. Jonás, A. Allerhand & H. S. Gutowsky*, J. chem. Physics *42*, 3396 (1965).

[13] *D. W. Mathieson*, 'Nuclear Magnetic Resonance for Organic Chemists', p. 152, Academic Press, London 1967.

[14] *A. Rassat, C. W. Jefford, J. M. Lehn & B. Waegell*, Tetrahedron Letters 243 (1964); *C. W. Jefford, D. T. Hill, L. Ghosez, S. Toppet & K. C. Ramey*, J. Amer. chem. Soc. *91*, 1532 (1969).

[15] *F. A. Bovey, E. W. Anderson, F. P. Hood, R. L. Kornegay &* J. chem. Physics *40*, 3099 (1964).

[16] *H. Friebolin, H. G. Schmid, S. Kabuss & W. Faisst*, Org. mag. Res. *1*, 147 (1969).

[17] *N. L. Allinger & M. A. Miller*, J. Amer. chem. Soc. *83*, 2145 (1961).

[18] *F. A. L. Anet & A. J. R. Bourn*, J. Amer. chem. Soc. *89*, 760 (1967).

[19] *J. E. Anderson & J. D. Roberts*, J. Amer. chem. Soc. *92*, 97 (1970).

[20] *A. Allerhand, H. S. Gutowsky, J. Jonás & R. Meinzer,* J. Amer. chem. Soc. *88,* 3185 (1966); *G. V. D. Tiers,* Proc. chem. Soc. *1960,* 389; *H. S. Gutowsky & F. M. Chen,* J. physic. Chemistry *69,* 3216 (1965).
[21] *G. Chiurdoglu & A. Maquestiau,* Bull. Soc. chim. belg. *63,* 357 (1954).
[22] *M. Fétizon & J. Goré,* Tetrahedron Letters *1966,* 471.
[23] *M. Fétizon, J. Goré, P. Laszlo & B. Waegell,* J. Org. Chemistry *31,* 4147 (1966).
[24] *W. R. Hasek,* 'Org. Syntheses', Vol. 41, p. 104, J. Wiley & Sons, Inc., New York 1961.
[25] *W. R. Hasek, W. C. Smith & V. A. Engleharдt,* J. Amer. chem. Soc. *83,* 543 (1961); *G. A. Yousif & J. D. Roberts, ibid. 90,* 6428 (1968).

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138. Reaction of 2-Methylnorborn-2-ene with N-Bromosuccinimide [1]

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(15. V. 70)

Summary. The reaction of 2-methylnorborn-2-ene with N-bromosuccinimide produced *exo*-3-bromo-2-methylenenorbornane and 2-methyl-3-bromonortricyclene in a 3:1 ratio. No 2-bromomethyl-norborn-2-ene was found. Most of the unreacted olefin was found to be isomerized to 2-methylenenorbornane.

The hydrolysis of 2-methyl-3-bromo-nortricyclene with silver acetate in a 50% mixture of acetone and water afforded the corresponding alcohol and acetate. *Exo*-3-bromo-2-methylene-norbornane on similar treatment gave the *exo*-3-hydroxy-2-methylene-norbornane and 2-hydroxymethyl-norbornane and 2-hydroxymethyl-norborn-2-ene and their corresponding acetates in a 3:2 ratio.

An ionic rather than a radical mechanism is proposed for the bromination reaction. In the solvolysis reactions of the resulting bromides the nature of the ionic intermediates is discussed.

Introduction. – The behaviour of N-bromosuccinimide (NBS) as a brominating agent towards bridged bicyclic olefins is capricious. When the allylic C-H bond lies in the nodal plane of the double bond, reactivity is usually directed towards the homoallylic position or the double bond itself [2]. When an allylic position is available, bromination is thought to proceed *via* allylic radicals which subsequently give the corresponding endocyclic allylic bromides [3].

As 2-methylnorborn-2-ene contains both these structural elements, its reactivity is of crucial interest. Furthermore, the properties of the bromides obtained relate to the problem of the nature of bridged cations.

Results. – 2-Methylnorborn-2-ene (I) and N-bromosuccinimide were allowed to react in boiling carbontetrachloride containing benzoyl peroxide. The resulting products were identified as *exo*-3-bromo-2-methylene-norbornane (II), 3-bromo-2-methyl-nortricyclene (III) and 2-methylenenorbornane (IV). The structures of II and III were assigned from a consideration of their NMR. and IR. spectra. The *exo* assignment of the bromine at C-3 in II was made on the basis of the magnitude of the coupling constant exhibited for C-3-H, ($^3J \sim 1.8$ Hz); a larger value (ca. 4 Hz) would

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