Free-Radical Reactions of Fluoroalkanesulfenyl Halides. II.[1] Free-Radical Reactions of Trifluoromethanesulfenyl Chloride with Alkanes

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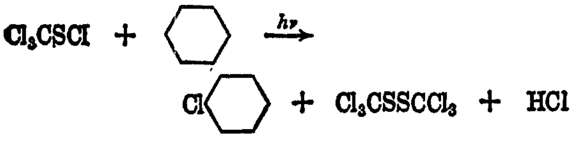
In free-radical chain reactions of trifluoromethanesulfenyl chloride with saturated hydrocarbons, the principal products are trifluoromethyl alkyl sulfides, chloroalkanes, hydrogen chloride, and bis(trifluoromethyl) disulfide. The ratio of sulfide to chloroalkane varies with the structure of the alkane.

Free-radical reactions of alkanes with several compounds containing sulfur–chlorine bonds, *e.g.*, sulfonyl chlorides,[2] thiocyanogen monochloride,[3] trichloromethanesulfenyl chloride,[4] and sulfur dichloride,[5] have been reported. The reactions may be divided into two groups according to the type of product derived from the alkane. In the first group, comprised of sulfonyl chlorides and trichloromethanesulfenyl chloride, the alkane-derived product is a chloroalkane, and the sulfur–chlorine reagent functions as a free-radical chlorinating agent (*e.g.*, eq 1). The products from the second group, where the reactants are sulfur dichloride and thiocyanogen monochloride, result from carbon–sulfur bond formation (*e.g.*, eq 2). All of these reactions are chain reactions involving alkyl radicals which perform the chain transfer. The difference in the reactions of the two groups can be traced to the nature of the chain-transfer step. In the reactions of the first group, the alkyl radical attacks the sulfur-bonded chlorine atom to form a chloroalkane and a radical, with the electron on sulfur, to carry on the chain (eq 3).



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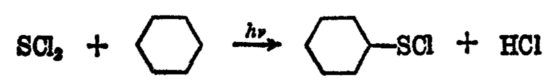


(2)

$$R\cdot + R'SCl \begin{cases} \rightarrow RCl + R'S\cdot & (3)\\ \rightarrow RSR' + Cl\cdot & (4)\end{cases}$$

In reactions of the second group, the alkyl radical attacks the sulfur atom to form a carbon–sulfur bond, concurrently generating a chlorine atom as the chain-carrying species (eq 4).

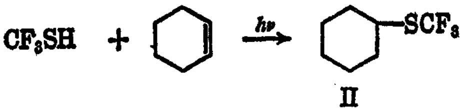
This paper reports the results of a study of free-radical reactions of trifluoromethanesulfenyl chloride (I) with alkanes. Unlike trichloromethanesulfenyl chloride, I exhibits both types of reactions, yielding chloroalkanes and trifluoromethyl alkyl sulfides, the latter usually predominating. After this work was completed, a report[6] appeared which shows that another sulfenyl chloride, pentachlorobenzenesulfenyl chloride, exhibits similar behavior.

Results

Cyclohexane.—The ultraviolet-initiated reaction of I with an excess of cyclohexane resulted in the formation of trifluoromethyl cyclohexyl sulfide (II), chlorocyclohexane (III), bis(trifluoromethyl) disulfide (IV), and hydrogen chloride as the only detected products (eq 5).

$$\underset{\text{I}}{CF_3SCl} + C_6H_{12} \xrightarrow{h\nu} \underset{\substack{\text{II}\\ 45\%}}{CF_3SC_6H_{11}} + \underset{\substack{\text{III}\\ 28\%}}{C_6H_{11}Cl} + \underset{\substack{\text{IV}\\ 35\%}}{CF_3SSCF_3} + HCl \quad (5)$$

The radical-chain nature of this reaction was indicated by the very short period of irradiation necessary to cause complete disappearance of 0.2 mole of the sulfenyl chloride and by the fact that the reaction could also be achieved by the use of 0.22 mole % of an azonitrile catalyst. Examination by gas chromatography (gc) of the reaction mixtures obtained from identical starting mixtures, one initiated by ultraviolet and the other by 5 mole % of α,α'-azobis(isobutyronitrile), showed that the products were formed in essentially the same ratios in the two experiments. The cyclohexane-derived products were isolated by preparative scale gc, and comparison of infrared spectra and gc retention times with those of authentic materials served for identification. An authentic sample of II was prepared by the ultraviolet-initiated addition of trifluoromethanethiol to cyclohexene (eq 6).



II

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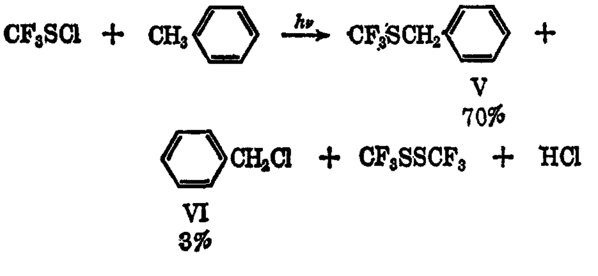
Toluene.—The ultraviolet-initiated reaction of I with excess toluene gave a 70% yield of trifluoromethyl benzyl sulfide (V) along with hydrogen chloride and bis(trifluoromethyl) disulfide (eq 7). No benzyl chloride (VI) was isolated, but the analysis of the sulfide in-



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[1] Paper I: J. F. Harris, Jr., *J. Am. Chem. Soc.*, **84**, 3148 (1962).

[2] E. S. Huyser and B. Giddings, *J. Org. Chem.*, **27**, 3391 (1962).

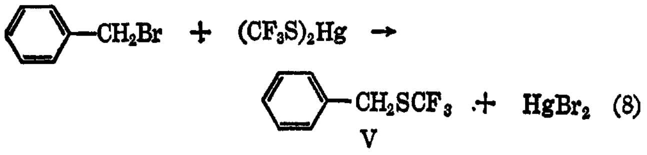
[3] (a) R. G. R. Bacon, R. G. Guy, R. S. Irwin, and T. A. Robinson, *Proc. Chem. Soc.*, 304 (1959); (b) R. G. R. Bacon and R. G. Guy, *J. Chem. Soc.*, 2428, 2436 (1961).

[4] (a) V. Prey, E. Gutschik, and H. Berbalk, *Monatsch. Chem.*, **91**, 556 (1960); (b) H. Kloosterziel, *Rec. Trav. Chim.*, **82**, 497, 508 (1963).

[5] E. Müller and E. W. Schmidt, *Ber.*, **96**, 3050 (1963).

[6] N. Kharasch and Z. S. Ariyan, *Chem. Ind.* (London), 929 (1964).

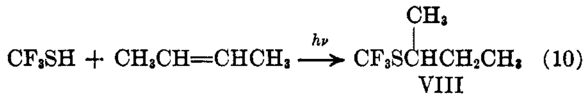
dicated that it contained about 3% of VI. The proton nmr pattern of V consisted of two unsplit resonances at τ 2.72 (C_6H_5) and 5.92 (CH_2) with the expected intensity ratio and was identical with the pattern of the compound prepared by the reaction of benzyl bromide with bis(trifluoromethylthio)mercury (eq 8).



n-Butane.—With n-butane, the major products included both possible sulfides (VII and VIII), 2-chlorobutane (IX), and bis(trifluoromethyl) disulfide (eq 9). About 1% of 1-chlorobutane (X) was detected.

$$CF_3SCl + CH_3CH_2CH_2CH_3 \xrightarrow{h\nu} \underset{\substack{VII\\13\%}}{CF_3SC_4H_9\text{-}n} + \underset{\substack{VIII\\46\%}}{CF_3SCH(CH_3)C_2H_5} + \underset{\substack{IX\\12\%}}{CH_3CHClCH_2CH_3} + \underset{\substack{X\\1\%}}{ClCH_2CH_2CH_2CH_3} + \underset{28\%}{CF_3SSCF_3} + HCl \quad (9)$$

The product composition was determined by gc, using samples of authentic materials for comparison. The product obtained in highest yield, VIII, was isolated by preparative scale gc, and its complicated proton nmr pattern was identical with that of the product obtained from the ultraviolet-initiated addition of trifluoromethanethiol to butene-2 (eq 10). An authentic sample of VII was prepared by the ultraviolet-initiated addition of trifluoromethanethiol to 1-butene (eq 11).



$$CF_3SH + CH_3CH{=}CHCH_3 \xrightarrow{h\nu} \underset{VIII}{CF_3SCH(CH_3)CH_2CH_3} \quad (10)$$

$$CF_3SH + CH_2{=}CHC_2H_5 \xrightarrow{h\nu} \underset{VII}{CF_3SC_4H_9\text{-}n} \quad (11)$$

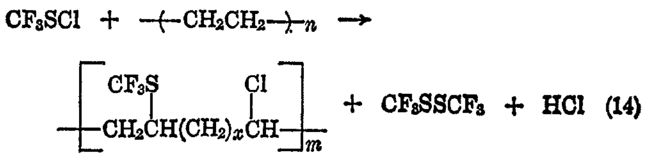
Isobutane.—The reaction of I with isobutane yielded both possible sulfides (XI and XII) and t-butyl chloride (XIII), but only traces of isobutyl chloride (XIV) (eq 12), and was thus similar to the n-butane reaction. The product composition was determined by gc, and samples of the three major components (exclusive of CF_3SSCF_3) were isolated by preparative scale gc. The highest yield component was identical with a sample of t-butyl chloride according to gc retention times and proton nmr patterns. The proton nmr pattern of the more prevalent of the sulfides contains resonances at τ 8.08 (CH, complicated splitting pattern), 7.25 (CH_2, doublet, J = 6.8 cps), and 8.96 (CH_3, doublet, J = 6.4 cps) in the expected ratios and is identical with the pattern of the sulfide obtained from the ultraviolet-initiated addition of trifluoromethanethiol to isobutylene (eq. 13). This product was thus assigned structure XII.

$$CF_3SCl + (CH_3)_3CH \xrightarrow{h\nu} \underset{\substack{XI\\24\%}}{CF_3SC(CH_3)_3} + \underset{\substack{XII\\12\%}}{CF_3SCH_2CH(CH_3)_2} + \underset{\substack{XIII\\33\%}}{(CH_3)_3CCl} + \underset{\substack{XIV\\1\%}}{(CH_3)_2CHCH_2Cl} + \underset{47\%}{CF_3SSCF_3} + HCl \quad (12)$$

$$CF_3SH + CH_2{=}C(CH_3)_2 \xrightarrow{h\nu} \underset{XII}{CF_3SCH_2CH(CH_3)_2} \quad (13)$$

The proton nmr pattern of the other sulfide contains a single resonance at τ 8.51 weakly split (J = 0.5 cps) to a quadruplet and is consistent with the assigned trifluoromethyl t-butyl sulfide structure (XI).

Polyethylene.—The free-radical reaction of CF_3SCl with polyethylene in benzene solution occurred readily with an azonitrile catalyst. The resulting polymer contained both trifluoromethylthio groups and chlorine atoms in about the same ratio as observed in the cyclohexane experiment (eq 14).



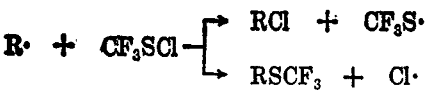
$$CF_3SCl + \left(CH_2CH_2\right)_n \rightarrow \left[CH_2CH(SCF_3)(CH_2)_xCH(Cl)\right]_m + CF_3SSCF_3 + HCl \quad (14)$$

Discussion

The chain mechanism shown in eq. 15–20 can be written for the reactions encountered in this study.

$$CF_3SCl \xrightarrow{h\nu} CF_3S\cdot + Cl\cdot \quad (15)$$

$$Cl\cdot + R{-}H \longrightarrow HCl + R\cdot \quad (16)$$



$$R\cdot + CF_3SCl \longrightarrow RCl + CF_3S\cdot \quad (17)$$

$$R\cdot + CF_3SCl \longrightarrow RSCF_3 + Cl\cdot \quad (18)$$

$$CF_3S\cdot + R{-}H \longrightarrow CF_3SH + R\cdot \quad (19)$$

$$CF_3SH + CF_3SCl \longrightarrow CF_3SSCF_3 + HCl \quad (20)$$

The initial step is the photolysis of the S–Cl bond of the sulfenyl chloride,[7] which gives a chlorine atom and a CF_3S radical (eq 15). Attack by the chlorine atom on the alkane yields HCl and an alkyl radical (eq 16), which chain transfers *via* a displacement on the chlorine of I to give a chloroalkane and a CF_3S radical (eq 17), as well as on the sulfur atom to give a trifluoromethyl alkyl sulfide and a chlorine atom (eq 18).[8] The chain is then repeated with eq 16, etc. It is obvious that the chlorine atoms produced in the chain transfer (eq 18) are alone insufficient to account for the kinetic chain lengths encountered. For example, in the reaction of cyclohexane with I, initiated by 0.22 mole % of α,α'-azobis(isobutyronitrile), at least 93 molecules of II were produced per radical derived from the initiator. With a kinetic chain of this magnitude and in view of the relatively large amount of chlorocyclohexane (III) produced in this reaction (III/II = 0.64), it is not possible that eq 17 is a chain-terminating process. It is thus necessary to postulate that the CF_3S radicals produced *via* eq 17 also contribute in some way to the length of the kinetic chain, possibly by abstracting hydrogen from

[7] The ultraviolet spectrum (gas phase) of CF_3SCl contains maxima at 2140 A (ϵ 270) and 3330 A (ϵ 27).

[8] A similar situation obtained in the free-radical chain addition of CF_3SCl to fluoro olefins in which attack by fluoroalkyl radicals was also observed to occur on both chlorine and sulfur of the sulfenyl chloride.[1]

the alkane as in eq 19. The sequence is then completed by a polar reaction of CF_3SCl with CF_3SH to give HCl and bis(trifluoromethyl) disulfide (eq 20).

The occurrence of the reaction represented by eq 19 is debatable. It is well known that thiyl radicals can abstract hydrogen from saturated carbon atoms (eq 21) in cases where the CH bond dissociation energy

$$RS\cdot + R'H \longrightarrow RSH + R'\cdot \qquad (21)$$

has been lowered by structural features to values in the vicinity of that of the SH bond in thiols (*i.e.*, 86–89 kcal),[9] thus making the reaction represented by eq 21 exothermic or at least only weakly endothermic.[10] The bond dissociation energies of the α-hydrogen atoms in toluene (78 kcal), and of the secondary and tertiary hydrogens in the alkanes used in this study (90–94 kcal) are probably low enough to permit inclusion of eq 19 in the chain sequence proposed above. Some additional help may also be available in these cases by virtue of the dissociation energy of the SH bond in CF_3SH, which is probably greater than 89 kcal, the value of which has been determined for methanethiol. There is some evidence from the product distributions obtained in reactions of I with *n*- and isobutane indicating that a species less reactive than the chlorine atom, presumably the CF_3S radical, is doing some of the hydrogen abstraction. For example, in the *n*-butane reaction the ratio of primary butyl radicals to secondary butyl radicals produced is about 1:4. In terms of the relative reactivity of primary *vs.* secondary hydrogen atoms, the ratio is 1:6. This preference for secondary hydrogen is higher by a factor of almost 2 than that reported previously for free-radical chlorination of alkanes in the liquid phase at about the same temperature[11] and indicates that some other less reactive species, *e.g.*, the CF_3S radical, is doing some of the hydrogen abstraction.[12] In the experiment with isobutane, the relative reactivity of primary *vs.* tertiary hydrogen is about 1:39. Since this ratio is about 1:7 in liquid phase chlorination of alkanes under similar conditions,[13] there is indication that in this case also the hydrogen abstraction is at least in part being accomplished by the CF_3S radical.

An alternative to abstraction of hydrogen by CF_3S radicals (eq 19) is a displacement process in which the CF_3S radical attacks the sulfenyl chloride to give bis(trifluoromethyl) disulfide and a chlorine atom (eq 22). Since the estimated dissociation energies of the S–Cl bond[14] and the S–S bond[9] are comparable (~70–73

$$CF_3S\cdot + CF_3SCl \longrightarrow CF_3SSCF_3 + Cl\cdot \qquad (22)$$

kcal), it seems reasonable that such a step could also be tolerated in a chain sequence. With the data thus far in hand a clear choice between these possibilities (*i.e.*, eq 19 and 22) is not possible, and indeed they may both be taking place in these reactions.

Examination of the results of the experiments described above reveals an apparent steric effect in the chain-transfer reaction involving attack by the alkyl radical on the sulfenyl chloride (eq 17 and 18). The primary radicals from *n*-butane, isobutane, and toluene give almost exclusively sulfides, only small amounts of the corresponding chlorides being formed in each case. The secondary radicals from cyclohexane and *n*-butane form both sulfides and chlorides in significant amounts, with sulfides predominating. The *t*-butyl radical from isobutane also forms both products in significant amounts, but in this case the chloride predominates. It thus appears that alkyl radicals intrinsically prefer to attack the sulfur atom of CF_3SCl and the primary radicals do so almost exclusively. Secondary and tertiary radicals, on the other hand, presumably experience steric difficulties in attacking the sulfur and to a significant extent attack the more accessible terminal chlorine atom. The difference in the behavior of CF_3SCl and Cl_3CSCl[4] in reactions with cyclohexane can also be attributed to steric effects; *i.e.*, the sulfur atom in Cl_3CSCl is less easily attacked by the cyclohexyl radical because of the greater size of the adjacent trichloromethyl group compared with the trifluoromethyl group, and consequently attack on Cl_3CSCl occurs only at the chlorine atom.

Experimental Section

I. Reaction of Trifluoromethanesulfenyl Chloride with Cyclohexane. A. Initiation by Ultraviolet Radiation at Atmospheric Pressure.—A mixture of 30 g (0.220 mole) of trifluoromethanesulfenyl chloride[15] and 60 ml (46.7 g, 0.556 mole) of Spectro Grade cyclohexane contained in a quartz reactor[16] fitted with an acetone–Dry Ice condenser and a magnetic stirrer was irradiated with a low-pressure mercury resonance lamp for 27 min. By this time the mixture was colorless. The mixture (70 g) was cooled to room temperature and then filtered to remove a trace of white solid which had formed during the irradiation. Examination of the filtrate by gc (10% Silicone 200 on firebrick) indicated the presence of bis(trifluoromethyl) disulfide, chlorocyclohexane, cyclohexane, and trifluoromethyl cyclohexyl sulfide. Upon distillation there was obtained 7.82 g (35.2%) of bis(trifluoromethyl) disulfide, 30.50 g of recovered cyclohexane, and a residue of 24.07 g which was shown by gas chromatography to consist of a 70:30 mixture of trifluoromethyl cyclohexyl sulfide (44.5% calculated on CF_3SCl) and chlorocyclohexane (28% calculated on CF_3SCl). Pure samples of these materials were separated by preparative scale gc (12-ft 20% Silicone 200 on Chromosorb, 90°, He flow rate of 1500 cc/min). These isolated materials were shown by comparison of infrared spectra to be identical with authentic samples.

B. Reaction in Sealed Pyrex Tubes.—In each case a mixture of 10 ml (7.8 g, 0.0926 mole) of cyclohexane, 2.82 g (0.0206 mole) of trifluoromethanesulfenyl chloride, and the indicated amount (Table I) of α,α'-azobis(isobutyronitrile) was sealed in a 23-ml, thick-walled Carius tube and heated at 80° for 8 hr. The mixtures which contained catalyst were colorless at this point, indicating complete consumption of trifluoromethanesulfenyl chloride. In one case, no catalyst was included, and the tube was irradiated with a G.E. sunlamp until the contents were colorless. The tubes were then cooled in Dry Ice, opened, and allowed to warm to room temperature, during which HCl was evolved. The residues were examined by gc (2-m, 20% diglyceride of ω-trifluorohexanoic acid on 60–80 mesh firebrick, 100°, He flow rate of 69 cc/min). The results of all of these experiments are summarized in Table I.

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[9] J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952).

[10] For example, butanethiyl radicals readily abstract hydrogen from isopropylbenzene. The activation energy of such processes is believed to be negligible. For further discussion of this and additional examples, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 322–326.

[11] C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

[12] It is, of course, possible that this apparent greater selectivity could be due to solvation effects of the constituents of the reaction mixture on the reactivity of the chlorine atom. No investigation of such effects has been carried out.

[13] H. B. Hass, E. T. McBee, and P. Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

[14] Reference 10, p 48.

[15] Trifluoromethanesulfenyl chloride was prepared as described by C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

[16] The reactor and procedure used here have been described previously: J. F. Harris and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961).

TABLE I

REACTIONS OF CF_3SCl WITH CYCLOHEXANE IN SEALED TUBES

Expt	Azo catalyst, g (mole)	Mole % based on CF_3SCl	Conditions	% yield	
				$CF_3SC_6H_{11}$	ClC_6H_{11}
1	0 (0)	0	80°, 8 hr	0	0
2	0 (0)	0	Ultraviolet, 4 min	33.4	20.6
3	0.1655 (1.01×10^{-3})	4.9	80°, 8 hr	33.1	20.7
4	0.0346 (2.10×10^{-4})	1.0	80°, 8 hr	37.6	23.9
5	0.0073 (4.44×10^{-5})	0.22	80°, 8 hr	41.0	26.2

II. Reaction of Trifluoromethanesulfenyl Chloride with *n*-Butane.—A mixture of 21 g (0.361 mole) of *n*-butane and 14.1 g (0.103 mole) of trifluoromethanesulfenyl chloride was irradiated at reflux for 1.25 hr. At the end of this time, the mixture was colorless. Most of the excess butane was distilled from the reaction mixture with a low-temperature packed still. The residue (14.16 g) was examined by gc (2-m 20% diglyceride of ω-trifluorohexanoic acid on 60–80 mesh firebrick, 52°, He flow rate of 78 cc/min) and was found by comparison with authentic samples to possess the composition (by weight) shown in Table II. A sample (bp 81.5–84°, $n^{25}D$ 1.3676) of the 53% peak was isolated by preparative-scale gc (12-ft 20% diglyceride of ω-trifluorohexanoic acid on Chromosorb A, 55°, He flow rate of 750 cc/min) and was shown by proton nmr spectroscopy to be identical with authentic trifluoromethyl *sec*-butyl sulfide, prepared by the ultraviolet-catalyzed addition of trifluoromethanethiol to 2-butene. The per cent yields (based on CF_3SCl) estimated from the gas chromatogram are given in Table II.

TABLE II

REACTION OF CF_3SCl WITH *n*-BUTANE

	% compn of reaction mixture	% yield (based on CF_3SCl)
CF_3SSCF_3	21	28
$CH_3CHClCH_2CH_3$	8	12
$CF_3SCH(CH_3)CH_2CH_3$	53	46
$ClCH_2CH_2CH_2CH_3$	1	1
$CF_3SCH_2CH_2CH_2CH_3$	15	13

III. Reaction of Trifluoromethanesulfenyl Chloride with Isobutane.—A mixture of 51 g (0.875 mole) of isobutane and 48 g (0.352 mole) of trifluoromethanesulfenyl chloride was irradiated at reflux for 1 hr and 4 min. At the end of this time, the mixture was colorless. After distillation of the excess isobutane, the residue (47.74 g) was found by gc (2-m 20% Kel-F ester on 60–80 mesh firebrick, 50°, He flow rate of 87 cc/min) to have the composition given in Table III. The 22, 28, and 14% peaks were separated by preparative-scale gc (12-ft 20% diglyceride of ω-trifluorohexanoic acid on Chromosorb A, 55°, He flow rate of 830 cc/min). The 22% peak was shown by proton nmr spectroscopy to be *t*-butyl chloride. The proton nmr pattern of the 14% peak (bp 78–79°, $n^{25}D$ 1.3652) was identical with that of trifluoromethyl isobutyl sulfide, prepared by the ultraviolet-initiated addition of trifluoromethanethiol to isobutylene. The elemental analysis of the 28% peak (bp 70–71°, $n^{25}D$ 1.3663) indicated that it was also a trifluoromethyl butyl sulfide and its proton nmr pattern, which consisted of a single resonance (see Results), indicated that it was trifluoromethyl *t*-butyl sulfide.

TABLE III

REACTION OF CF_3SCl WITH ISOBUTANE

Product	% compn of reaction mixture	% yield (based on CF_3SCl)
CF_3SSCF_3	35	47
$(CH_3)_3CCl$	22	33
$(CH_3)_2CHCH_2Cl$	1	1
$(CH_3)_3CSCF_3$	28	24
$(CH_3)_2CHCH_2SCF_3$	14	12

Anal. Calcd for $C_5H_9F_3S$: C, 38.0; H, 5.7; F, 36.0. Found: C, 38.5; H, 5.8; F, 35.9.

IV. Reaction of Trifluoromethanesulfenyl Chloride with Toluene.—A mixture of 26 g (0.190 mole) of trifluoromethanesulfenyl chloride and 60 ml (51.7 g, 0.562 mole) of toluene was irradiated for 3 hr. A gas chromatogram of the crude reaction mixture (10% Silicone 200 on firebrick, 115°) contained a single, large product peak in addition to a small peak corresponding to bis(trifluoromethyl) disulfide. The large product peak corresponds in retention time to both benzyl chloride and trifluoromethyl benzyl sulfide. Upon distillation of the reaction mixture through a small spinning-band still, there was obtained 33.7 g of recovered toluene [bp 42–47° (58 mm)] and 26.3 g of a fraction boiling from 86° (58 mm) to 73° (13 mm), $n^{25}D$ 1.4721–1.4731. Analysis indicated that this fraction was trifluoromethyl benzyl sulfide[17] containing about 3% benzyl chloride.

Anal. Calcd for $C_8H_7F_3S$: F, 29.7. Found: F, 27.8; Cl, 0.83.

V. Reaction of Trifluoromethanesulfenyl Chloride with Polyethylene.—A mixture of 12 g of nonlinear polyethylene [Alathon-14, η_{inh} (0.1% in tetralin at 125°) 1.09], 0.66 g of α,α′-azobis(isobutyronitrile), 200 ml of benzene, and 12 g (0.088 mole) of trifluoromethanesulfenyl chloride was charged into a 400-ml stainless steel shaking autoclave and heated at 80° for 8 hr. The resulting mixture was heated to reflux, and benzene was added at reflux until the polymer was completely dissolved. After being filtered hot, the solution was poured slowly into methanol. The resulting precipitated polymer was dried in a vacuum oven at room temperature overnight and then at 50° for a few hours. The dried polymer weighed 12.54 g and had η_{inh} (0.1% in tetralin at 125°) 0.95.

Anal. Found: Cl, 6.79; F, 10.07; S, 5.72.

VI. Preparation of Sulfides. A. Trifluoromethyl *sec*-Butyl Sulfide.—A mixture of 9.5 g (0.169 mole) of 2-butene and 18 g (0.176 mole) of trifluoromethanethiol was irradiated at reflux from a Dry Ice filled condenser for about 5 min. Upon distillation through a small spinning-band still, there was obtained 17.25 g (65%) of trifluoromethyl *sec*-butyl sulfide distilling at 85–86°, $n^{25}D$ 1.3671. The forerun (bp 79–85°, 8.20 g) was shown by gas chromatography to be almost entirely the same product. Including this material, the yield was 95%.

Anal. Calcd for $C_5H_9F_3S$: C, 38.0; H, 5.7; F, 36.0; S, 20.3. Found: C, 38.5; H, 5.9; F, 36.0; S, 20.3.

B. Trifluoromethyl *n*-Butyl Sulfide. 1. From Bis(trifluoromethylthio)mercury and *n*-Butyl Iodide.—A mixture of 25 g (0.136 mole) of *n*-butyl iodide and 41 g (0.102 mole) of bis(trifluoromethylthio)mercury was heated under reflux until precipitation began. Heating was continued for 0.5 hr, and then the mixture was allowed to stand overnight. The product was removed from the reactor by evacuating the reaction mixture through two Dry Ice–acetone cooled traps. The trap contents were dissolved in carbon disulfide, and anhydrous hydrogen chloride was passed through the mixture until no more mercuric chloride precipitated. After filtration, the mixture was distilled through a small spinning-band still to give 9.61 g (45%) of trifluoromethyl *n*-butyl sulfide distilling at 90–93°, $n^{25}D$ 1.3677–1.3681.

Anal. Calcd for $C_5H_9F_3S$: C, 38.0; H, 5.7; F, 36.0; S, 20.3. Found: C, 38.3; H, 6.2; F, 35.5; S, 20.7.

2. From Addition of Trifluoromethanethiol to 1-Butene.—A mixture of 22 g (0.215 mole) of trifluoromethanethiol and 15 ml of 1-butene (liquid at −76°) was irradiated for 0.5 hr. Upon distillation of the reaction mixture through a small spinning-band still, there was obtained 25.6 g (75%) of a fraction (1:1 adduct) distilling at 86–93°, $n^{25}D$ 1.3687–1.3689. A gas chromatogram indicated that two materials in an approximately 95:5 ratio constituted this fraction. The portion boiling at 93° was essentially pure (with respect to the major component).

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[17] Trifluoromethyl benzyl sulfide has been described previously: bp 172° [E. H. Man, D. D. Coffman, and E. L. Meutterties, *J. Am. Chem. Soc.*, **81**, 3575 (1959)].

The major product has a proton nmr pattern identical with that of the product obtained from bis(trifluoromethylthio)mercury and *n*-butyl iodide and must, therefore, be trifluoromethyl *n*-butyl sulfide.

Anal. Calcd for $C_5H_9F_3S$: C, 38.0; H, 5.7; F, 36.0; S, 20.3. Found: C, 38.3; H, 5.9; F, 36.5; S, 20.7.

C. Trifluoromethyl Isobutyl Sulfide.—A mixture of 15.4 g (0.275 mole) of isobutylene and 32 g (0.313 mole) of trifluoromethanethiol was irradiated for 5 min. Upon distillation of the reaction mixture through a small spinning-band still, there was obtained 34.10 g (78%) of trifluoromethyl isobutyl sulfide distilling at 85°, $n^{25}D$ 1.3647–1.3649.

Anal. Calcd for $C_5H_9F_3S$: C, 38.0; H, 5.7; S, 20.3. Found: C, 37.6; H, 5.9; S, 20.1.

D. Trifluoromethyl Cyclohexyl Sulfide.—A mixture of 45 g (0.493 mole) of cyclohexene and 52 g (0.508 mole) of trifluoromethanethiol was irradiated for 5 hr. Upon distillation of the reaction mixture through a large spinning-band still, there was obtained 64.5 g (69%) of trifluoromethyl cyclohexyl sulfide distilling at 72° (60 mm), $n^{25}D$ 1.4180.

Anal. Calcd for $C_7H_{11}F_3S$: C, 45.6; H, 6.0; S, 17.4. Found: C, 45.9; H, 6.3; S, 17.2.

E. Trifluoromethyl Benzyl Sulfide.—This procedure is similar to that described by Man, *et al.*[17]

A mixture of 30 g (0.0744 mole) of bis(trifluoromethylthio)-mercury was placed in a flask fitted with an addition funnel and a reflux condenser, and heated by an oil bath. The bath was heated to 95°, and then 25 g (0.146 mole) of benzyl bromide was added dropwise. A precipitate formed immediately. The heating was continued for 1 hr after the addition was completed, and then the mixture was worked up as described in B, 1. Upon distillation through a small spinning-band still, there was obtained 18.3 g (65%) of benzyl trifluoromethyl sulfide distilling at 56° (8 mm), $n^{25}D$ 1.4709.

Studies on the Azidoazomethine–Tetrazole Equilibrium. IV. Azidopurines[1]

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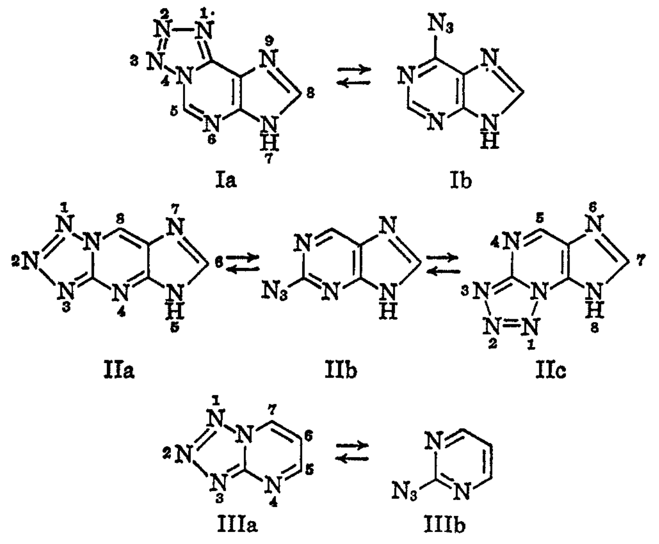
The azidoazomethine–tetrazole equilibrium for the systems tetrazolo[5,1-*i*]purine (Ia)–6-azidopurine (Ib) and tetrazolo[1,5-*a*]purine (IIa)–2-azidopurine (IIb)–tetrazolo[5,1-*b*]purine (IIc) has been examined by means of infrared and proton magnetic resonance spectrometry. II is the first example in which all three tautomers (IIa, b, and c) have been detected in a single medium. Tetrazole stabilization is shown to be greater in Ia than in IIa and IIc. The heats of tautomerization of IIa–IIb and IIc–IIb, respectively, are found to be +4.7 ± 0.2 and +2.7 ± 0.2 kcal/mole. In addition, the magnitude of the heat of tautomerization of tetrazolo[1,5-*a*]pyrimidine (IIIa) to 2-azidopyrimidine (IIIb), +5.1 ± 0.1 kcal/mole, is the same as that of IIa–IIb. An increase in entropy is observed in each case on going from the tetrazolo tautomer to the azido, as expected, and in the temperature range studied the entropy effects compete with the enthalpy effects in controlling the position of equilibrium.

In previous papers we have reported on the azidoazomethine–tetrazole equilibrium in pyrimidines,[2] and we now report some observations on the analogous equilibrium in purines. The preparations of both 6- and 2-azidopurines (Ib and IIb) have been claimed,[3,4] but for I evidence was later presented in favor of the tricyclic structure, tetrazolo[5,1-*i*]purine (Ia).[4,5] Recently, the preparations of some mono-, di-, and triazidopurines have been reported[6,7] in which one of the main considerations in assigning the structures has been the presence of one or more azido infrared absorption bands in the 2200–2100-cm.$^{-1}$ region. Our results indicate that the presence of an azido absorption band in the infrared spectrum of a sample does not preclude the possibility that the tetrazole tautomer is also present.

In this paper the effects of solvent and temperature on the equilibria between tetrazolo[5,1-*i*]purine (Ia) and 6-azidopurine (Ib) and among tetrazolo[1,5-*a*]purine (IIa), 2-azidopurine (IIb), and tetrazolo[5,1-*b*]purine (IIc) are examined. In addition to infrared and proton magnetic resonance (pmr) spectra, support for the assignment of tautomers in system II of Scheme I was provided by data on the equilibrium between tetrazolo[1,5-*a*]pyrimidine (IIIa) and 2-azidopyrimidine (IIIb).[2c]

Scheme I



Experimental Section

I,[3] II,[4] and III[8] were prepared by the nitrosation of the corresponding hydrazino derivatives. The infrared spectra were

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[1] This investigation was supported by funds from the C. F. Kettering Foundation and the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, Contract No. PH-43-64-51.

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