TABLE I

RATES OF INVERSION (k) OF TROPILIDENE AT VARIOUS
TEMPERATURES

Temp., °C.	Peak sepn., c.p.s.	Corr. line width,[a] c.p.s.	k, sec.$^{-1}$
−150	76.0		55
−148	71.0		82
−145	49		140
−143	0		180
−133		7.8	1300
−130		6.2	1650

[a] 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,[11] the low barrier to inversion of tropilidene is understandable. From the published[7] 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[3,4] 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-cyclononatriene.[10,12] Different chemical shifts for the methylene protons are

(11) On the other hand, the suggestion[10] that 1,4,7-cyclononatriene 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[13] 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,[14] 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[1,6] 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.[15] The audiophase detector of the Varian integrator was employed in the way suggested by L. F. Johnson.[16] 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[8] $k = \pi\nu^2/2(\nu_2 - \nu_1)$, where ν is the relative chemical shift (in c.p.s.) in the absence of exchange, and ν_2 and ν_1 are full line widths at half-height in the presence and absence of exchange, respectively. The value of ν_1 was taken to be approximately equal to the line width of tetramethylsilane at the temperature where ν_2 was being measured. At −130° and −133°, ν_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

BY THOMAS J. DOUGHERTY

Products resulting from both "normal" addition (*i.e.*, to CH₂) and "abnormal" addition (to CHF) have been identified among the reaction products of vinyl fluoride and trifluoromethyl iodide. Addition by CF₃ radical is highly specific with $k_{CH_2}/k_{CHF} \approx 11$, 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$_2$ClCFClI[1] has been shown recently by v.p.c. techniques to yield also 20–30% of the isomeric iodide CFCl$_2$CF$_2$I.[2] Similarly, the thermal telomerizations of perfluoropropene with CF$_3$I and with n-C$_3$F$_7$I have been found to yield products resulting from addition to both positions of the double bond[2] and not exclusively those in which the attacking radical becomes attached to the CF$_2$ group as originally reported.[3]

(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$_1$R$_2$C = CH$_2$ (R = halogen or hydrogen) radical addition has been found to occur exclusively at the methylene group.[4] Vinyl fluoride is reported to be no exception. Thus the benzoyl peroxide-initiated addition of CF$_2$Br$_2$,[5] CF$_2$BrCFClBr,[6] and the photochemical-initiated addition of CF$_2$=CFI[7] and CF$_3$I[8] to this olefin have all been reported to yield only products of the type RCH$_2$CHFX. We now report that in the benzoyl peroxide-induced telomerization of vinyl fluoride (VF) with trifluoromethyl iodide CF$_3$ 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).

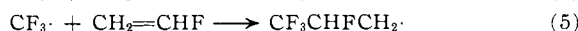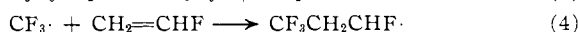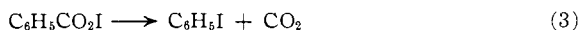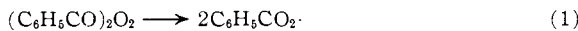(8) R. N. Haszeldine, *J. Chem. Soc.*, 1199 (1953).

TABLE I

PRODUCT DISTRIBUTION IN REACTION OF VINYL FLUORIDE AND TRIFLUOROMETHYL IODIDE[a,b]

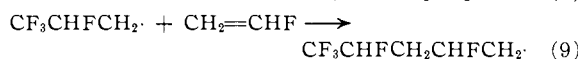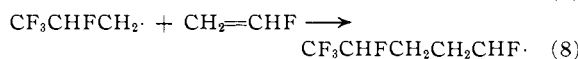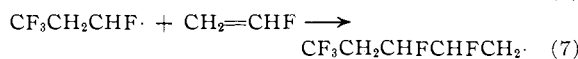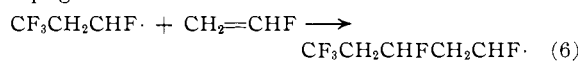|	Moles VF/CF$_3$I = 0.33			Moles VF/CF$_3$I = 4.8	
Fract. I[f]	Run 1[c]	Run 2[d]	Run 3[e]	Run 4[d]	Run 5[e]
1a	81.7	86.5	73	0.7	0.4
1b	5.3	6.5	7.4	4.0	4.7
Fract. II					
2a	~0	~0	~0	1.7	2.1
2b	5.9	5.1	6.8	22.2	18.0
2c	0.5	0.43	1.05	9.7	9.9
2d	0.45	0.28	0.85	7.6	6.6
2e	5.9	5.7	6.0	2.5	2.5
2f	0.3	0.28	~0	~0	~0
Fract. III					
3a	0	0	1.9	37.0	38.1[g]
3b[h]	0	0	1.0	14.8	16.9
3c					

[a] Values are relative % of area of component peak in vapor phase chromatogram compared to total area of peaks for 1:1, 2:1, and 3:1 telomers. In runs 1, 2, and 3, all products are represented by the indicated areas, whereas in runs 4 and 5 there is 26.5 and 44.5 wt. %, respectively, of telomers >3:1. The areas of the telomers were found to be proportional to their weights. [b] Components are listed in order of retention times. [c] $T = 90°$. [d] $T = 95°$. [e] $T = 100°$. [f] Relative areas determined from F[19] n.m.r. spectra. [g] Approximately 1% of an unidentified material was eluted just ahead of 3a. [h] The areas of 3b and 3c appear to be nearly equal.

but *does* occur at CHF with a rate approximately one-eleventh that of addition to the methylene group. Perhaps more significantly, however, it has been found that the propagating radical, $CF_3(CH_2CHF)_2$, *adds at the methylene group with a rate only twice that of addition at CHF.*[9] The reaction scheme may be summarized as
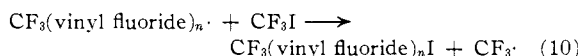
Initiation

$$(C_6H_5CO)_2O_2 \longrightarrow 2C_6H_5CO_2\cdot \qquad (1)$$

$$C_6H_5CO_2\cdot + CF_3I \longrightarrow C_6H_5CO_2I + CF_3\cdot \qquad (2)$$

$$C_6H_5CO_2I \longrightarrow C_6H_5I + CO_2 \qquad (3)$$

$$CF_3\cdot + CH_2{=}CHF \longrightarrow CF_3CH_2CHF\cdot \qquad (4)$$

$$CF_3\cdot + CH_2{=}CHF \longrightarrow CF_3CHFCH_2\cdot \qquad (5)$$

Propagation

$$CF_3CH_2CHF\cdot + CH_2{=}CHF \longrightarrow$$
$$CF_3CH_2CHFCH_2CHF\cdot \qquad (6)$$

$$CF_3CH_2CHF\cdot + CH_2{=}CHF \longrightarrow$$
$$CF_3CH_2CHFCHFCH_2\cdot \qquad (7)$$

$$CF_3CHFCH_2\cdot + CH_2{=}CHF \longrightarrow$$
$$CF_3CHFCH_2CH_2CHF\cdot \qquad (8)$$

$$CF_3CHFCH_2\cdot + CH_2{=}CHF \longrightarrow$$
$$CF_3CHFCH_2CHFCH_2\cdot \qquad (9)$$

Chain transfer

$$CF_3(\text{vinyl fluoride})_n\cdot + CF_3I \longrightarrow$$
$$CF_3(\text{vinyl fluoride})_nI + CF_3\cdot \qquad (10)$$

Termination may occur by various radical coupling reactions.

Reactions between vinyl fluoride and trifluoromethyl iodide were carried out in shaker tubes using benzoyl peroxide initiator as described in the Experimental. The reaction products could be partially separated by distillation under reduced pressure. Table II describes product distribution as a function of reactant ratio. Examination of each of the telomer fractions by v.p.c. indicated a complex mixture of isomers as indi-

(9) The referee has suggested that free radical rearrangements such as those discussed by F. R. Mayo, *J. Am. Chem. Soc.*, **84**, 3964 (1962) [n-ClPrCl $\longrightarrow$ CH$_3$ĊHCH$_2$Cl $\longrightarrow$ CH$_3$CHClCH$_2$· $\xrightarrow{\text{HCl}}$ CH$_3$CHClCH$_3$], could account for some of the "abnormal" product. Although this seems unlikely in this system, it cannot be ruled out at this time.

cated in Table I. By use of preparative scale v.p.c., certain of these components were obtained in sufficient quantity for structural examination.

Although v.p.c. indicated a single constituent of the 1:1 fractions, the F[19] n.m.r. spectra clearly established the presence of both 1:1 telomers, the ratio being a function of the mole ratio of reactants (Table I). The CF$_3$ group resonance at $\phi^{10} = 66.0$ (two sets of overlapping triplets, $J = 9.65$ separated by $J = 7.35$ c.p.s.) in all spectra was three times the area of the –CHFI resonance at $\phi = 144.8$ (complex splitting pattern) while the CF$_3$ group resonance at $\phi = 80.0$ (two sets of overlapping doublets, $J \approx 5.0$ c.p.s. separated by $J \approx 5.0$ c.p.s.) was in all cases three times the area of the –CHF resonance at $\phi = 193$ (complex splitting pattern). The former spectrum established the structure 1,3,3,3-tetrafluoropropyl iodide, CF_3CH_2CHFI (1a), and the latter that of its isomer 2,3,3,3-tetrafluoropropyl iodide, CF_3CHFCH_2I (1b).

The two main components of fraction II in runs 1, 2, and 3 (2b and 2e, Table I) were separated by preparative v.p.c. for identification. Compound 2e was shown by its infrared spectrum to be iodobenzene, apparently arising from chain transfer of the benzoyloxy radical with CF_3I (eq. 2 and 3), while 2b was identified by n.m.r. as the 2:1 head–tail telomer 1,3,5,5,5-pentafluoroamyl iodide, $CF_3(CH_2CHF)_2I$. The elemental analysis and infrared and ultraviolet spectra were consistent with this assignment.

Preparative v.p.c. allowed separation of fraction III (Table I) into 3a and a mixture of approximately equal amounts of 3b and 3c. The elemental analysis and the infrared, ultraviolet, and n.m.r. spectra of 3a showed the structure to be that of the 3:1 head–tail telomer 1,3,5,7,7,7-hexafluoroheptyl iodide, $CF_3(CH_2CHF)_3I$. While the analysis and various spectra indicated that mixture 3b–3c was isomeric with 3a, the structure could not be totally assigned. Thus, the n.m.r. spectrum showed a CF$_3$ group of the same type as in 3a (*i.e.*, CF$_3$ adjacent to CH$_2$–, $\phi \approx 65$), a single type fluorine resonance at $\phi = 198.5$ and 209[11] of area one-third that of the CF$_3$ group, and a set of three peaks, $\phi = 182, 185, 187.5$, of total area two-thirds that of the CF$_3$ group; no fluorine on carbon with iodine was indicated. The structure thus can be partially determined from these data to be $CF_3CH_2CHF(VF)CHFCH_2I$. To determine the mode of attachment of the second vinyl fluoride unit, the following series of reactions was carried out. Reaction of mixture 3b–3c with triethylamine in ethanol afforded what appeared by v.p.c. and n.m.r. to be a single olefinic product $C_7H_8F_6$. That both 3b and 3c gave this product was determined by following the reaction to completion by v.p.c. Ozonolysis of the olefin followed by mild hydrolysis and oxidative work-up yielded an acid, $C_6H_7F_5O_2$, whose infrared spectrum indicated an α-fluoro substituent.[12] It thus appears that 3b and 3c are diasterioisomers of 2,3,5,7,7,7-hexafluoroheptyl iodide, $CF_3(CH_2CHF)_2$-$CHFCH_2I$. The F[19] n.m.r. spectrum was consistent with this assignment.

The relative rate of reaction of the CF$_3$ radical at the two terminal positions of vinyl fluoride at 100° can be obtained from run 3 by comparing the relative

(10) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(11) Double sets of chemically shifted peaks were often observed since the compounds in most cases were mixtures of diastereoisomers. This spectrum is of a 10% solution in DMSO; that in the Experimental is of a CCl$_4$ solution.
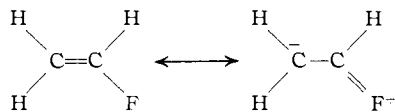
(12) The carbonyl absorption was at 5.7 μ compared to CF$_3$CO$_2$H, 5.60 μ; C$_2$F$_5$CO$_2$H, 5.64 μ; C$_3$F$_6$CO$_2$H, 5.61 μ; C$_9$F$_{19}$CO$_2$H, 5.68 μ (R.N. Haszeldine, *J. Chem. Soc.*, 4026 (1954)) and saturated aliphatic acids, 5.80–5.87 μ (L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 162).

amounts of telomers containing the grouping CF_3CH_2- with those containing the CF_3CHF- moiety. This information can be easily obtained from the F^{19} n.m.r. spectrum of the telomer mixture since CF_3 adjacent to $-CH_2-$ shows resonance at approximately $\phi = 65$ while CF_3 adjacent to $-CHF-$ is found at about $\phi = 80$. In this way $k_{CH_2}/k_{CHF} = 11.3$ for CF_3 radical addition to vinyl fluoride.

The value of this ratio for the propagating radical $CF_3(CH_2CHF)_2$ can be estimated from the relative amounts of $CF_3(CH_2CHF)_2CH_2CHFI$ (3a) and $CF_3(CH_2CHF)_2CHFCH_2I$ (3b and 3c) in run 3 since no telomers of higher molecular weight were formed in this reaction. Thus $k_{CH_2}/k_{CHF} = 1.9$ for $CF_3(CH_2CHF)_2$ radicals.

Transfer constants $(C_n = k_{transfer}/k_{propagation})$ for the various radicals involved can be determined from the data of Table I if it is assumed that the telomer iodides do not act as chain transfer agents competitively with CF_3I. This assumption was tested by carrying out a telomerization in which CF_3CH_2CHFI was added at the start. By comparing the product distribution with a control run, it was determined that approximately half of the telomer iodide had reacted. Reactions such as $CF_3(VF)I + R\cdot \rightarrow RI + CF_3(VF)\cdot$ must, therefore, be added to the above reaction scheme. Since this reaction in effect converts lower molecular weight telomers to higher molecular weight products, results of calculations of transfer constants based on the data of Table I are misleading.

The high selectivity for addition to vinyl fluoride shown by the CF_3 radical is best explained on the basis of its high degree of electrophilicity amply demonstrated in the work of Stefani and Szwarc.[13] The propagating radicals of the type RCH_2CHF, on the other hand, are expected to be considerably less electrophilic than CF_3 radicals and thus show less specificity for addition at the position of highest electron density in vinyl fluoride (i.e., at the methylene group).

$$\underset{H}{\overset{H}{\diagdown}}C=C\underset{F}{\overset{H}{\diagup}} \longleftrightarrow \underset{H}{\overset{H}{\diagdown}}\overset{-}{C}-C\underset{F^-}{\overset{H}{\diagup}}$$

The small size of the fluorine atom will minimize the steric differences in the transition states for the two modes of addition, thus also leading to a lower degree of specificity.

It may be concluded, therefore, that the direction of radical addition to olefins will depend greatly upon the relative importance of various polar structures in the transition states (as well as steric factors) and thus ultimately upon the polarization (and/or polarizability) of both the olefin *and the attacking radical*.[13a]

Experimental[14]

Telomerizations were carried out typically as follows. A 500-ml. stainless steel rocker bomb containing benzoyl peroxide (2.5 wt. % based on trifluoromethyl iodide) was cooled in a Dry Ice bath and an evacuation–nitrogen flush sequence performed several times. Trifluoromethyl iodide (Columbia Organic Chemicals

(13) A. P. Stefani, L. Herb, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961); A. P. Stefani and M. Szwarc, *ibid.*, **84**, 3661 (1962).

(13a) Note Added in Proof.—We have recently become aware of work by C. W. Wilson, III, and E. R. Santee, Jr., Fourth OCEANS Conference, Pittsburgh, Penna., Feb. 28–March 2, 1963, in which the F^{19} n.m.r. spectrum of polyvinyl fluoride indicates two distinct types of fluorine atoms. The data presented herein, together with that of R. C. Golike of this Laboratory on the F^{19} n.m.r. spectrum of polyvinyl fluoride (private communication), leave no doubt that the higher field set of peaks is attributable to "head–head" links, *i.e.*, $-CHFCHF-$. It is of interest to note that the amount of fluorine occurring in this way in the polymer (25–30%) can be closely predicted on the basis of the relative selectivity of the $CF_3(CH_2CHF)_2$ radical.

(14) Nuclear magnetic resonance spectra were obtained on a Varian dual purpose 60 spectrometer operated at 30 or 56.4 Mc. using neat samples except for 5–10% Freon-11 as reference.

Co., 108 g., 0.55 mole) was then transferred as a gas into the bomb and allowed to freeze. Vinyl fluoride (supplied uninhibited by the Central Research Dept., of the du Pont Co., 120 g., 2.61 moles) was condensed into the bomb which was then allowed to warm to room temperature and inserted into a reciprocating shaking device. While shaking, the mixture was heated to reaction temperature rapidly and held there for approximately 4 half-lives of initiator (90°, 6 hr.; 95°, 3.5 hr.; 100°, 2 hr.). After cooling to room temperature, the gases were vented and the contents of the bomb analyzed by vapor phase chromatography and fractionally distilled under reduced pressure: b.p. 1:1 adduct, 22° (5 mm.); b.p. 2:1, 55° (12 mm.); b.p. 3:1, 49° (0.1 mm.); 4:1 and greater not distilled.[15] Retention times on an 8-ft. stainless steel analytical column, packed with Carbowax 1500 (10% on Chromosorb) with a helium flow rate of 150 ml./min., operated at 90° for 16 min. and then programmed at 4.6°/min. to 220°, are: 1a, 1b, 11 min.; 2a, 35 min.; 2b, 38 min.; 2c, 39 min.; 2d, 40 min.; 2e, 42 min.; 3a, 49 min.; 3b, 50.8 min.; 3c, 60.2 min. (see Table I). Table II indicates the molecular weight distribution as a function of mole ratio of reactants for several runs.

To obtain sufficient amounts of material for structural determination, several 0.5-ml. samples of the individual fractions were separated on an 8-ft. preparative v.p.c. column packed with Carbowax 1500 on firebrick with a helium flow rate of >600 ml./min. and operated at 200° for the 3:1 fractions and 175° for the 2:1 fractions. In this way, components 2b, 2e, 3a, 3b, and 3c were separated.

Table II

Molecular Weight Distribution as a Function of Mole Ratio of Reactants[a]

VF, g.	CF₃I, g.	Moles VF/CF₃I	Yield, g.	1:1	2:1	3:1	>3:1
8.4	108	0.33[c]	28.9	82.4	14.7	2.9	0
33.5	65	2.0	72.3	45.8	46.0	8.2	0
45	65	3.0	76.7	16.5	64.7	13.7	5.1
120	108	4.8[d]	160.4	2.4	22.7	30.4	44.5
120	108	4.8[b]	193.9	3.7	29.3	31.4	35.6
92	65	6.0	57.1	23.6	39.6	21.0	15.8
120	65	8.0	50.8	4.93	46.1	19.9	29.1

(Column header spanning: %—by wt. of telomers— over 1:1, 2:1, 3:1, >3:1)

[a] The weight ratio of benzoyl peroxide to CF_3I was kept constant at 2.5%, $T = 100°$. [b] Several runs made at this mole ratio of reactants gave ratios of >3:1 telomers/2:1 telomer of ~1.0. The relative amounts of 1:1 and 3:1 telomers in these runs were unchanged, however. [c] Run 3, Table I. [d] Run 5, Table I.

1:1 **Telomer fractions** obtained from fractionation of runs at 100° were examined by F^{19} n.m.r., which indicated a mixture of the two 1:1 telomer iodides, 1,3,3,3-tetrafluoropropyl iodide, CF_3CH_2CHFI (1a) and 2,3,3,3-tetrafluoropropyl iodide, CF_3CHFCH_2I (1b), the ratio being a function of mole ratio of reactants (Table I). The ultraviolet spectra in ethanol showed λ_{max} 256.5 mμ ($\epsilon \approx 330$). All fractions gave satisfactory elemental analyses.

2:1 **Telomer fractions** from runs 1, 2, and 3 (Table I) at 100° were obtained from fractionation and examined by F^{19} n.m.r. which indicated the presence of CF_3CH_2- ($\phi \approx 65$) and CF_3CHF- ($\phi \approx 80$) in ratios of approximately 100:0, 100:0, and 98.4:1.5, respectively. Components 2b and 2e were obtained from preparative v.p.c. and examined individually. The infrared spectrum of 2e unequivocally identified it as iodobenzene by comparison with its published spectrum.[16] The F^{19} n.m.r. spectrum of 2b showed CF_3 (ϕ 66, area 3), $-CHF-$ (ϕ 190, area 1), and $-CHFI$ (ϕ 143, 148.5; area 1), thus establishing the structure as 1,3,5,5,5-pentafluoroamyl iodide, $CF_3(CH_2CHF)_2I$. The ultraviolet spectrum of the 2:1 fraction showed λ_{max} 257 mμ, $\epsilon \approx 305$. Elemental analyses were satisfactory.

3:1 **Telomer fractions** obtained from fractionation of runs 3 and 4 (Table I) contained CF_3CH_2- ($\phi \approx 65$) and CF_3CHF ($\phi \approx 80$) in approximate ratios of 97:3 and 97.4:4.2.6, respectively, as obtained from their F^{19} n.m.r. spectra. These fractions were then passed through the preparative v.p.c. column and separated into component 3a and a mixture of approximately equal quantities of 3b and 3c (Table I). The F^{19} n.m.r. spectrum of 3a showed it to be 1,3,5,7,7,7-hexafluoroheptyl iodide, $CF_3(CH_2CHF)_3I$; CF_3 (ϕ 64.7, area $\approx$ 3), CHF (ϕ 187.5, area $\approx$ 3), and CHFI (ϕ 140.5, 145, area $\approx$ 1). The n.m.r. spectrum of 3b-3c (solid, m.p. 65°) determined on a 10% solution in carbon tetrachloride indicated CF_3 (ϕ 64.6, area $\approx$ 3), CHF (ϕ 185, area $\approx$ 2),

(15) Reference 6 reports: b.p. 1:1 adduct, 86.2° (757 mm.), b.p. 2:1 adduct, 64° (20 mm.).

(16) American Petroleum Institute, Infrared Spectral Tables, Serial No. 1291.

and CHF (ϕ 191, 194.5, 201, 206; area $\approx$ 1), but no –CHFI.[11] The 3:1 fractions in ethanol showed $\lambda_{max} \approx 256$ mμ, $\epsilon \approx 370$.

Anal. Calcd. for $C_7H_9F_6I$: C, 25.1; H, 2.69; F, 34.2; I, 38.0. Found: C, 24.9; H, 2.58; F, 34.1; I, 37.8.

The elimination reaction of 3b–3c was carried out by dissolving the mixture (18.0 g., 0.054 mole) in ethanol (60 ml.) containing triethylamine (10.0 g., 0.099 mole) and refluxing. After 7 days, v.p.c. analysis indicated almost complete reaction with formation of a single, new peak (retention time 7.8 min. at 125°, helium flow rate 150 ml./min. with analytical column described above). The reaction mixture was poured into water (200 ml.) causing separation of a red oil which was washed with cold water (3 × 25 ml.), dilute hydrochloric acid (2 × 25 ml.), and dilute sodium carbonate solution (2 × 25 ml.). The organic layer was steam distilled and the colorless oil which separated in the distillate dried over anhydrous sodium carbonate to yield an olefin, $C_7H_5F_6$ (6.8 g., 62% yield); C=C in infrared spectrum at 5.9 μ.

Anal. Calcd. for $C_7H_8F_6$: C, 40.7; H, 3.89; F, 55.4. Found: C, 40.7; H, 4.05; F, 55.2.

Ozonization was carried out by dissolving the olefin (0.50 g., 2.43 × 10⁻³ mole) in a mixture of chloroform (10 ml.) and methylene chloride (2 ml.), cooling to –78° in a Dry Ice trap, and passing in O_3 (3% in O_2) until the solution turned blue (40 min.). The solution of ozonide was poured slowly into water (10 ml.) and stirred 45 min. To the solution was added sodium hydroxide (0.2

g., 4.0 × 10⁻³ mole) and silver oxide (2.0 g., 5.0 × 10⁻³ mole) and the mixture heated in a steam bath for 1 hr. After filtering the reaction mixture, the organic solvents were removed under vacuum and the aqueous solution strongly acidified with hydrochloric acid. The filtrate was extracted with ether (3 × 50 ml.), the ether solution dried ($CaCl_2$) and evaporated to yield an acid, $C_6H_7F_5O_2$ (0.45 g., 90% yield), which was recrystallized from chloroform; m.p. 97–95° (partly), >285° (remainder). The infrared spectrum showed carbonyl absorption at 5.70 μ indicating an α-fluoro substituent.[12] The F^{19} n.m.r. spectrum was consistent with this assignment but was not in itself definitive.

Anal. Calcd. for $C_6H_7F_6O_2$: C, 34.9; H, 3.4; F, 46.1; neut. equiv., 206. Found: C, 35.3; H, 3.5; F, 45.8; neut. equiv., 210.

Telomerization in the Presence of CF_3CH_2CHFI.—This run was carried out as run 5, Table I, except that 10.0 g. of 1:1 telomer CF_3CH_2CHFI was also added. Fractionation yielded 8.6 g. of 1:1 telomer compared to control runs yielding 4–7 g. Therefore, at least half of the initial 10.0 g. of telomer must have reacted, presumably by chain transfer.

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Hydrogen Chemical Shifts of 3-Alkyl and 3-Phenyl Sydnones

By K. D. Lawson, Wallace S. Brey, Jr., and L. B. Kier

Proton resonance spectra of five 3-alkyl sydnones and 3-phenyl sydnone have been determined in acetone and in chloroform solution. The ring hydrogen chemical shifts in chloroform solution are strongly concentration dependent in a manner which indicates that the chloroform solvent is breaking down aggregates of solute molecules. The resonances of the hydrogens in the substituent group which are α to the sydnone ring fall strikingly far downfield, indicating an unshielding by the aromatic ring current as well as by the electronegative effect of the nitrogen atom in the ring.

The sydnone ring system is an unusual one, for it cannot be represented satisfactorily by any canonical structure which does not place formal charges somewhere in the ring. The conventional formulation of a 3-substituted sydnone is

$$
\begin{array}{c}
\text{CH—C} \diagup \overset{\ominus}{\text{O}} \\
\mid \quad \oplus \quad \diagdown \text{O} \\
\text{R —N——N} \diagup
\end{array}
$$
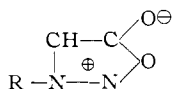
The chemical and spectroscopic properties of molecules containing the sydnone ring have been interpreted to indicate a six-electron aromatic system, delocalized over the five atoms of the ring.[1] It appeared of importance to determine the relationship of the n.m.r. chemical shifts in various sydnones substituted in position 3 to the behavior of these compounds as aromatic molecules. Of interest also is the relation of the physical properties of these materials to their pharmacological activity as central nervous system stimulants.[2–4]

Experimental

Preparation of the materials was described in an earlier paper,[3] and various physical properties of the compounds which had not been previously reported were tabulated there. Nuclear magnetic spectra of solutions of several sydnones substituted in position 3 were determined for the compounds in solution in acetone and in deuterated chloroform, using a Varian HR-60 Model V4300-2 spectrometer operating at 60.0 Mc. The shift of the ring hydrogen in each of the compounds was very carefully determined by superimposing the audiofrequency sideband of the internal reference, tetramethylsilane (TMS), on the appropriate sydnone

resonance peak, and observing the superimposed peaks on the oscilloscope. The audiofrequency used was measured simultaneously with an electronic counter. The average of replicate measurements was computed; the average deviation of ten replications was 0.2 to 0.3 c.p.s. The shifts were extrapolated to infinite dilution from results on solutions of varying concentration. Some determinations were also made of the shifts of hydrogens in the substituent alkyl and phenyl groups, and of the resonance position of the proton in $CHCl_3$ as the solvent for isopropyl sydnone.

Figures 1 and 2 show the data for the ring hydrogen chemical shifts in the two solvents. In these figures, the frequency difference from TMS is plotted as measured, in order to represent accurately the numerical values obtained. The extrapolated values are compiled in Table I. In the discussion which follows, and in Table II, which represents the data for the shifts of the substituent groups, the results are given for convenience as τ-values,[5] although it is to be noted that this is not quite legitimate, since the τ-scale was originally defined in terms of the shift at low concentrations in carbon tetrachloride as the solvent.

Table I

Chemical Shifts of the Ring Hydrogens of 3-Substituted Sydnones, Extrapolated to Infinite Dilution

Substituent	Shift from TMS in acetone, c.p.s.	Shift from TMS in $CDCl_3$, c.p.s.
Methyl	−401.5	−382.5
Ethyl	−405.5	−381.5
Isopropyl	−405.9	−379.3
t-Butyl	−407.9	−377.0
t-Octyl[a]	−413.2	−376.5
Phenyl	−438.9	−405.8

[a] $\alpha,\alpha,\gamma,\gamma$-Tetramethylbutyl.

Discussion

The first feature of the spectra to be considered is the general location of the ring hydrogen resonance.

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(5) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).