9.93 m, 10.07 m, 10.11 i, 11.84 m, 12.29 m, 12.29 m, 12.79 i, 13.75 i, and 14.29 μ m.

Anal. Calcd for $C_{14}H_{28}N_2O_3S$: C, 55.23; H, 9.27; N, 9.20; S, 10.53; amine neut equiv, 152. Found: C, 55.49; H, 9.29; N, 9.23; S, 10.56; amine neut equiv, 152.

In the absence of pyridine, ill-defined mixtures were obtained, probably indicating ring cleavage.

Registry No.—**3a**, 13156-04-2; **3b**, 13156-01-9; **3c**, 13156-03-1; **3d**, 13156-06-4; **3e**, 13156-07-5; 1-*t*-butyl-2-methyl-3-azitidinol, 13619-15-3; 1-*t*-butyl-3-azetidinyl acetate, 13619-16-4; 1-(1,1,3,3-tetramethylbutyl)-3-azetidinyl acetate, 13619-17-5; 1-*n*-octylamino-3-chloro-2-propanol, 13619-18-6; 1-*t*-butylamino-3-chloro-2-propanol, 13156-02-0; 3-chloro-1-*t*-octylamino-2-propanol, 13156-05-3; 1-*t*-butylamino-3-chloro-2-propyl acetate, 13619-21-1; 3-chloro-1-(1,1,3,3-tetramethylbutylamino)-2-propyl acetate, 13619-22-2; bis(1-*t*-butyl-3-azetidinyl) sulfite, 13619-23-3.

Nuclear Magnetic Resonance Spectra of Bicyclo[*n*.1.0]alkane Derivatives[1]

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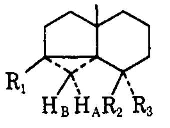
Chemical shifts and coupling constants for geminal and vicinal protons of a cyclopropane ring have been determined for 35 bicyclo[*n*.1.0]alkane derivatives. It has been found that for systems having the general structure XI (R = H or alkyl; R′ = alkyl; *n* = 3) the geminal proton with the *endo* configuration resonates at a lower field than the *exo* proton. In various bicyclo[4.1.0]heptan-2-ols, similar results are found. Possible reasons for this inversion of the expected chemical shifts, such as diamagnetic anisotropy and van der Waals interacetions, are discussed.

The utility of nmr spectroscopy as a method for identifying cyclopropane rings has been firmly established. Many studies have been made with cyclopropyl compounds having electronegative substituents on the ring,[3-9] but few studies have been made on compounds where the cyclopropane ring has no such grouping.[10-13]

In the present study, the nmr spectra of three simple alkylcyclopropanes and 35 compounds containing a fused cyclopropane ring were analyzed. The chemical shifts and coupling constants obtained are summarized in Table I. The *endo* proton is designated as H_A and the *exo* proton as H_B. The *endo* proton is always *trans* to H_X, the bridgehead proton, for all compounds (structures I–X) in Table I.

The reported parameters were derived from the experimental line positions with the aid of a computer program utilizing the equations of Bernstein, Pople, and Schneider[14] for the ABX systems and the equations of Cohen and Sheppard[15] for the ABX_2 systems. The proton, H_X, on the bridgehead of the cyclopropane ring fusion (structure XI, p 2978) could not be assigned in the most cases because of overlapping absorption by the methylene protons of the rest of the molecule. Not being able to assign H_X did not prevent the analysis of the AB portion of the spectra in the ABX and ABX_2 cases.



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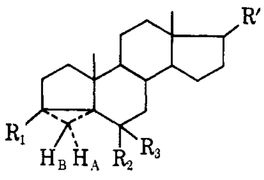

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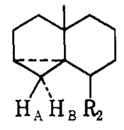

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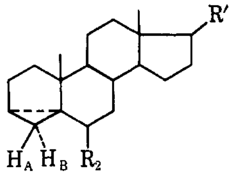

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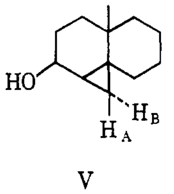

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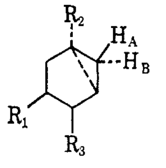

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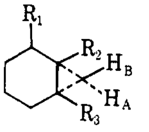

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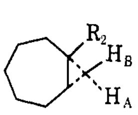

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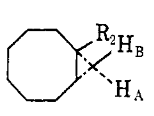

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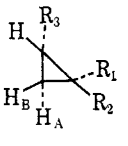

X

In the spectra of compounds 32–36, the H_X absorptions overlap with those from H_A and H_B. From these spectra an estimate of the coupling constants and chemical shifts was made. From these parameters a theoretical spectrum was calculated using a modified Reilly–Swalen program.[16] The parameters were adjusted until a best fit was obtained between theoretical and observed spectra. The average deviation of the final calculated spectrum from the observed spectrum in all compounds analyzed was never greater than 0.4 cps and was usually less than 0.1 cps.

The assignment of the methylene protons of the cyclopropane ring was made on the basis of the *cis*

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[1] This work was supported in part by Public Health Service Grant No. AM-709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

[2] National Institute of Health Predoctoral Fellow, 1963–1965.

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TABLE I

NMR OF BICYCLO[n.1.0] DERIVATIVES

Compound no.	Registry no.	Structure				Chemical shift, τ			Coupling constant, cps		
			R_1	R_2	R_3	H_A	H_B	H_X	J_{AX}	J_{BX}	J_{AB}
1	13388-42-6	I	H	OMe	H	9.71	10.22		2.70	7.40	−4.27
2	13388-43-7	I	Me	OMe	H	9.47	10.46				−4.50
3	13388-44-8	I	H	OMe	Me	9.83	10.02		3.10	8.00	−5.12
4	13388-45-9	I	H	OH	H	9.62	10.08		2.58	6.92	−3.95
5	13441-21-9	I	H	OH	H	9.58	D[m]		2.6		
6	13388-46-0	I	H	Δ^6		9.54	9.82		2.69	7.41	−4.57
7	13388-47-1	I	H	═O		9.28	9.64		3.68	8.72	−3.97
8		II	H	OEt	H	9.73	10.23		2.8	8.00	−4.5
9		II	Me	OEt	H	9.55	10.47				−4.5[a]
10		II	H	Δ^6		9.52	9.87		2.8	7.5	−4.5
11		II	Me	Δ^6		9.41	10.08				−5.0[a]
12		II	Me	H	H	9.56	10.35				−4.45[a]
13	13388-48-2	III		OMe		9.42	9.65		3.34	8.36	−4.77
14	13388-49-3	III		OH		9.51	9.71		4.13	8.57	−5.27
15	13421-35-7	III		═O		9.40	9.10		3.0		−4.5
16		IV		β-OMe		9.42	9.62		3.32	8.18	−4.82
17		IV		β-OH		9.56	9.78		3.3	7.8	−4.4[b]
18		IV		β-OH		D[m]	9.77			8.5	...[b]
19		IV		α-OH		9.80	9.5		3.0		−5.0
20		IV		Δ^6		9.57	9.87		2.8	7.5	−4.5
21	13421-36-8	V				9.35	9.98		4.35	9.02	−4.45
22	694-44-0	VI	OH-*trans*	H		10.02	9.70		4.5	7.0	−4.5[c]
23	694-43-9	VI	OH-*cis*	H		9.57	9.50		4.0	8.0	−4.0[c]
24	13388-51-7	VI	CO_2H	H		10.00	9.68		4.1	8.0	−5.5[d]
25	13388-52-8	VI	CO_2H	H	Δ^2	9.92	8.91		4.5	7.6	−3.5[e]
26	13388-53-9	VI	Δ^2	CO_2Et		9.53	8.34		4.5	8.3	−3.1[e]
27	4625-24-5	VI	H	Me		9.70[i]	9.85		3.62	7.98	−4.82
28	13388-55-1	VII	OH	Me	Me	9.34	10.06				−4.65
29	13388-56-2	VII	OH	Me	H	9.58	9.71		4.17	9.03	−4.55
30	13388-57-3	VII	OH	H	Me	9.45	9.75		4.46	9.34	−4.90
31	7432-49-7	VII	OH	H	H	9.67[k]	9.49		4.4	8.6	−4.6
32	286-08-8	VII	H	H	H	10.04[l]	9.37		4.5	9.3	−4.5
33		VII	H	Me	H	9.95[j]	9.82		5.58	8.52	−3.97
33		VII	H	Me	H	9.81[i,j]	9.66	9.33	5.33	9.02	−4.20
34	13388-61-9	VIII		Me		9.84[i,j]	9.54	9.49	3.41	8.09	−3.27
35	13388-60-8	IX		Me		10.10[i,j]	9.66	9.59	2.37	7.53	−3.22
36	4127-45-1	X	Me	Me	Me	10.17[i,j]	9.59	9.55	3.76	8.0	−4.6
37	1630-94-0	X	Me	Me	H	9.80	9.80		5.4	9.2	−4.5[f]
38	75-19-4	X	H	H	H	9.78[g]	9.78		6.2	9.2	−5.6[h]

[a] G. Just and V. DiTullio, *Can. J. Chem.*, **52,** 2153 (1964). [b] C. C. Leznoff and G. Just, *ibid.*, **42,** 2801 (1964). [c] S. Winstein and E. C. Friedrich, personal communication. [d] Reference 11. [e] Reference 12. [f] Reference 10. [g] Reference 4. [h] T. Schaefer, F. Hruska, and G. Kotowycz, *Can. J. Chem.*, **43,** 75 (1965). [i] Benzene was used as solvent. All other spectra were run in CCl_4. [j] ABC analysis was used. [k] ABX_2 analysis was used. [l] ABC_2 analysis was used. [m] D means deuterium has replaced H_B.

coupling constant, J_{BX}, being larger than the *trans* coupling constant, J_{AX}. The evidence in the literature indicates that this is a valid criterion for assignment, there being no exception to date to this generality in the spectra of cyclopropyl derivatives.[17] Vicinal couplings in Table I range from 6.9 to 9.3 cps when the protons are *cis* oriented and from 2.6 to 5.6 cps when *trans* oriented. Using the Karplus equations[18] and the calculated dihedral angles of 0° and 131–134°,[10] one obtains the predicted values of 8.2 and 3.8–4.3 cps for the *cis* and *trans* couplings, respectively. Thus, the observed values of vicinal couplings agree with those predicted by theory and also with those previously reported[10–13] for cyclopropyl derivatives with no electronegative substituents directly attached to the three-membered ring.

The geminal couplings are assumed to be negative from the results of previous workers.[9,10,19,20] The average of −4.51 cps from Table I is in agreement with values for similar compounds.[11,21]

Chemical Shifts.—In a previous study of the nmr spectra of substituted cyclopropanes,[22] it was found that for many substituents (excluding carboxyl) the cyclopropyl proton *cis* to the substituent was upfield from the proton *trans* to the substituent. A similar relationship would be expected with alkyl groups. In a compound with the cyclopropane ring fused to another ring, the methylene groups of the larger ring which are attached to the cyclopropane ring function as the substituents. For example, in bicyclo[4.1.0]heptan-7-ol

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[17] One apparent exception has been reported by G. L. Closs, *J. Am. Chem. Soc.*, **82,** 5723 (1960). This report has been corrected: G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84,** 4985 (1962).

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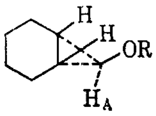
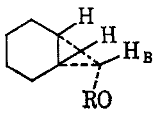
[21] See Table I, footnote *h*.

[22] K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86,** 762 (1964).



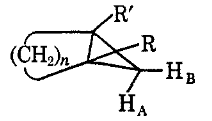
τ 7.25 ppm
J = 3 cps
39



τ 7.10 ppm
J = 6.5 cps
40

derivatives **39** and **40**,[5] the *endo* proton H_A in **39** is *cis* to two substituents and appears at 0.15 ppm higher field than the *exo* proton which is *trans* to the substituents.

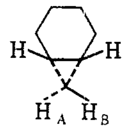
Examination of the data in Table I shows that the chemical shifts for the *endo* (H_A) and the *exo* (H_B) protons fall into two patterns. In compounds **15**, **19**, **22–26**, **31–36** the *endo* proton resonates at a higher field than the *exo*, while in the remaining compounds in Table I, the *endo* proton appears at a lower field than the *exo*. To gain some insight into the factors which control the chemical-shift differences, various structural features of the general structure XI have been examined.



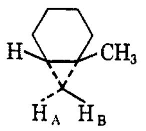
XI

In Table I, all of the compounds in which the *endo* protons (H_A) of the methylene group of the cyclopropane ring resonate at a lower field than the *exo* protons (H_B) have either a bicyclo[3.1.0]pentane nucleus and one ring juncture substituent (XI, n = 3; R′ = alkyl; R = H) or a bicyclo[4.1.0]hexane nucleus with one ring juncture substituent and hydroxyl group on the six-membered ring (XI, n = 4; R′ = alkyl). Thus, the deshielding of the *endo* proton is related both to the ring size and the number of substituents on the ring system.

Considering this latter problem first, with the simple hydrocarbons **32** and **33**, it is found, as expected, that the addition of a methyl group brings about a large upfield shift for the H_B proton which is *cis* to the new methyl group and a small downfield shift for the *trans* H_A proton; thus, the difference in chemical shift between these two protons is greatly diminished, but the *endo* proton still resonates at higher field. The addition of a second alkyl substituent would be expected to bring about the inversion. This change in chemical shift must be due solely to the diamagnetic anisotropic shielding of a proton by a C–C bond, since no change in conformations of the ring system would be expected.

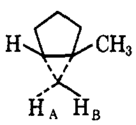


τ 10.04 9.37
32

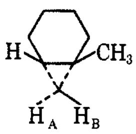


τ 9.95 9.82
33

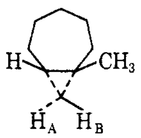
Second, the value of the difference in chemical shifts appears to be related to the size of the ring to which the cyclopropane ring is fused, as is seen by comparison of compounds **27** and **33–35**. As the major ring size decreases from eight to six, the chemical-shift difference between the *exo* proton and the *endo* proton diminishes, but the latter proton still resonates at a higher field. However, when the ring is five-membered and the compound has one substituent at the bridgehead, the *endo* proton resonates at a lower field than the *exo* proton. One possible reason for this ring-size effect can be the different spacial relationships of the various C–C bonds in the molecules which induce diamagnetic anistropic shielding of the cyclopropane protons. An approximation of the magnitude of such an effect was obtained by calculation of the shielding effect for all C–C bonds other than those of the three-membered ring using the McConnell equation.[23] The angles and distances needed in the equation were measured from Dreiding models of the ring system. The conformation chosen was that which had a minimum of H–H eclipsing or which, by other studies, had been suggested to be preferred. These conformations are shown in XII–XIII.[24] From the calculated values it is seen that, although the effect works in the desired direction, the inversion when the ring size reaches five would not be expected, and an additional interaction must be present in the smaller ring to bring about further deshielding of the *endo* proton.



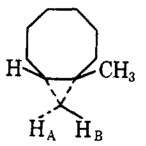
τ 9.70 9.85
27



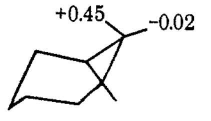
9.81 9.66
33



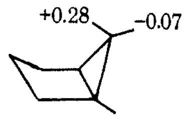
9.84 9.54
34



10.10 9.66
35

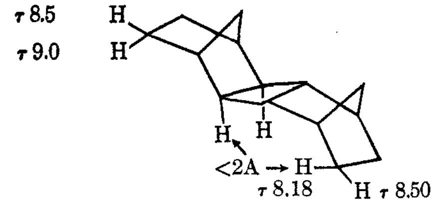


XII



XIII

An additional effect can be van der Waals interaction; *i.e.*, the close approach of a nonbonded group may cause downfield shifts of interacting protons.[25–27] For example, in norbornane the *endo* proton absorbs at 0.54 ppm higher field than the *exo*, but in norbornene dimer XV, where the *endo* proton–cyclobutane proton distance is less than 2 A, the *endo* proton appears at lower field than the *exo* by 0.32 ppm making a total shift of 0.86 ppm. The magnitude of this deshielding



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[23] H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957). The value for ΔX used in the calculations was -5.5×10^{-6} A³.

[24] If other conformations are used, the exact numerical value of the shielding changes but in all cases the *endo* proton is shielded and the *exo* proton is deshielded.

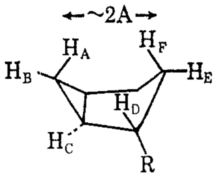
[25] T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41**, 2969 (1963).

[26] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2569 (1965).

[27] M. A. Batfiste and M. E. Brennen, *Tetrahedron Letters*, 5857 (1966).

effect should vary with the distance separating the atoms and be related to the conformation which the molecule adopts. Thus, the importance of this deshielding could be related to ring size.

In the bicyclo[3.1.0]hexane series, where the *endo* proton absorbs at lower field, it has been suggested[28] that the ring system is slightly boat shaped, and in such a conformation the H_A–H_F separation is minimal. A

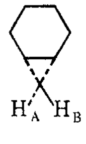


XVI

similar conformation has been postulated for the bicyclo[3.1.0]hexan-3-ols[29] and for the thujane derivatives.[13] It has been estimated from the coupling constants that the H_C–C–C–H_D dihedral angle is 80°, and the H_D–C–C–H_F angle is 20°.[28] Using these angles to establish the conformation of a Dreiding model, the measured distance between H_A and H_F is 2 A (XV). In the bicyclo[4.1.0]heptanes derivatives the closest approach of the *endo* proton to a proton across the ring is 2.25 A. Thus, the extra deshielding seen in the five-membered ring series discussed above could be due to this van der Waals interaction. The deshielding reduces the *endo–exo* chemical-shift difference and, when combined with the usual substituents effect of an alkyl group, is sufficient to cause the inversion when $n = 3$.

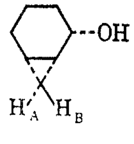
The finding that the chemical shift of the *endo* proton is at lower field in the simple bicyclo[3.1.0]hexanes is also seen in the more complex fused-ring systems (in types) I–IV. It is interesting to note that the inversion is not dependent upon the relative configuration of the cyclopropane ring and the angular methyl group.

Finally, the effect of a substituent not on the cyclopropane ring is worthy of evaluation. Examination of the results in the table shows that a hydroxyl group on a carbon α to the cyclopropane ring can exert an effect on the chemical shifts of the methylene protons. The magnitude and sign of the effect varies with the steric relationship of the cyclopropyl hydrogen atoms and the hydroxyl group. Four examples, **32**, **31**, **17**, and **19**, are shown below and in these cases the cyclopropyl proton *cis* to the hydroxyl group is strongly deshielded.



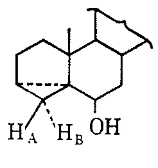
τ 10.04 9.37

32



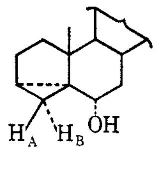
9.67 9.49

31



9.56 9.78

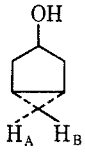
17



9.80 9.50

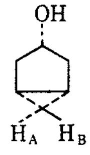
19

The only examples of a hydroxyl group β to a cyclopropane ring are found in the bicyclo[3.1.0]hexane system; four typical examples are shown below. When the hydroxyl group is *cis* to the cyclopropane ring, both methylene protons on the cyclopropane ring resonate at lower field than when the hydroxyl group is *trans* to the ring. At present, in these hydroxyl group effects it is not known whether the substituent effect is due to transannular shielding or is due to changes in the conformation of the ring system.



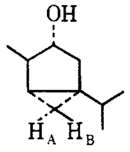
10.02 9.70

22

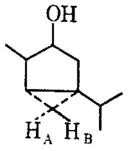


τ 9.57 9.50

23



9.20 9.62



9.90 9.70

Long-Range Coupling.—Long-range coupling across four bonds between the *exo* proton of the cyclopropane ring and the proton on C-2 which is *trans* to the cyclopropane ring (labeled R in XVI) has been reported in various derivatives of thujane (1-isopropyl-4-methylbicyclo[3.1.0]hexane)[13] and in bicyclo[3.1.0]hexan-3-one and -3-ol.[19] It might be expected therefore that 1-methylbicyclo[3.1.0]hexane (**27**) would also show long-range coupling for the *exo* proton. The spectrum does not show any resolvable fine splitting, however, and the width at half-height $W_{1/2}$ of the *exo* proton is no larger than that of the *endo* proton (1.8 cps). That the line width of the two cyclopropyl protons is equal may also be an indication that both protons are coupling long range, the *exo* with the 2-*trans* proton, and the *endo* with the bridgehead methyl group. No resolvable long-range coupling was observed in the bicyclo[4.1.0]heptanes.

The decalins of type I and steroids of type II do seem to show some broadening of the *exo* cyclopropyl proton. The line width of the high-field doublet of doublets has the value $W_{1/2} = 1.3$ cps. Thus, the *exo* proton is probably coupling with the 2β proton since H_β–C_4–C_3–C_2–H_β forms a "W", apparently the necessary geometrical requirement for the long-range coupling.[30] The *endo* proton would form a "W" with the 6β hydrogen, were there one, but this particular hydrogen is absent owing to the 6β-methoxyl group in **1**. The *endo* proton, therefore, does not become broadened. Since the chemical-shift difference between the 2β and 3β hydrogens is greater than the related coupling constants of these protons, the broadening of the *exo* proton band cannot be due to second-order (or virtual) coupling.[31]

Conclusion

Bicyclo[3.1.0]hexane and, in some cases, bicyclo[4.1.0]heptane derivatives having an alkyl group on the bridgehead exhibit the *exo* proton at higher field than the *endo* proton in their nmr spectra. This observation is explained by the substituent effect of the alkyl group on the bridgehead in combination with a van der Waals deshielding of the *endo* proton by transannular interaction.

Experimental Section

Nmr Procedure.—The spectra were taken in either carbon tetrachloride or chloroform using a Varian A-60 spectrometer with tetramethylsilane as an internal standard. In a few cases where greater peak separation was required the spectra were also taken on a Varian HA-100 spectrometer. The spectra were al-

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[28] P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

[29] E. C. Friedrich, personal communication.

[30] J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

[31] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

ways determined first by scanning the region 9.5–10.0 without TMS; then TMS was added, the peaks were realigned, and the TMS peak was recorded. A calibration sample was run each day that a spectrum was determined.

Source of Compounds.—Except where references to other workers appear, all materials employed were prepared in this laboratory and the syntheses of these materials will appear in a separate publication.

Halomethyl Metal Compounds. XIII. The Preparation of *gem*-Difluorocyclopropanes by Iodide Ion Induced CF_2 Transfer from Trimethyl(trifluoromethyl)tin[1,2]

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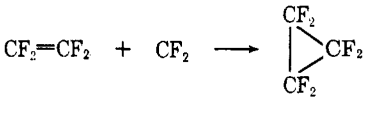
The action of sodium iodide on trimethyl(trifluoromethyl)tin in DME in the presence of an olefin gives *gem*-difluorocyclopropanes in yields ranging from moderate to excellent according to the equation $Me_3SnCF_3 + NaI + \text{olefin} \rightarrow Me_3SnI + NaF +$ *gem*-difluorocyclopropane. It is suggested that the mechanism of this reaction involves nucleophilic attack by iodide ion on tin to displace the trifluoromethyl anion, which then loses fluoride ion to form difluorocarbene. The latter subsequently reacts with the olefin to give the *gem*-difluorocyclopropane. The formation of fluoroform when the $Me_3SnCF_3 + NaI$ reaction was carried out in acetone-DME provides indirect evidence in favor of such a mechanism. Nineteen new *gem*-difluorocyclopropanes were prepared by this route, including difluorocyclopropyl derivatives of silicon, germanium, and tin. Noteworthy is the observation ahat CF_2 does not insert into C–H bonds, even into those which are very reactive toward CCl_2. The pyrolysis of Me_3SnCF_3 in the presence of benzoic acid gave difluoromethyl benzoate in 50% yield.

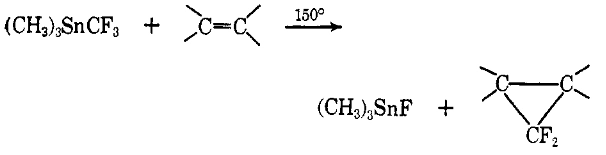
In 1960 Stone and co-workers[6] and Clark and Willis[7] reported the preparation of trimethyl(trifluoromethyl)tin by the reaction of hexamethylditin with iodotrifluoromethane. Of great interest was the finding of the latter group that Me_3SnCF_3 decomposed on being heated in a sealed tube at 150° for 20 hr with almost quantitative conversion to trimethyltin fluoride and hexafluorocyclopropane. The formation of the latter was rationalized in terms of initial α elimination of trimethyltin fluoride, followed by dimerization of the difluorocarbene thus generated and CF_2 addition to the resulting tetrafluoroethylene (eq 1–3). Indeed, pyrolysis of Me_3SnCF_3 in the presence of added tetrafluoroethylene gave the expected quantity of hexafluorocyclopropane. The possibility that Me_3SnCF_3 might serve in a general preparation of *gem*-difluorocyclopropanes (eq 4) was not investigated by these workers.

$$(CH_3)_3SnCF_3 \longrightarrow (CH_3)_3SnF + CF_2 \qquad (1)$$

$$2CF_2 \longrightarrow CF_2{=}CF_2 \qquad (2)$$



(3)



(4)

Subsequently, the pyrolysis of trifluoromethyl derivatives of iron,[8] phosphorus,[9] and germanium[10] has been observed to generate CF_2. The pyrolysis of $CF_3Fe(CO)_4I$ in the presence of ethylene was reported to give 1,1-difluorocyclopropane, but neither yield data nor experimental details were provided.[8] Also of interest is that $(CF_3)_3As$ and $(CF_3)_3Sb$ underwent thermal decomposition at 180–220° to give a mixture of products containing 10% tetrafluoroethylene and hexafluorocyclopropane.[11] Successful transfer of CF_2 to olefins has been achieved *via* decarboxylation of sodium chlorodifluoroacetate in 1,2-dimethoxyethane (DME) or diglyme in the presence of olefins[12,13] or by thermolysis or photolysis of difluorodiazirine in the presence of olefins.[14,15]

Of the CF_2 transfer reagents mentioned above, $ClCF_2CO_2Na$ was the most useful. The others were somewhat less practical, either because their preparation was difficult or was achieved in only poor yield, or because their pyrolysis required temperatures too high to allow their general application in *gem*-difluorocyclopropane synthesis.

In our work with phenyl(trihalomethyl)mercury compounds we found that phenyl(trichloromethyl)mercury (which releases CCl_2 to olefins at 80°, but which requires rather long reaction times for quantitative decomposition at that temperature) reacts rapidly with sodium iodide in DME at 80° as shown in eq 5.[1,2] The

$$C_6H_5HgCCl_3 + Na^+I^- \longrightarrow C_6H_5HgI + Na^+CCl_3^- \qquad (5)$$

trichloromethide ion thus produced loses chloride ion, giving dichlorocarbene. If this displacement is carried

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[1] Part XII: D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 959 (1967).

[2] Preliminary communication: D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, *ibid.*, **87**, 681 (1965).

[3] Alfred P. Sloan Foundation Fellow, 1962–1966.

[4] National Institutes of Health Predoctoral Fellow, 1963–1966.

[5] Postdoctoral Research Fellow, 1963–1965; on leave from the Nitto Chemical Industrial Co., Ltd., Osaka, Japan.

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[11] P. B. Ayscough and H. J. Emeléus, *J. Chem. Soc.*, 3381 (1954).

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