

Photochemically Initiated Reactions of Bistrifluoromethyl Disulphide with Olefins

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Bistrifluoromethyl disulphide reacts in a Pyrex vessel with olefins to give adducts which are best described as formed by attack of $\text{CF}_3\text{S}\cdot$ radicals on the olefin. Ethylene gives $\text{CF}_3\text{S}\cdot\text{CH}_2\text{CH}_2\text{S}\cdot\text{CF}_3$; propene $\text{CF}_3\text{S}\cdot\text{CH}(\text{CH}_3)\text{CH}_2\text{S}\cdot\text{CF}_3$; tetrafluoroethylene $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CF}_2)_2\text{S}\cdot\text{CF}_3$ and $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CF}_2)_n\text{S}\cdot\text{CF}_3$ (n large); hexafluoroisopropene $\text{CF}_3\text{S}\cdot\text{S}[\text{CF}(\text{CF}_3)\text{CF}_2]_n\text{S}\cdot\text{CF}_3$ ($n = 1, 2$); 1,1-difluoroethylene $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CH}_2)_n\text{S}\cdot\text{CF}_3$ ($n = 1-6$); trifluoroethylene $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CFH})_n\text{S}\cdot\text{CF}_3$ ($n = 1-7$); chlorotrifluoroethylene $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CFCl})_n\text{S}\cdot\text{CF}_3$ ($n = 1-4$) and also $\text{CF}_2\text{CFCl}\cdot\text{CF}_2\text{CFCl}\cdot\text{S}$ and $\text{CF}_3\text{S}\cdot\text{CF}_2\text{CFCl}\cdot\text{CF}_3$. In most cases the isomers present have been identified.

BISTRIFLUOROMETHYL DISULPHIDE, $\text{CF}_3\text{S}\cdot\text{S}\cdot\text{CF}_3$, has been reported to give bis(trifluoromethylthio)mercury, $(\text{CF}_3\text{S})_2\text{Hg}$, on irradiation in the presence of mercury,¹ trifluoromethylthiodifluoramine, $\text{CF}_3\text{S}\cdot\text{NF}_2$, on irradi-

in the presence of oxalyl chloride.³ All of these reactions are postulated to proceed through $\text{CF}_3\text{S}\cdot$ radicals produced by homolytic cleavage of the S-S bond; $\text{CF}_3\text{S}\cdot$ radicals also being postulated as intermediates in the

TABLE 1

Olefin	(mmole)	$\text{CF}_3\text{S}\cdot\text{SCF}_3$ (mmole)	Re- action time (h)	% Con- version olefin	Products (yield expressed as % total products)	B.p. in K at 760 mmHg ^a	Vapour pressure mmHg at 298 K	<i>M</i> Found	<i>M</i> Calc.				
$\text{CH}_2=\text{CH}_2$	5.69	5.51	44	48.8	(1) $\text{CF}_3\text{S}\cdot\text{CH}_2\text{CH}_2\text{S}\cdot\text{CF}_3$ (100)	383—384 (383) ^b	16.18	230	230				
$\text{CH}_2\text{CH}=\text{CH}_2$	5.91	6.06	20	59.9	(2) $\text{CF}_3\text{S}\cdot\text{CH}(\text{CH}_3)\text{CH}_2\text{S}\cdot\text{CF}_3$ (100)	390—391	17.05	244	244				
$\text{CF}_2=\text{CF}_2$	4.53	4.27 ^c	16	100	(3) $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CF}_2)_2\text{S}\cdot\text{CF}_3$ (3)	400—402	5.25	402	402				
$\text{CF}_3\text{CF}=\text{CF}_2$	6.56	5.32	184	48.5	(4) $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CF}_2)_n\text{S}\cdot\text{CF}_3$	n large (97)	Solid						
					(5) $\text{CF}_3\text{S}\cdot\text{S}[\text{CF}(\text{CF}_3)\text{CF}_2]_n\text{S}\cdot\text{CF}_3$	$n = 1$ (9.5)	369—371 (373) ^c	45.26	352	352			
$\text{CF}_2=\text{CH}_2$	5.92	5.82	26	100	(6)	$n = 2$ (90.5)	426—428 (429—432) ^d	0.64	502	502			
					(7) $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CH}_2)_n\text{S}\cdot\text{CF}_3$	$n = 1$ (67.8)	389—390	14.79	266	266			
					(8) "	$n = 2$ (19.5)	439—440	0.21	330	330			
					(9) "	$n = 3$	Grease		394	394			
					(10) "	$n = 4$ (7.0)	Grease		458	458			
					(11) "	$n = 5$	Grease		522	522			
$\text{CF}_2=\text{CFH}$	6.24	5.78	28	100	(12) "	$n = 6$ (5.5)	Grease		586	586			
					(13) $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CFH})_n\text{S}\cdot\text{CF}_3$	$n = 1$ (36.8)	362—364	51.77	284	284			
					(14) "	$n = 2$ (25.6)	388—390	8.53	366	366			
					(15) "	$n = 3$ (16.8)	435—437	0.09	448	448			
					(16) "	$n = 4$ (12.5)	535—537		530	530			
					(17) "	$n = 5$	Grease		612	612			
					(18) "	$n = 6$ (8.3)	Grease		694	694			
					(19) "	$n = 7$	Grease		776	776			
					$\text{CF}_2=\text{CFCl}$	6.08	5.87 ^e	24	100	(20) $\text{CFCl}\cdot\text{CF}_2\text{CFCl}\cdot\text{S}\cdot\text{CF}_3$	(26)	367—372	Mixture
(21) $\text{CF}_3\text{S}\cdot\text{CF}_2\text{CFCl}\cdot\text{CF}_3$	286	286											
(22) $\text{CF}_3\text{S}\cdot\text{S}(\text{CF}_2\text{CFCl})_n\text{S}\cdot\text{CF}_3$	$n = 1$	318	318										
(23) "	$n = 2$ (24.8)	431—432	0.46	434						434			
(24) "	$n = 3$ (22.2)	469—481		550						550			
(25) "	$n = 4$ (19.9)	Grease		666						666			
(26) "	$n > 4$ (7)	Solid											

^a All boiling points were recorded in semi-micro apparatus at atmospheric pressure and corrected to 760 mmHg. ^b Ref. 8. ^c Ref. 5. ^d Ref. 7. ^e In these cases reactions were also carried out with a 1 : 5 ratio of olefin to disulphide. No new products were observed.

ation in the presence of tetrafluorohydrazine,² and trifluoromethylsulphenyl chloride, $\text{CF}_3\text{S}\cdot\text{Cl}$, on irradiation

¹ G. A. R. Brandt, H. J. Emel us, and R. N. Haszeldine, *J. Chem. Soc.*, 1952, 2198.

² E. C. Stump, jun. and C. D. Padgett, *Inorg. Chem.*, 1964, **3**, 610.

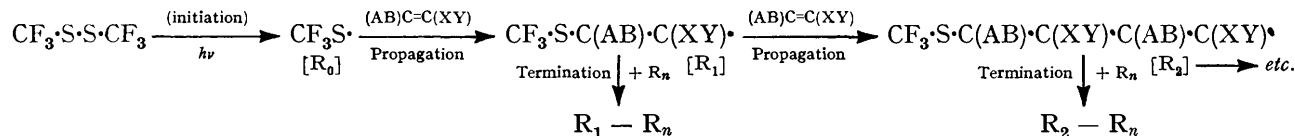
formation of bistrifluoromethyl sulphide, $(\text{CF}_3)_2\text{S}$, on irradiation of $\text{CF}_3\text{S}\cdot\text{S}\cdot\text{CF}_3$ in the absence of mercury.

We have now shown that on irradiation in Pyrex glass

³ B. W. Tattershall and G. H. Cady, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2819.

in the presence of olefins bistrifluoromethyl disulphide undergoes addition and telomerisation reactions (Table 1) which can be readily rationalised in terms of the reactions between trifluoromethylthiyl radicals and the olefins. It is noteworthy that irradiation in quartz does not produce clean products and it appears that the filtering action of the Pyrex towards high energy radiation promotes the formation of the $\text{CF}_3\text{S}\cdot$ radicals. There appears to be no reaction between bistrifluoromethyl disulphide and the olefins in the absence of irradiation.

The reactions can be conveniently discussed in terms of the generalised scheme:



It should be emphasised that the evidence for the successive steps in this scheme is based mainly on the nature of the observed products and not upon kinetic data; however, the scheme is in accord with similar reaction schemes, for example the reaction of trichloromethyl radicals and fluoroethylenes.⁴ The scheme is written with head-to-tail secondary propagation as is generally followed. With partially and fully fluorinated derivatives there is a tendency for telomerisation which is not found with the hydrocarbon analogues so that with the fluoro-olefins the propagation step is being favoured over a termination step. The nature of the products suggests that radical combination is the terminating process in many cases although radical displacement from bistrifluoromethyl disulphide is also a possible terminating step. Radical-displacement steps have been previously postulated in reactions involving trifluoromethylsulphenyl chloride⁵ and dimethyl tetrasulphide.^{6a} Similar reaction schemes have been applied to other examples of addition of disulphides to olefins.^{6c}

Most of the $\alpha\omega$ -bis(trifluoromethylthio)alkanes produced in this study are new although some of the derivatives have been formed previously by the reaction of trifluoromethylsulphenyl chloride with hexafluoropropene [product (5)],⁵ the reaction of trifluoromethanethiol with hexafluoropropene [product (6)],⁷ and the reaction of bis(trifluoromethylthio)mercury with 1,2-dibromoethane [product (1)].⁸

Qualitative identification of trifluoromethylthioalkanes was possible using the characteristic i.r. frequencies

already known for these compounds^{8,9} but these i.r. bands are not sufficiently precise to enable identification of individual compounds; * more precise characterisation was made by n.m.r. spectroscopy and details of chemical shifts are given in Table 2 and of coupling constants in Table 3. In general, the spectra are complex because of coupling along the chain and the fine structure could not be interpreted in all cases. The coupling $^4J(\text{F}_3\text{CSCCH})$ could not be measured and is less than 0.25 Hz. The mass spectra are particularly useful in establishing structure. All of the trifluoromethylthio-derivatives show a relatively strong parent ion (Table 1) and one mode of breakdown appears to be loss of a

CF_3S group from the end of the molecule at which the α -carbon has the least electronegative substituents. Further breakdown appears to occur mainly by successive loss of groups from this end of the molecule although there is also β -fission¹⁰ in which CF_3SCAB^+ groups are formed. The mass spectral data used in detailed assignment of structure have been given below.*

With ethylene and propene there is no detectable telomerisation and from the present results it cannot be determined whether the initial attack of the $\text{CF}_3\text{S}\cdot$ radical is on the CH or CH_2 of propene since the same final product would be formed in either case. The pentafluorosulphur (from SF_5Cl)¹¹ and trifluoromethyl (from CF_3I)¹² radicals are believed to attack the CH_2 groups in reactions with $\text{CH}_3\cdot\text{CH}=\text{CH}_2$. The ^1H n.m.r. spectrum of $\text{CF}_3\cdot\text{S}\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{S}\cdot\text{CF}_3$ (2) is very complex, a situation comparable to that found for $\text{SF}_5\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_3$. This latter spectrum was analysed as an $\text{AB}_4\text{P}_3\text{XYZ}$ system¹³ but (2) should be an $\text{A}_3\text{D}_3\text{P}_3\text{XYZ}$ system and an analysis of the ^1H n.m.r. spectrum was not possible.

When bistrifluoromethyl disulphide reacts with tetrafluoroethylene the only products are $\text{CF}_3\cdot\text{S}\cdot(\text{CF}_2\text{CF}_2)_n\cdot\text{S}\cdot\text{CF}_3$ with $n = 2$ and $n =$ a large number. Even when the ratio of $\text{CF}_3\cdot\text{S}\cdot\text{S}\cdot\text{CF}_3$ to $\text{CF}_2=\text{CF}_2$ is increased to 5 : 1 the only liquid product isolated is $\text{CF}_3\cdot\text{S}\cdot(\text{CF}_2\cdot\text{CF}_2)_2\cdot\text{S}\cdot\text{CF}_3$ and $\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CF}_3$ was never isolated from the reaction. The $\text{CF}_3\cdot\text{S}\cdot\text{S}\cdot\text{CF}_3$ -induced polymerisation of tetrafluoroethylene¹⁴ under high pressures and with high

⁷ J. F. Harris, jun., and F. W. Stacey, *J. Amer. Chem. Soc.*, **1961**, **83**, 840.

⁸ J. F. Harris, jun., *J. Org. Chem.*, **1967**, **32**, 2063.

⁹ S. N. Nabi and N. Sheppard, *J. Chem. Soc.*, **1959**, 2429.

¹⁰ E. J. Levy and W. A. Stahl, *Analyt. Chem.*, **1961**, **33**, 707.

¹¹ J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, **1961**, 2066.

¹² R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, **1953**, 1199.

¹³ N. Boden, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **1963**, **59**, 620.

¹⁴ U.S.P. 3,023,196 (*Chem. Abs.*, **1962**, **57**, 10,038d).

* Full data for all compounds have been deposited with the National Lending Library SUP. No. 20197 (29 pp., 1 microfiche). See note about Supplementary Publications in Notice to Authors, No. 7, in the index issue of *J. Chem. Soc. (C)*, 1970.

⁴ J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, **1966**, **62**, 1859.

⁵ J. F. Harris, jun., *J. Amer. Chem. Soc.*, **1962**, **84**, 3148.

⁶ (a) T. L. Pickering, K. J. Saunders, and A. V. Tobolsky; (b) C. G. Krespan, 'The Chemistry of Sulphides,' ed. A. V. Tobolsky, Interscience, New York, **1968**, p. 61, 211; (c) F. W. Stacey and J. F. Harris, *Org. Reactions*, **1963**, **13**, 151.

temperatures may well give trifluoromethylthio-containing polymers analogous to the telomers formed in the present reaction.

The reaction between bistrifluoromethyl disulphide and hexafluoropropene gives two products, $\text{CF}_3\cdot\text{S}[\text{CF}(\text{CF}_3)\cdot\text{CF}_2]_n\cdot\text{S}\cdot\text{CF}_3$ [$n = 1$ and 2 , (5) and (6)]. For (5) the structure is unambiguous and the n.m.r.

the CF_3S group is a broad triplet confirming (6a), containing a $\text{CF}_3\cdot\text{S}\cdot\text{CF}_2$ group, as the structure. The CF_2 group appears as a close-spaced 1:1 doublet showing non-equivalence. The mass spectrum shows an intense peak at m/e 151 attributed to $\text{CF}_3\text{SCF}_2^+$ again confirming (6a), the structure which would be expected from previous results of radical additions to hexafluoro-

TABLE 2
Chemical shifts in ^{19}F and ^1H n.m.r. spectra

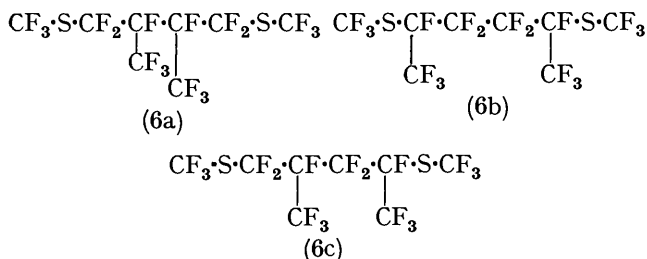
	$\delta_{\text{CF}_3\text{S}}$	δ_{CF_3}	δ_{CF}	δ_{CF_2}	δ_{CH_2}	δ_{CH}	δ_{CH_3}	
(1) $\text{CF}_3\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CF}_3$	+41.9				+2.94		+1.33	
(2) $\text{CF}_3\cdot\text{S}\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{S}\cdot\text{CF}_3$	(ii) +40.3							
(i) (ii)	(i) +42.1							
(3) $\text{CF}_3\cdot\text{S}\cdot(\text{CF}_2\cdot\text{CF}_2)_2\cdot\text{S}\cdot\text{CF}_3$	(i) +35.3	(ii) +85.5						
(i) (ii) (iii)	(iii) +118.7							
(5) $\text{CF}_3\cdot\text{S}\cdot\text{CF}(\text{CF}_3)\cdot\text{CF}_2\cdot\text{S}\cdot\text{CF}_3$	(i) +33.6	+78.2	+156.9	+74.1				
(i) (ii)	(ii) +35.2							
(6a) $\text{CF}_3\cdot\text{S}[\text{CF}(\text{CF}_3)\cdot\text{CF}_2]_2\cdot\text{S}\cdot\text{CF}_3$	+36.4	+71.5	+164.7	+69.1				
(7) $\text{CF}_3\cdot\text{S}[\text{CF}_2\cdot\text{CH}_2]_2\cdot\text{S}\cdot\text{CF}_3$	(i) +37.2	+73.7			+3.65			
(i) (ii)	(ii) +42.4	+71.3						
(8a) $\text{CF}_3\cdot\text{S}\cdot\text{CH}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CF}_3$	+42.4	+113.0			} +3.78			
(8b) $\text{CF}_3\cdot\text{S}\cdot\text{CH}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CH}_2\cdot\text{CF}_2\cdot\text{S}\cdot\text{CF}_3$	(iv) +36.0	(iii) +62.1				} +2.41		
(i) (ii) (iii) (iv)	(i) +42.0	(ii) +89.9						
(13) $\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CFH}\cdot\text{S}\cdot\text{CF}_3$	(i) +36.2	+74.7	+221.1			+6.32		
(i) (ii)	(ii) +40.6							
(14a) $\text{CF}_3\cdot\text{S}\cdot\text{CFH}\cdot\text{CF}_2\cdot\text{CF}\cdot\text{H}\cdot\text{CF}_2\cdot\text{S}\cdot\text{CF}_3$	(i) +36.7	(iii) +117.5	(ii) +198.9		} +7.02—6.30			
(i) (ii) (iii) (iv) (v) (vi)	(vi) +41.7	(v) +75.4	(iv) +212.1			} +6.17—5.15		
(i) (ii) (iii) (iv) (v) (vi)	+41.3	+121.5	+222.2				} +5.02—4.23	
(14b) $\text{CF}_3\cdot\text{S}\cdot\text{CFH}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CFH}\cdot\text{S}\cdot\text{CF}_3$		(i) +94.3	(ii) +68.2					
(20) $\text{CF}_2\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{S}\cdot\text{CFCl}\cdot\text{CF}_2$	(iii) +64.6	(iv) +78.7						
(i) (ii)								
(21) $\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{CF}_3$	+35.4	+78.7	+75.7	+90.8				
(23a) $\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{S}\cdot\text{CF}_3$	(i) +37.1	(ii) +73.6	(iii) +73.4					
(i) (ii) (iii) (iv) (v) (vi)	(vi) +33.4	(iv) +118.7	(v) +80.3					
(23b) $\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{S}\cdot\text{CF}_3$	+35.5	+76.5	+78.4					
(24b) $\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{CFCl}\cdot\text{CF}_2\cdot\text{S}\cdot\text{CF}_3$	+35.0	+76.6	+78.2					
		+119.8						
(25c) $\text{CF}_3\cdot\text{S}(\text{CF}_2\cdot\text{CFCl})_2(\text{CFCl}\cdot\text{CF}_2)_2\cdot\text{S}\cdot\text{CF}_3$	+34.8	+71.5	+125.6					

TABLE 3

Coupling constants (Hz)

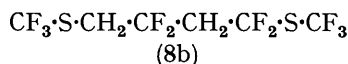
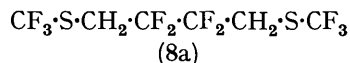
Compound	$J_{\text{CF}_3\cdot\text{S}\cdot\text{CF}_2}$	$J_{\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}_2}$	$J_{\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2}$	$J_{\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2}$	$J_{\text{H}_1\text{F}_1}$	$J_{\text{H}_1\text{F}_2}$	$J_{\text{F}_1\text{F}_2}$
$\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}(\text{CF}_3)\cdot\text{S}\cdot\text{CF}_3$	10.4	3.8	11.2	5.5			
$\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CF}(\text{CF}_3)\cdot\text{CF}(\text{CF}_3)\cdot\text{CF}_2\cdot\text{S}\cdot\text{CF}_3$	10.3						
$\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CF}_3$	10.9	5.8				14.1	
$\text{CF}_3\cdot\text{S}\cdot\text{CF}_2\cdot\text{CFH}\cdot\text{S}\cdot\text{CF}_3$	10.7	3.6	10.9	3.7	56.4	5.8	13.1

spectrum is in agreement with that in the literature.⁵ For $n = 2$ there are three possible structures [(6a)—(6c)].



propene where preferential reaction is with the CF_2 group.¹⁵⁻¹⁷

The reaction between bistrifluoromethyl disulphide and 1,1-difluoroethylene ($\text{A}=\text{B}=\text{H}$, $\text{X}=\text{Y}=\text{F}$) gives the series of adducts $\text{CF}_3\cdot\text{S}(\text{CH}_2\cdot\text{CF}_2)_n\cdot\text{S}\cdot\text{CF}_3$ ($n = 1-6$). There are three possible structures for the $n = 2$ compound but only two of these (8a) and (8b) have been



identified in the mixture of products. Compound (8a) is

¹⁶ J. M. Tedder and J. C. Walton, *Trans. Faraday Soc.*, 1967, **63**, 2678.

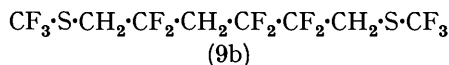
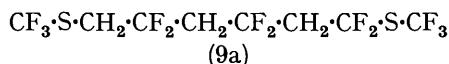
¹⁷ R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1954, 923.

The ^{19}F n.m.r. spectrum is simple and indicates the presence of only one isomer, for which four signals imply a symmetrical structure. The ^{19}F signal attributed to

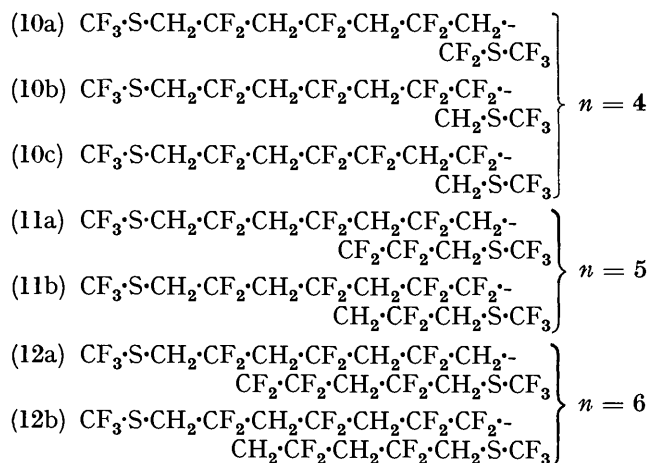
¹⁵ G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1963, 1083.

identified by the chemical shifts $\delta_{\text{CF}_3\text{S}} = 42.4$ p.p.m. typical of a $\text{CF}_3\text{S}\cdot\text{CH}_2$ group and $\delta_{\text{CF}_2} = 113.0$ p.p.m. typical of a $\text{CF}_2\text{CF}_2\cdot\text{CH}_2$ group. The presence of (8b) is shown by $\delta_{\text{CF}_3\text{S}\cdot\text{CF}_2} = 36.0$ p.p.m., $\delta_{\text{CF}_3\text{S}\cdot\text{CH}_2} = 42.0$ p.p.m., $\delta_{\text{CF}_2\text{S}\cdot\text{CF}_2\text{CH}_2} = 62.1$ p.p.m., and $\delta_{\text{OH}\cdot\text{CF}_2\text{CH}_2} = 89.9$ p.p.m. From the ^{19}F n.m.r. spectrum the approximate relative proportion of (8a) to (8b) is 4 to 1. The mass spectrum of the mixture shows a high abundance of the $\text{CF}_3\text{SCH}_2^+$ ion (m/e 115, relative abundance 100) with a trace of the $\text{CF}_3\text{SCF}_2^+$ ion (m/e 151, relative abundance 1).

The $n = 3, 4$ and $n = 5, 6$ compounds occur as two separable fractions but it was not possible to separate the individual components of the mixture. The yields are relatively low and good n.m.r. spectra could not be obtained. The signals of $\text{CF}_3\text{S}\cdot\text{CH}_2$ groups could be identified in the ^{19}F n.m.r. spectra and the ^1H spectra are very similar to those of the $n = 2$ compounds, (8a) and (8b). The mass spectral breakdown patterns, however, allow some indication to be obtained of the structures of the $n = 3, 4, 5,$ and 6 compounds. For $n = 3$, (9), the parent ion is observed at m/e 394 and ions are observed corresponding to loss of CF_3S ($m/e = 293$), CF_3SCH_2 ($m/e = 279$), $\text{CF}_3\text{S}\cdot\text{CH}_2\cdot\text{CF}_2$ ($m/e = 229$), $\text{CF}_3\text{S}\cdot\text{CH}_2\cdot\text{CF}_2\cdot\text{CH}_2$ ($m/e = 215$), $\text{CF}_3\text{S}\cdot\text{CH}_2\cdot\text{CF}_2\cdot\text{CF}_2$ ($m/e = 179$), $\text{CF}_3\text{S}\cdot\text{CH}_2\cdot\text{CF}_2\cdot\text{CH}_2\cdot\text{CF}_2$ and $\text{CF}_3\text{S}\cdot\text{CH}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CH}_2$ ($m/e = 165$), $\text{CF}_3\text{S}(\text{CH}_2\cdot\text{CF}_2)_2\cdot\text{CH}_2$ ($m/e = 151$), and $\text{CF}_3\text{S}(\text{CH}_2\cdot\text{CF}_2)_2\cdot\text{CF}_2$ ($m/e = 115$). This breakdown pattern suggests that (9) consists of the isomers (9a) and (9b) although traces of other isomers would



clearly not be identified by this method. In a similar manner the structures of the other compounds making up these fractions were deduced to be

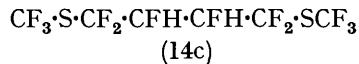
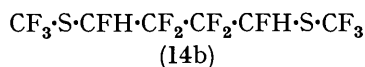
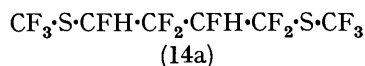


The free radical addition reactions to 1,1-difluoroethylene have been extensively investigated^{4,15,17-19}

¹⁸ J. F. Harris, jun. and F. W. Stacey, *J. Amer. Chem. Soc.*, 1963, **85**, 749.

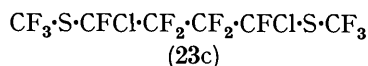
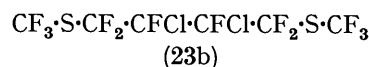
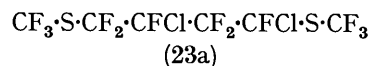
the systems studied including the reactions of $\text{CF}_3\text{S}\cdot$ radicals produced from trifluoromethanethiol.⁸ In every case the radical was found to add exclusively to the CH_2 end of the olefin as appears to be the case in the present work. No trace was found of higher telomers although there seems no reason why these should not be present. They would be relatively involatile and this could be the reason for the failure to identify them.

It has been previously shown that free-radical addition to trifluoroethylene occurs by radical attack at both ends of the olefin although predominant attack is at the CHF end.^{4,8,18,20} In the reaction between bistrifluoromethyl disulphide and trifluoroethylene products $\text{CF}_3\text{S}(\text{CHF}\cdot\text{CF}_2)_n\text{S}\cdot\text{CF}_3$, $n = 1$ to 7 are obtained. The $n = 2$ fraction is shown by ^{19}F n.m.r. spectra and by mass spectroscopy to consist of two, (14a) and (14b), of the three possible isomers; (14c) was not observed in



the fraction. In view of the complexity of the system it is not possible to make positive identification of all of the higher telomers formed in this reaction. Both identified products would be formed by radical attack on the CHF end of trifluoroethylene.

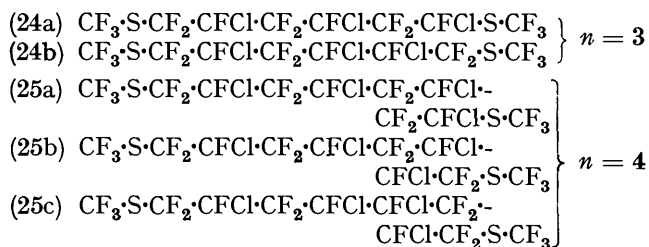
Previous studies on free-radical addition to chlorotrifluoroethylene have shown that for most radicals, addition takes place exclusively at the CF_2 end of the olefin.^{5,8,18,20} In the reaction between bistrifluoromethyl disulphide and chlorotrifluoroethylene ($\text{A}=\text{B}=\text{X}=\text{F}$, $\text{Y}=\text{Cl}$) the initial reaction appears to be exclusively at the CF_2 end of the olefin. $\text{CF}_3\text{S}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{S}\cdot\text{CF}_3$ (22) is not formed in any great quantity even when the ratio of disulphide to olefin is raised to 5:1. The $n = 2$ component is found by ^{19}F n.m.r. and mass spectroscopy to consist of a mixture of the isomers (23a) and (23b), (23c) being absent as would be expected if initial attack of the $\text{CF}_3\text{S}\cdot$ radical were in the



¹⁹ P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 1955, **77**, 2783; P. Tarrant and M. R. Lilyquist, *ibid.*, p. 3640; R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 1956, 61; S. E. Braslavsky, F. Casas, and O. Cifuentes, *J. Chem. Soc. (B)*, 1970, 1059.

²⁰ R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1957, 2800; A. T. Coscia, *J. Org. Chem.*, 1961, **26**, 2995; T. J. Dougherty, *J. Amer. Chem. Soc.*, 1964, **86**, 461; R. E. Banks, R. N. Haszeldine, and W. D. Morton, *J. Chem. Soc. (C)*, 1969, 1947; H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Trans. Faraday Soc.*, 1970, **66**, 2038.

direction indicated. The $n = 3$ and $n = 4$ components have been shown by mass spectroscopy to consist of isomers (24a) and (24b), and (25a), (25b), and (25c) respectively, n.m.r. spectroscopy showing a preponderance of (24b) and (25c) in the two fractions



A low yield of high telomers was found but was not separated or identified.

The $n = 1$ compound is found in the least amount in a mixture containing 1,3-dichlorohexafluorothioloan (20), and 1-trifluoromethylthio-2-chlorohexafluoropropane (21). The presence of these two rather unexpected products can be accounted for by a mechanism similar to that invoked to explain the surprisingly large amounts of octafluorothioloan produced during the copolymerisation of tetrafluoroethylene with tetrafluoroethiiran.⁶⁶ A $\text{CF}_3 \cdot \text{S} \cdot \text{CF}_2 \cdot \text{CFCl} \cdot \text{CF}_2 \cdot \text{CFCl} \cdot$ radical can undergo conventional reactions as already indicated but could undergo intramolecular attack on sulphur to form the thioloan (20) with elimination of a $\text{CF}_3 \cdot$ radical which could be picked up by $\text{R}_1 \cdot$ to give the propane (21).

EXPERIMENTAL

Materials were handled in a Pyrex vacuum system using standard vacuum techniques. The gas phase, room-

⁶⁶ R. H. Pierson, A. H. Fletcher, and E. St. Clair Gantz, *Analyt. Chem.*, 1956, **28**, 1218.

temperature reactions were carried out in Pyrex flasks (*ca.* 120-ml volume and 40-mm diameter) fitted with Rotaflo Teflon stop-cocks. Irradiation was carried out with a Hanovia 12277 medium-pressure mercury-arc lamp. I.r. spectra were recorded in the gas phase or in carbon tetrachloride and dioxan solutions over the range 4000—250 cm^{-1} with a Perkin-Elmer 457 spectrophotometer. ^1H and ^{19}F n.m.r. spectra were recorded, generally on neat liquid samples, with a Perkin-Elmer R10 spectrometer operating at 60 and 56.4 MHz respectively. Tetramethylsilane and trichlorofluoromethane were used as external references. Mass spectra were recorded on A.E.I. MS 12 and MS 9 mass spectrometers; molecular weights were generally determined by mass spectrometry.

Commercial bistrifluoromethyl disulphide (Peninsular ChemResearch Inc.), was purified by trap-to-trap distillation. The i.r. spectrum of the ethylene ²¹ (Matheson Co.) showed some ethane present as impurity but the propene ²¹ (Matheson Co.), tetrafluoroethylene,²² hexafluoropropene,²² 1,1-difluoroethylene,²² trifluoroethylene,²² and chlorotrifluoroethylene ²² (Peninsular ChemResearch Inc.) were pure according to their i.r. spectra.

The general procedure was as follows. Known quantities in a 1:1 molar ratio of the olefin and bistrifluoromethyl disulphide were condensed into the reaction flask so that at room temperature the total pressure of the reactants was *ca.* 1 atmos. The flask and contents were irradiated until no more liquid product was seen to collect at the bottom of the flask. The contents of the flask were fractionated and examined by standard techniques. The detailed quantities of reactants are given in Table 1. Where full analyses (by Bernhardt) were carried out on the products the results confirm the suggested formulae of the compounds.

We thank the Ministry of Defence for financial support for this work.

[1/1209 Received, July 14th, 1971]

²² J. H. Simons, ed., 'Fluorine Chemistry,' vol. II, Academic Press, New York, 1954, p. 476.