2-substituted butadienes offer a sensitive probe to distinguish between a diradical intermediate and a concerted pathway. Encumbrance of the dipolarophilic center and diradical stabilization lead to opposite predictions for the activity of substituted *vs.* unsubstituted double bonds.

Other 1,3 dipoles show analogous phenomena. Diphenylnitrilimine adds to the less encumbered double bond of isoprene 4.0 times faster than to the one bearing the methyl group.[61]

Historical Note.—The cycloadditions of aliphatic diazo compounds were discovered[62] in 1888, and those of organic azides[63] in 1893. In a very valuable paper, published in 1938, Smith[64] collected the available data on 1,3 additions without differentiating between additions of bases H–B and cycloadditions. The special driving force for the cyclic reaction path stemming from a fundamentally dissimilar mechanism was not recognized. In 1938 (as in 1900) only cycloadditions of diazoalkanes and azides were known.

That Staudinger's nitrenes[65] and nitrones were considered in this paper[64] as formally derived from ketenes and allenes did not contribute to a clear classification of dipolar reagents. Perhaps for this reason, Smith's review did not attract much attention as shown by the small number of papers on the subject published between 1938 and 1958.

We have reported elsewhere the train of thought which led to the general concept of 1,3-dipolar cycloaddition in 1958;[66] the original mechanistic consideration concerned the addition of diazoalkanes to angle-strained double bonds.

Another generalization recently revealed a synthetic principle which makes accessible a large number of six-membered heterocycles.[67] The term *1,4-dipolar cycloaddition* should not be misinterpreted; there is good experimental evidence and theoretical reason to characterize this scheme as a two-step process passing through a zwitterionic intermediate.[68] The *1,4 dipole* combines only with those dipolarophiles which display pronounced electrophilic or nucleophilic reactivity. This limits severely the range of applicable dipolarophiles.[69]

Just the opposite is observed for *1,3-dipolar cycloaddition.* Here nearly every multiple-bond system including heteroatoms can act as a dipolarophile. The result is an amazingly wide scope of this synthetic principle[16] which is far from being exhausted. It is a fascinating idea that 1,3-dipolar addition owes this wide scope to the concerted mechanism which avoids the necessity of charge separation along the reaction pathway.

The position that 1,3-dipolar cycloadditions, at least those studied so far, do *not* conform to one general mechanism is unfounded.

---

[61] Experiments by W. Fliege, München, 1967.

[62] E. Buchner, *Ber. Deut. Chem. Ges.*, **21**, 2637 (1888).

[63] A. Michael, *J. Prakt. Chem.*, [2] **48**, 94 (1893).

[64] L. I. Smith, *Chem. Rev.*, **23**, 193 (1938).

[65] Staudinger's nitrenes had another structure. Cycloadditions of azomethine ylids *alias* nitrenes were first described by R. Huisgen, R. Grashey, and E. Steingruber, *Tetrahedron Lett.*, 1441 (1963).

[66] R. Huisgen, *Proc. Chem. Soc.*, 357 (1961).

[67] R. Huisgen and K. Herbig, *Ann.*, **688**, 98 (1965).

[68] R. Huisgen, M. Morikawa, K. Herbig, and E. Brunn, *Chem. Ber.*, **100**, 1094 (1967).

[69] A brief review on 1,4-dipolar cycloaddition will be published in the Proceedings of the First International Congress of Heterocyclic Chemistry, Interscience Publishers, Inc., New York, N. Y., 1968.

Photochemistry of Cyclic Mercaptoles[1]

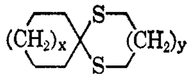
James D. Willett,[2] John R. Grunwell, and Glenn A. Berchtold[3]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received October 11, 1967

The photochemistry of the mercaptoles **1**–**4** has been investigated. The major pathway for reaction of the ethylene mercaptoles **1** and **2** involved elimination of the elements of ethylene sulfide to form the corresponding cyclic thione which was isolated as the dimer in the case of **1**. The thione or its dimer underwent secondary photochemical reactions to form the corresponding disulfide, sulfide, and mercaptan. The major pathway for reaction of the propylene mercaptoles, **3** and **4**, involved over-all isomerization of one of the geminal sulfur atoms to an adjacent carbon atom; the ratio of *cis/trans* product in each case was approximately 8:1.

The ultraviolet spectra of mercaptals and mercaptoles show an absorption band in the region of 235–250 $m\mu$ ($\epsilon \sim 250$–850) which has been attributed to an excited state involving sulfur–sulfur interaction.[4,5] In view of this excited-state interaction, the photochemistry of mercaptoles has been investigated to determine the nature of products from excitation at this long-wavelength absorption band. The compounds selected for study were the ethylene and propylene mercaptoles **1**–**4**. Mercaptole **1** was studied under a variety of conditions to determine those which gave optimum yield of the major products; these conditions were then applied to mercaptoles **2**–**4**.



1, $x = 1$; $y = 0$　**3**, $x = 1$; $y = 1$

2, $x = 0$; $y = 0$　**4**, $x = 0$; $y = 1$

The photolysis of 1,4-dithiaspiro[4.5]decane (**1**) under various conditions yielded the product mixtures listed in Table I. Runs 5–7 were analyzed only for the major product (**7**). A thin film of brown polymer coated the walls of the reaction vessel when the Hanovia high-pressure Hg lamp was used; no such polymer formation was observed with the low-pressure Hg lamps. Cyclohexane, n-hexane, and Freon-113 were satisfactory solvents. The formation of a similar product mixture in these three solvents indicates that no significant amount of products arises from reaction with solvent. No reaction was observed in anhydrous methanol.

---

[1] Supported by National Science Foundation Grant No. GP-5761.

[2] National Institutes of Health Predoctoral Fellow.

[3] Alfred P. Sloan Fellow, 1963–1967.

[4] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, **71**, 84 (1949).

[5] S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 437 (1964).

SCHEME I

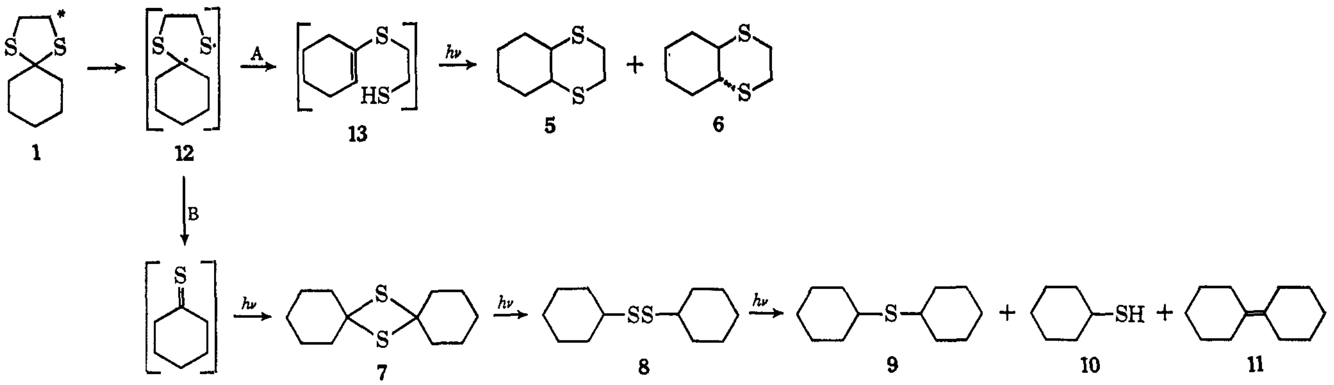


TABLE I

PRODUCTS FROM PHOTOLYSIS OF 1

Reaction no.	Light source[a]	Solvent	Concn, *M*	Time, hr	Products, % yield 5	6	7	8	9	10	11	Unreacted 1
1	A	Cyclohexane	0.112	94.5	<1	1	9	11	4	2	2	66
2	B	Cyclohexane	0.16	9	<1	<1	14	2	2	1	1	76
3	B	*n*-Hexane	0.12	8	<1	<1	23	3	1	<1	<1	68
4	B	Freon-113	0.12	12	1	2	13	<1	2	1	<1	75
5	A	Cyclohexane	0.08	5			5					
6	A	Cyclohexane	0.034	10			4					
7	A	Methanol	0.20	16			0					

[a] A means a Hanovia type A, 550-W lamp; B means Rayonet photochemical reactor, 2537-Å, low-pressure Hg vapor lamps.

The major product was 7,14-dithiadispiro[5.1,5.1]-tetradecane (**7**) and it was the first product detected when the reaction was followed by gas chromatography. The yield of **7** reached its maximum value at 8–12 hr; continued photolysis slowly decreased the yield of **7** but increased the yield of **8–11**. Since this behavior indicates **7** was undergoing further photochemical reaction, the photolysis of **7** was investigated. After a period of 8 hr, **7** was converted in 8.5% yield into the disulfide **8**. Photolysis of this disulfide (**8**) produced **9** (1%), **10** (2%), **11** (1%), and **7** (2%). The remainder of the reaction mixture was unreacted disulfide. These results are in agreement with the previously reported photochemical studies of disulfides.[6-8]

It appears that photo-excited mercaptole **1** fragments to the diradical **12** which undergoes further reaction by either one of two pathways (Scheme I, A or B). Evidence for the intermediacy of **12** rests on the esr spectrum[9] obtained during photolysis of pure **1** at liquid nitrogen temperatures. The spectrum shows an unsymmetrical pattern with five distinct *g* values: three are indicative of the primary sulfur radical[10] (2.0261, 2.0056, 1.9968) and the remaining (2.0168, 1.9831) may be due to the tertiary carbon radical adjacent to sulfur. Although no evidence exists for the intermediacy of **13**, it would appear to be a reasonable intermediate in the formation of the dithians **5** and **6**, particularly in view of the ratio of *cis/trans* isomers obtained in the photolysis of mercaptoles **3** and **4** as described later. Intermediate **13** could arise from **12** through intramolecular hydrogen atom abstraction by the primary sulfur radical. The possibility of a concerted migration of the sulfur atom or hydrogen atom can not be excluded by the data available.

The formation of **7** undoubtedly proceeds through initial formation of cyclohexanethione. Solutions of **1** immediately turn pink on irradiation; cyclohexane thione is deep red in color, λ_{max} 495 mμ (ϵ 10).[7,11] Products **8–11** arise from **7** as described earlier. The formation of **7** in the photolysis of the disulfide **8** undoubtedly proceeds through formation of cyclohexanethione. Rosengren[8] has shown that **8** is converted into cyclohexanethione on photolysis in a rigid glass at 77°K.

The conditions selected for photolysis of **2–4** were cyclohexane solvent and the Rayonet 2537-Å low-pressure Hg vapor lamp source. The results are listed in Table II.

The photochemistry of 1,4-dithiaspiro[4.4]nonane, **2**, appeared to be essentially the same as **1**. The presence of dithians **14** and **15** was indicated by comparison of the mass spectra of samples collected by gas chromatography with authentic samples. The small quantities available from the photochemical reaction, however, were not pure and could not be separated from the contaminating materials.

The predominant reaction involves elimination of the elements of ethylene sulfide with formation of cyclopentanethione (**16**). Although the dimer of thione **16** has been isolated from other photochemical reactions,[12] there was no evidence for its formation in this reaction. Either the dimer undergoes photochemical reaction as rapidly as it is formed or the excited thione reacts to form **17–19** in preference to dimerization. The major product in this reaction, **19**, arises from reaction of thione **16** with solvent. Although **17** could arise from

---

[6] C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **81**, 1137 (1959).

[7] K. Rosengren, *Acta Chem. Scand.*, **16**, 1401 (1962).

[8] K. Rosengren, *ibid.*, **16**, 2284 (1962).

[9] We wish to thank Professor K. Bowers of this department for measuring the spectrum.

[10] J. J. Windle, A. K. Wiersema, and A. L. Tappel, *J. Chem. Phys.*, **41**, 1996 (1964).

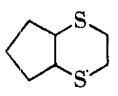
[11] M. J. Janssen, *Rec. Trav. Chim. Pays-Bas*, **79**, 464 (1960).

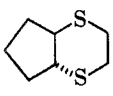
[12] M. C. Panek and G. A. Berchtold, unpublished work from these laboratories.

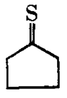
TABLE II

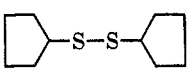
PRODUCTS FROM PHOTOLYSIS OF 2–4

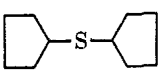
Mercaptole	Concn, *M*	Time, hr	Products (% yield)							Unreacted starting material (%)
2	0.121	18	**14** (<3)	**15** (<1)	**16** (4)	**17** (5)	**18** (3)	**19** (14)	**20** (1)	**2** (64)
3	0.182	42.5	**21** (40)	**22** (6)						**3** (12)
4	0.113	8	**23** (39)	**24** (5)						**4** (55)

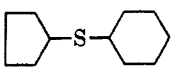

14

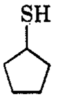

15

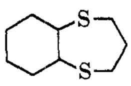

16

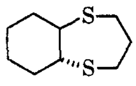

17

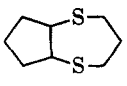

18

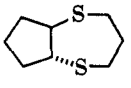

19


20


21


22


23


24

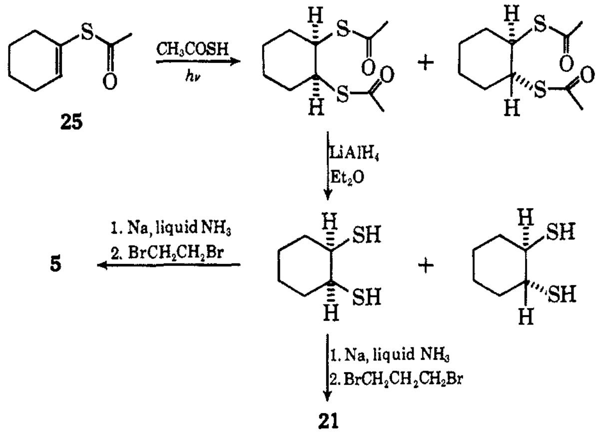
the thione dimer, it is probably formed from dimerization of the cyclopentane thiyl radical.

1,5-Dithiaspiro[5.5]undecane, **3**, undergoes photochemical reaction to the two isomers, **21** and **22**, listed in Table II. These two products and unreacted mercaptole **3** account for 58% of the starting material. There are at least 13 other components in the reaction mixture, all of which are formed only in minor yield. The rate of formation of **21** and **22** leveled off after approximately 8 hr. In a similar fashion, the photolysis of 1,5-dithiaspiro[5.4]decane, **4**, showed little change after 8 hr and produced **23** and **24** as the major products with only slight traces of minor products.

Thus, it appears that the major pathway for reaction of the diradical, initially formed from the propylene mercaptoles, involves hydrogen atom abstraction by the primary thiyl radical to form the 3-mercaptopropylthiocycloalkene which then undergoes cyclization. The ratio of *cis/trans* isomers from mercaptoles **3** and **4** are essentially that which one would expect from radical addition of mercaptan to the substituted olefinic system.[13]

The structures of all photochemical products except **7** and **16** were established by comparison with authentic samples. The structure of **7** was unambiguous from the spectral data and analysis. The structure of thione **16** was assigned on the basis of its visible spectrum, $\lambda_{\max}^{\mathrm{EtOH}}$ 495 mμ, and its gas chromatographic retention time. It rapidly polymerized on standing. The synthesis of all authentic samples was straightforward (see Experimental Section) except for the *cis* isomers **5**, **14**, **21**, and **23**. The authentic samples of **5** and **21** were prepared as follows. Pyrolysis of the diacetate of 1,1-cyclohexanedithiol produced 1-cyclohexene thiolacetate (**25**) which was converted into an 85:15 mixture of *cis*- and *trans*-1,2-cyclohexane bisthiolacetates by the light-catalyzed addition of thiolacetic acid. Reduction of the mixture with lithium aluminum hydride gave a similar mixture of *cis*- and *trans*-1,2-cyclohexanedithiols in quantitative yield which were separated by distillation. Cyclization of the bis sodium salt of the *cis* isomer with 1,2-dibromoethane and with 1,3-dibromopropane produced **5** and **21**, respectively (Scheme II).

SCHEME II



The authentic samples of **14** and **23** were prepared in a similar fashion from 1-cyclopentene thiolacetate except that the *cis–trans* isomers were separated by distillation as the diacetates and the pure *cis*-1,2-cyclopentane bisthiolacetate was reduced to the *cis*-dithiol.

Experimental Section[14]

Photolysis of 1,4-Dithiaspiro[4.5]decane (1). **A.**—A solution of 11.15 g (0.064 mol) of 1[15] [$\lambda_{\max}^{\mathrm{EtOH}}$ 242 mμ (ϵ 316)] in 350 ml of reagent grade cyclohexane[16] was irradiated for a period of 9 hr in a Rayonet photochemical reactor[17] using lamps with a maximum output at 2537 Å. A stream of oxygen-free, dry nitrogen was passed through the solution during the photolysis and then through a Dry Ice–acetone trap followed by a solution of bromine in carbon tetrachloride. After 30 min the solution had turned from colorless to bright pink; after 4 hr the solution had become and remained pale orange. At no time was any insoluble polymeric material noted. The crude photolysis solution was concentrated *in vacuo* to yield 9.94 g of an orange liquid. The mixture was analyzed by gas chromatography; the temperature was programmed from 100–230° at a rate of 2°/min. Comparison with authentic samples showed the mixture to consist of the components listed with reaction no. 2 of Table I. The Dry Ice–acetone trap contained only solvent and a trace of white polymeric material. The bromine in CCl_4 solution contained 1,2-dibromoethane corresponding to an 18% yield of ethylene as determined by integrating the nmr spectrum of a known volume of

---

[13] N. A. LeBel and A. DeBoer, *J. Amer. Chem. Soc.*, **89**, 2784 (1967), and references cited therein.

[14] All melting points are corrected, and all boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 237 or 337 recording spectrophotometer. The ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The nmr spectra were recorded on a Varian A-60 nmr spectrometer, and chemical-shift data are given in parts per million (ppm) downfield from tetramethylsilane as an internal standard. Mass spectra were recorded on a Consolidated Electrodynamics Model 21-130 mass spectrometer with an ionizing potential of 68 V and are recorded in percentages relative to the most intense peak as 100%. Elemental analyses were performed by Scandinavian Microanalytical Laboratory or Galbraith Laboratories, Inc. Gas chromatograms were recorded on an F & M Model 810 gas chromatograph and were calibrated with bicyclohexyl as an internal standard; the column used was an 8-ft 20% SE-30 on Chr P, 80–100 mesh.

[15] H. Fuhrer and H. Günthard, *Helv. Chim. Acta*, **45**, 2036 (1962).

[16] Passed through Merck acid-washed alumina prior to use.

[17] Southern New England Ultraviolet Co., Middletown, Conn., Model RPR 100: 35 W; reactor barrel, 10 in. (diameter) by 15 in. (depth).

solution containing a known amount of *p*-dichlorobenzene as a reference standard.

The structure of **7** was established from the following data: mp 128–129° (lit.[18] 132–133°); $\nu_{max}^{CCl_4}$ 2955, 2945, 2930, 2855, 2845, 1450, 1435, 1425, 1270, 1255, 1245, and 1195 cm^{-1}; λ_{max}^{EtOH} 285 mμ (ϵ 34); mass spectrum, *m/e* 228 (11%), 185 (2%), 114 (100%), 109 (4%), 81 (87%), and 71 (39%).

Anal. Calcd for $C_{12}H_{20}S_2$: C, 63.09; H, 8.82; S, 28.07. Found: C, 63.19; H, 8.81; S, 28.09.

B.—A solution of 10 g (0.056 mol) of **1** in 500 ml of cyclohexane[16] was irradiated with a 550-W Hanovia, type A, mercury arc lamp contained in a water-cooled quartz immersion well. The solution was swept continuously with a stream of oxygen-free, dry nitrogen. The nitrogen stream was passed through a Dry Ice–acetone trap and then through a solution of bromine in CCl_4. The irradiation was continued for a period of 94.5 hr; it was necessary to clean the immersion well of a thin brown polymeric film 11 times during the course of the photolysis. At the end of the photolysis the clear golden yellow solution was concentrated *in vacuo* to yield 9.80 g of orange-brown liquid which was analyzed by gas chromatography as described in A. The results are listed with reaction 1 in Table I.

The other photolyses of **1** listed in Table I were carried out as described in part A or B depending on the light source used.

Photolysis of 2, 3, and 4.—The photolysis of **2**[19] [λ_{max}^{EtOH} 245 mμ (ϵ 274)], **3**[20] [λ_{max}^{EtOH} 247.5 mμ (ϵ 833)], and **4** [$\lambda_{max}^{isooctane}$ 251 mμ (ϵ 732)] was carried out as described in section A for the photolysis of **1**. The conditions and the product analyses are listed in Table II.

1,5-Dithiaspiro[5.4]decane (**4**).—To a refluxing solution of 77.7 g (0.924 mol) of cyclopentanone in 300 ml of benzene containing 0.5 g of *p*-toluenesulfonic acid was added, dropwise with stirring, 100 g (0.924 mol) of 1,3-propanedithiol. The water formed in the reaction was removed as the benzene azeotrope by a Dean–Stark trap. The brownish solution was washed with three 25-ml portions of 10% aqueous sodium hydroxide and three 250-ml portions of water. The organic layer was dried (Na_2SO_4), the benzene was removed *in vacuo*, and the resulting yellow liquid was distilled to yield 132 g (82%) of clear, colorless liquid: bp 86–87° (0.05 mm); $\nu_{max}^{CCl_4}$ 2955, 2910, 2880, 1450, 1430, 1310, 1280, 1245, 1185, 1170, 1120, 1040, 1005, 950, 910, 870, and 680 cm^{-1}; $\lambda_{max}^{isooctane}$ 251 mμ (ϵ 732); nmr (CCl_4), δ 2.92 (triplet with fine splitting, 4 H) and 2.0 ppm (multiplet, 10 H); mass spectrum, *m/e* 174 (29%), 145 (18%), 141 (8%), 113 (7%), 100 (63%), 71 (32%), 67 (100%), 45 (42%), and 41 (65%).

Anal. Calcd for $C_8H_{14}S_2$: C, 55.10; H, 8.09; S, 36.80. Found: C, 55.30; H, 8.10; S, 36.85.

Photolysis of 7, 14-Dithiadispiro[5.1,5.1]tetradecane (**7**).—A solution of 400 mg (0.0031 mol) of **7** in 20 ml of *n*-hexane was irradiated for a period of 12 hr as described in section A for the photolysis of **1**. The brown solution was concentrated *in vacuo*, dissolved in the minimum amount of methylene chloride and the resulting solution was analyzed by gas chromatography. The only material present other than starting material in a 1% yield was dicyclohexyl disulfide (absolute yield 8%).

Photolysis of Dicyclohexyl Disulfide (**8**).—A solution of 6.5 g (0.028 mol) of **8** in 350 ml of cyclohexane[16] was irradiated for 12 hr as described in section A for the photolysis of **1**. The solvent was removed *in vacuo*, and the residue was analyzed by gas chromatography. The products present were **7** (2%), **9** (1%), **10** (2%), and **11** (1%).

Dicyclohexyl disulfide (**8**) was prepared in 57% yield as previously reported,[21] bp 100° (0.05 mm).

Dicyclopentyl disulfide (**17**) was prepared in 54% yield as previously reported,[22] bp 69° (0.05 mm).

Dicyclopentyl sulfide (**18**) was prepared in 30% yield as previously reported,[22] bp 164° (21 mm).

Cyclohexyl cyclopentyl sulfide (**19**) was prepared in 84% yield as previously reported,[22] bp 136–137° (13 mm).

Cyclopentyl mercaptan (**20**) was prepared in 50% yield as previously reported,[22] bp 130°.

trans-**1,2-Cyclohexanedithiol** was prepared in 80% yield from *trans*-cyclohexane-1,2-dithiol trithiocarbonate[23] as previously reported,[24] bp 94–98° (9 mm).

trans-**2,5-Dithiabicyclo[4.4.0]decane** (**6**).—Sodium metal (0.70 g) was added to 2 g (0.0134 mol) of *trans*-1,2-cyclohexanedithiol in 50 ml of liquid NH_3. To this blue solution was added 2.63 g (0.014 mol) of 1,2-dibromoethane, the blue color being discharged immediately. The NH_3 was evaporated after standing for 2 hr, the residue was treated with ether and water, and the layers were separated. The ethereal layer was washed with water, with 6 *N* HCl, and again with water. It was dried ($MgSO_4$) and concentrated *in vacuo* to give 2 g (86%) of a white crystalline solid, mp 72–74°. Chromatography on alumina and sublimation *in vacuo* at room temperature gave 1.04 g (45%) of product: mp 76–77°; $\nu_{max}^{CCl_4}$ 2940, 2915, 2860, 1450, 1420, 1335, 1295, 1280 and 1110 cm^{-1}; λ_{max}^{EtOH} shoulder at 230 mμ (ϵ 200); nmr (CCl_4), δ 1.50 (multiplet, 8 H) and 2.93 ppm (multiplet, 6 H); mass spectrum, *m/e* 174 (56%), 146 (10%), 131 (13%), 114 (60%), 105 (23%), 81 (100%), 67 (22%), 61 (37%), 59 (46%), 45 (47%), and 41 (30%).

Anal. Calcd for $C_8H_{14}S_2$: C, 55.12; H, 8.09; S, 36.78. Found: C, 54.91; H, 8.26; S, 36.90.

trans-**2,6-Dithiabicyclo[5.4.0]undecane** (**22**).—This compound was prepared from 2.20 g (0.015 mol) of *trans*-1,2-cyclohexanedithiol and 4.60 g (0.0156 mol) of 1,3-diiodopropane except that pentane was used in place of ether as the organic solvent. The pentane layer was dried (Na_2SO_4) and concentrated *in vacuo* to give 1.01 g of white crystalline material which was chromatographed on alumina (hexane solvent) to give 507 mg (17%) of product: mp 57–58°; $\nu_{max}^{CCl_4}$ 2950, 2930, 2915, 2870, 2860, 1460, 1430, 1320, 1280, 1220, 1200, 1120, 1055, 995, and 880 cm^{-1}; λ_{max}^{EtOH} 225 mμ (ϵ 309); nmr (CCl_4), δ 2.90 (multiplet, 6 H) and 1.59 ppm (multiplet, 10 H); mass spectrum, *m/e* 188 (52%), 146 (6%), 119 (11%), 114 (34%), 106 (100%), 81 (55%), 73 (35%), 45 (50%), and 41 (67%).

Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 57.11; H, 8.56; S, 34.26.

trans-**1,2-Cyclopentanedithiol.**—To a slurry of 2.6 g (0.068 mol) of $LiAlH_4$ in 50 ml of dry ether was added, dropwise with stirring, under an atmosphere of N_2, 7.4 g (0.042 mol) of *trans*-1,2-cyclopentanedithiol trithiocarbonate[23] in 150 ml of dry dimethoxyethane. The mixture was stirred overnight at room temperature, the excess $LiAlH_4$ was decomposed with water, and the mixture was acidified with 10% HCl. The organic layer was separated and the aqueous layer was extracted with 75 ml of pentane. The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*, and the residue was distilled to give 3.13 g (55%) of product: bp 97–98°(21 mm); $\nu_{max}^{CCl_4}$ 2985, 2885, 2570, 1475, 1460, 1330, and 1235 cm^{-1}; nmr, δ 1.93 (broad multiplet, 8 H), 1.78 (singlet, 1 H), and 1.72 ppm (singlet, 1 H).

Anal. Calcd for $C_5H_{10}S_2$: C, 44.73; H, 7.50; S, 47.76. Found: C, 44.63; H, 7.52; S, 47.95.

trans-**2,5-Dithiabicyclo[4.3.0]nonane** (**15**).—To a solution of 1.0 g of *trans*-1,2-cyclopentanedithiol in 50 ml of liquid NH_3 is added 0.50 g (0.0218 g-atom) of Na. After hydrogen ceases to evolve, the blue solution is treated with 1.90 g (0.0102 mol) of 1,2-dibromoethane. The blue color disappears and a white precipitate forms. The NH_3 was evaporated after 2 hr and the residue was dissolved in H_2O and hexane. The hexane layer was separated, dried ($MgSO_4$), filtered, and evaporated. The resulting colorless liquid was chromatographed on 50 g of Merck acid-washed alumina (elution with hexane), and the major fraction was distilled to give 0.26 g (21%) of **15** which solidified and was sublimed at 25° (0.05 mm): mp 45–46°; bp 67° (0.3 mm); ν_{max}^{KBr} 2960, 2950, 2920, 2900, 2880, 2860, 1450, 1410, 1325, 1305, 1295, 1255, 1220, 1160, 1060, 940, 925, 880, 870, 825, and 680 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 225 mμ (ϵ 280); nmr (CCl_4), δ 2.4–3.3 (multiplet, 6 H) and 0.9–2.3 ppm (multiplet, 6 H); mass spectrum, *m/e* 160 (66%), 132 (16%), 113 (7%), 100 (78%), 67 (100%), 45 (63%), and 41 (31%).

Anal. Calcd for $C_7H_{12}S_2$: C, 52.45; H, 7.54; S, 40.01. Found: C, 52.87; H, 7.70; S, 39.64.

trans-**2,6-Dithiabicyclo[5.3.0]decane** (**24**).—In a 100-ml, round-bottomed, three-necked flask equipped with stirrer, gas inlet tube, Dry Ice condenser, and rubber septum was placed 1.15 g (0.05 g-atom) of sodium metal and 0.04 g of $FeCl_3$. Liquid NH_3 (75 ml) was condensed in the flask. After 30 min all of the blue color had disappeared and a slate gray precipitate of $NaNH_2$ was present. To this stirred suspension was added dropwise

---

(18) A. R. Katritzky, *et al.*, *J. Chem. Soc.*, 5953 (1965).

(19) E. E. Reid and A. Jelinek, *J. Org. Chem.*, **15**, 448 (1950).

(20) H. Hauptmann and M. M. Campos, *J. Amer. Chem. Soc.* **72**, 1405.

(21) K. Rosengren, *Acta Chem. Scand.*, **16**, 1401 (1962).

(22) I. N. Tits-Skvortsova, A. I. Leonova, and S. Y. Levina, *Zh. Obshch. Khim.*, **22**, 135 (1952); *Chem. Abstr.*, **49**, 5330 (1955).

(23) C. C. J. Culvenor, W. Davies, and K. H. Pansacker, *J. Chem. Soc.*, 1050 (1946).

(24) S. M. Igbal and L. N. Owen, *ibid.*, 1030 (1960).

3.1 g (0.023 mol) of *trans*-1,2-cyclopentanedithiol, followed by 10 g (0.034 mol) of 1,3-diiodopropane. The reaction vessel was kept at room temperature until the NH_3 evaporated. The mixture was treated with water and extracted with pentane. The pentane extract was washed with 10% HCl and water, dried, and concentrated *in vacuo*. Distillation of the residue gave 1.54 g (25%) of product: $\nu_{\max}^{CCl_4}$ 2975, 2935, 2880, 1465, 1425, 1315, 1270, 1230, 1080, 1070, 855, and 730 cm^{-1}; nmr (CCl_4), δ 3.10 (multiplet, 6 H) and 2.00 ppm (multiplet, 8 H); mass spectrum, *m/e* 174 (21%), 141 (24%), 100 (23%), 81 (21%), 79 (21%), 67 (100%), 55 (25%), 45 (36%), and 41 (77%).

Anal. Calcd for $C_8H_{14}S_2$: C, 55.10; H, 8.09; S, 36.80. Found: C, 54.93; H, 8.04; S, 37.01.

1-Cyclohexene Thiolacetate (25).—To a solution of 76 g (0.52 mol) of 1,1-cyclohexanedithiol[25] in 700 ml of pyridine at 0° was added 84 g (1.07 mol) of acetyl chloride over a period of 1 hr with stirring. The pyridinium hydrochloride precipitated at once and the reaction was very exothermic. The mixture was stirred 4 hr and filtered, and the pyridine was evaporated *in vacuo*. The residue was dissolved in 500 ml of hexane and extracted with 200-ml portions of 10% HCl until the aqueous layer remains colorless. The hexane layer was washed with water, dried ($MgSO_4$), and evaporated to give 95 g (79%) of pale yellow diacetate: $\nu_{\max}^{\text{film}}$ 3360, 2925, 2850, 1685, 1450, 1350, 1270, 1250, 1185, 1105, 1000, 940, 890, 875, 860, 820, and 750 cm^{-1}. This oil (95 g, 0.41 mol) was dissolved in 700 ml of hexane and passed through an 8-in. column of glass helices maintained at 500° with N_2 as the carrier gas. The rate of addition was adjusted to maintain the temperature in the tube but also to allow the effluent gases to be condensed in a trap maintained at 0°. After three-fourths of the hexane solution was pyrolyzed, the hexane in the trap was evaporated and the residue was distilled. The low-boiling fraction (product) was separated from the high-boiling starting material which was added to the remaining hexane solution. The pyrolysis was continued to completion, the hexane was removed *in vacuo*, and the residue was distilled. The low-boiling fractions were combined and redistilled to give 40.5 g (62%) of product: bp 54° (0.05 mm); $\nu_{\max}^{\text{film}}$ 3375, 3020, 2930, 2870, 2850, 2825, 1700, 1450, 1430, 1350, 1260, 1135, 1125, 1050, 1015, 940, 920, 915, 830, 790, and 725 cm^{-1}; $\lambda_{\max}^{\text{hexane}}$ 227 mμ (ϵ 4750); nmr (CCl_4), δ 6.10 (multiplet, 1 H), 2.22 (singlet, 3 H), 2.15 (multiplet, 4 H), and 1.68 ppm (multiplet, 4 H); mass spectrum, *m/e* 156 (20%), 114 (100%), 81 (95%), 71 (13%), and 43 (78%).

Anal. Calcd for $C_8H_{12}OS$: C, 61.50; H, 7.74; S, 20.52. Found: C, 61.60; H, 7.87; S, 20.46.

***cis*- and *trans*-1,2-Cyclohexane Bisthiolacetates.**—A solution of 27.7 g (0.18 mol) of **25** and 134.5 g (1.77 mol) of thiolacetic acid in a 250-ml quartz vessel was irradiated with a 500-W GE sun lamp for 48 hr. The excess thiolacetic acid was removed *in vacuo* and the residue was distilled to give 15.7 g, bp 105° (0.05 mm), of product which was shown by gas chromatography to be 84% *cis* and 16% *trans* adduct. Distillation through a 36-in. Teflon annular still gave 13.3 g (31%) but failed to effect separation of the isomers: $\nu_{\max}^{\text{film}}$ 3365, 2945, 2855, 1690, 1450, 1355, 1275, 1135, 1110, 995, 955, 910, 880, 835, 755, and 705 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 233 mμ (ϵ 9000).

Anal. Calcd for $C_{10}H_{16}O_2S_2$: C, 51.69; H, 6.94; S, 27.60. Found: C, 51.94; H, 6.95; S, 27.39.

***cis*-1,2-Cyclohexanedithiol.**—A solution of 12.2 g (0.05 mol) of the mixture of *cis*- and *trans*-1,2-cyclohexane bisthioacetates in 100 ml ether was added with stirring over a period of 1 hr to a solution of 4.0 g (0.11 mol) of $LiAlH_4$ in 500 ml of ether. The mixture was stirred an additional 30 min, and the excess $LiAlH_4$ was destroyed by addition of water. The precipitate was dissolved by addition of HCl, and the ether layer was separated, washed with water, dried, and evaporated to give 7.6 g of crude dithiols. Gas chromatography analysis indicated the mixture to be 84% *cis* and 16% *trans*-dithiol (preparation of pure *trans* isomer reported above). Distillation through a 36-in. Teflon annular still gave 3.5 g of pure *cis* isomer: bp 107–108° (8 mm); $\nu_{\max}^{\text{film}}$ 2950, 2900, 2860, 2555, 1450, 1350, 1330, 1290, 1275, 1225, 1190, 1080, 1000, 930, 880, 825, 805, 740, 715, and 675 cm^{-1}; nmr ($CDCl_3$), δ 3.25 (multiplet, 2 H), 2.50–1.0 (multiplet, 8 H), and 1.86 ppm (doublet, J = 7.5 Hz, 2 H).

Anal. Calcd for $C_6H_{12}S_2$: C, 48.59; H, 8.16; S, 43.25. Found: C, 48.88; H, 8.21; S, 42.89.

***cis*-2,5-Dithiabicyclo[4.4.0]decane (5).**—This compound was prepared from 1.0 g (0.0068 mol) of *cis*-1,2-cyclohexanedithiol, 0.4 g (0.018 g-atom) of sodium metal, and 1.4 g (0.0075 mol) of 1,2-dibromoethane in 50 ml of NH_3 as described for the preparation of **6** except that hexane was used as the organic solvent instead of ether. Chromatography on 50 g of Merck acid-washed alumina (hexane solvent) and sublimation at 25° (0.2 mm) gave 0.5 g (43%) of **5**: mp 61–62°; $\nu_{\max}^{\text{KBr}}$ 2940, 2850, 1440, 1405, 1285, 1270, 990, 924, 910, 875, 850, 825, 740, 690, and 680 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 225 mμ (ϵ 440); nmr ($CDCl_3$), δ 3.10 (multiplet, 2 H), 2.80 (multiplet, 4 H), and 1.15–2.60 ppm (multiplet, 8 H); mass spectrum, *m/e* 174 (43%), 131 (3%), 113 (30%), 105 (9%), 92 (20%), 81 (100%), 67 (14%), 61 (10%), 45 (32%), and 41 (24%).

Anal. Calcd for $C_8H_{14}S_2$: C, 55.12; H, 8.09; S, 36.79. Found: C, 55.26; H, 8.20; S, 36.20.

***cis*-2,6-Dithiabicyclo[5.4.0]undecane (21).**—This compound was prepared from 2.0 g (0.014 mol) of *cis*-1,2-cyclohexanedithiol, 0.77 g (0.034 g-atom) of sodium metal, and 2.9 g (0.014 mol) of 1,3-dibromopropane in 50 ml of NH_3 as described for the preparation of 5. The product was obtained as white crystals in a yield of 0.94 g (37%): mp 44–45°; $\nu_{\max}^{\text{KBr}}$ 2935, 2855, 1445, 1410, 1305, 1285, 1275, 1220, 1200, 1180, 1000, 905, 880, 855, 835, 735, and 680 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 225 mμ (ϵ 490); nmr ($CDCl_3$), δ 2.4–3.4 (multiplet, 6 H) and 1.2–2.4 ppm (multiplet, 10 H); mass spectrum, *m/e* 188 (25%), 106 (100%), 81 (16%), 73 (12%), 45 (25%), and 41 (32%).

Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 57.71; H, 8.64; S, 33.80.

1-Cyclopentene Thiolacetate.—This compound was prepared from 110 g of 1,1-cyclopentanedithiol[25] by the same procedure used to prepare **25**. The crude diacetate, 126 g (71%), slowly decomposed on standing. The yield of product was 41 g (53%): bp 42° (0.05 mm); $\nu_{\max}^{\text{film}}$ 3400, 3060, 2970, 2905, 2850, 1710, 1470, 1445, 1360, 1320, 1295, 1240, 1210, 1140, 1110, 1060, 1040, 1020, 950, 900, and 810 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 238 mμ (ϵ 4320), 224 mμ (ϵ 5040); nmr ($CDCl_3$), δ 6.00 (multiplet, 1 H), 2.45 (multiplet, 4 H), 2.22 (singlet, 3 H), and 1.98 ppm (multiplet, 2 H); mass spectrum, *m/e* 142 (14%), 100 (38%), 71 (16%), 67 (77%), 43 (100%), and 41 (40%).

Anal. Calcd for $C_7H_{10}OS$: C, 59.12; H, 7.08; S, 22.55. Found: C, 59.56; H, 7.21; S, 22.01.

***cis*-1,2-Cyclopentane Bisthiolacetate.**—A solution of 36.5 g (0.275 mol) of 1-cyclopentene thiolacetate and 56 g (0.735 mol) of freshly distilled thiolacetic acid was stirred for 10 hr and then irradiated 40 min with a 500-W GE sun lamp. The excess thiolacetic acid was evaporated *in vacuo* and the residue was distilled to give 44 g, bp 95° (0.05 mm), of product which was shown by gas chromatography to be 79% *cis* and 21% *trans* isomer. Distillation through a 36-in. Teflon annular still gave 13 g (22%) of pure *cis* isomer: bp (0.05 mm) 95°; $\nu_{\max}^{\text{film}}$ 3370, 2970, 2930, 2880, 1690, 1470, 1450, 1420, 1350, 1315, 1255, 1130, 1105, 1000, 950, 880, and 810 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 234 mμ (ϵ 8660); nmr ($CDCl_3$), δ 4.08 (multiplet, 4 H), 2.30 (singlet, 6 H), and 1.75 ppm (multiplet, 6 H).

Anal. Calcd for $C_9H_{14}O_2S_2$: C, 49.51; H, 6.46; S, 29.37. Found: C, 49.52; H, 6.48; S, 29.29.

***cis*-1,2-Cyclopentanedithiol.**—This compound was prepared from 11 g (0.055 mol) of *cis*-1,2-cyclopentane bisthiolacetate and 3.0 g (0.079 mol) of $LiAlH_4$ by the same procedure used to prepare *cis*-1,2-cyclohexanedithiol. The yield was 5.76 g (86%): bp (0.3 mm) 37°; $\nu_{\max}^{\text{film}}$ 2960, 2875, 2550, 1460, 1440, 1305, 1295, 1275, 1250, 1215, 1125, 1025, 1000, 940, 920, 890, 840, 790, and 740 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 219 mμ (ϵ 420); nmr ($CDCl_3$), δ 3.25 (multiplet, 2 H), 1.5–2.5 (multiplet, 6 H), and 1.80 ppm (doublet, J = 6 Hz, 2 H).

Anal. Calcd for $C_5H_{10}S_2$: C, 44.73; H, 7.51; S, 47.76. Found: C, 44.82; H, 7.47; S, 47.64.

***cis*-2,5-Dithiabicyclo[4.3.0]nonane (14).**—This compound was prepared from 2.5 g (0.0187 mol) of *cis*-1,2-cyclopentanedithiol, 0.97 g (0.042 g-atom) of sodium metal, and 3.76 g (0.020 mol) of 1,2-dibromoethane in 50 ml of NH_3 as described for the preparation of **5**. After chromatography the product was distilled to give 1.3 g (44%): bp 71° (0.25 mm); $\nu_{\max}^{\text{film}}$ 2980, 2940, 2910, 2870, 2800, 1470, 1440, 1420, 1320, 1300, 1280, 1250, 1215, 1200, 1165, 1125, 1115, 1015, 995, 940, 920, 880, 850, 800, and 680 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 225 mμ (ϵ 270); nmr ($CDCl_3$), δ 3.15 (multiplet, 2 H), 2.75 (multiplet, 4 H), and 1.90 ppm (multiplet, 6 H); mass spectrum, *m/e* 160 (45%), 99 (34%), 92 (20%), 67 (100%), and 45 (35%).

---

[25] J. Jentzsch, J. Fabian, and R. Mayer, *Chem. Ber.*, **95**, 1764 (1962).

Anal. Calcd for $C_7H_{12}S_2$: C, 52.45; H, 7.54; S, 40.01. Found: C, 52.80; H, 7.64; S, 39.74.

cis-**2,6-Dithiabicyclo[5.3.0]decane (23).**—This compound was prepared from 2.5 g (0.0187 mol) of *cis*-1,2-cyclopentanedithiol, 0.92 g (0.04 g-atom) of sodium metal, and 4.0 g (0.0191 mol) of 1,3-dibromopropane in 40 ml of NH_3 as described for the preparation of **5**. After chromatography the product was distilled to give 1.67 g (51%): bp 91° (0.25 mm); ν_{max}^{film} 2970, 2920, 2860, 2800, 1465, 1445, 1410, 1330, 1310, 1265, 1240, 1215, 1140, 1070, 1050, 1020, 1000, 965, 940, 925, 910, 880, 850, 790, 735, and 680 cm^{-1}; uv end absorption only; nmr ($CDCl_3$) δ 3.10–3.50 (multiplet, 2 H), 2.30–3.05 (multiplet, 4 H), and 1.50–2.20 ppm (multiplet, 8 H); mass spectrum, *m/e* 174 (25%), 106 (100%), 73 (16%), 67 (36%), 45 (40%), and 41 (60%).

Anal. Calcd for $C_8H_{14}S_2$: C, 55.12; H, 8.09, S, 36.79. Found: C, 55.35; H, 8.10; S, 36.55.

Registry No.—**4,** 15077-17-5; **5,** 16214-56-5; **6,** 16291-03-5; **7,** 4410-24-6; **14,** 16214-58-7; **15,** 16214-59-8; **21,** 16214-71-4; **22,** 16214-60-1; **23,** 16214-61-2; **24,** 16214-62-3; **25,** 15786-82-0; *cis*-1,2-cyclopentanedithiol, 16214-64-5; *trans*-1,2-cyclopentanedithiol, 2126-11-6; *cis*-1,2-cyclohexene bisthiolacetate, 16214-66-7; *trans*-1,2-cyclohexane bisthiolacetate, 16214-67-8; *cis*-1,2-cyclohexanedithiol, 2242-71-9; 1-cyclopentene thiolacetate, 16214-69-0; *cis*-1,2-cyclopentane bisthiolacetate, 16214-70-3.

Multiple Multicenter Reactions of Perfluoro Ketones with Olefins

W. H. Urry, J. H. Y. Niu, and L. G. Lundsted

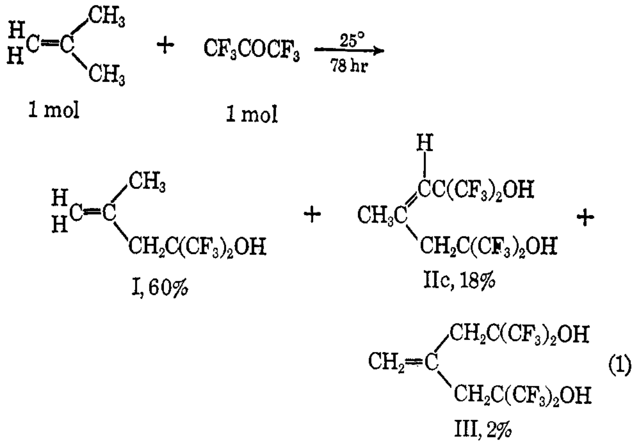
George Herbert Jones Laboratory, University of Chicago, Chicago, Illinois,
and Research Department, Wyandotte Chemicals Corporation, Wyandotte, Michigan

Received December 11, 1967

Hexafluoroacetone gives stepwise reactions with olefins [$>CHC{=}CH + CF_3COCF_3 \rightarrow -C{=}CCHC(CF_3)_2OH + CF_3COCF_3 \rightarrow HO(CF_3)_2CCC{=}CC(CF_3)_2OH$] some of which, surprisingly, occur at 25°. Products in a 2:1 ratio are general, and 2-methylpropene also gives a 3:1 product. Terminal olefins are the most reactive with 2-methyl-1-alkenes giving faster rates than 1-alkenes. Otherwise, olefin reactivity is decreased with increased alkyl substitution of their unsaturated carbon atoms. With such tri- and tetrasubstituted olefins or 1:1 products, acid-catalyzed isomerizations (product fluoro alcohols are acidic) occur prior to further reaction with hexafluoroacetone. Reactions giving 2:1 products are stereospecific owing to steric effects.

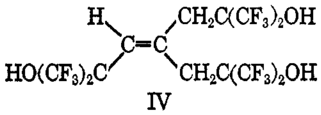
The facile reactions of perfluoro ketones with olefins are known to give 1:1 products;[1-6] and, with 2-methylpropene,[4,5] 2-phenylpropene,[5] and allene,[6] 2:1 products have been reported. The current work shows that the successive reactions occur with comparable rates, and hence 2:1 products are always formed. Indeed, these results suggest that further study of related reactions of olefins with maleic anhydride,[7,8] maleates,[8] fumarates,[8] methylene malonates,[8] pyruvates,[9] or azodicarboxylates[7] may reveal that they also yield such multiple products.

With 2-methylpropene (eq 1), this reaction is unique in its ease and extent (all yields given below are based on olefin used), and the specificity common to them is observed. All of the hexafluoroacetone was consumed (over-all yields based upon it were 100%). Hence, higher ketone/olefin ratios gave more IIc and III, and their yields approached equality at higher reaction temperatures (a ketone/olefin ratio of 2.6 at 25° for 72 hr gave 72% IIc and 8% III; a ratio of 2.0 at 180° for 72 hr gave 56% IIc and 38% III). The reaction of 1,3-dichloro-1,1,3,3-tetrafluoropropanone (2.2 molar excess) with 2-methylpropene at 120° for 72 hr gave products analogous to IIc (54%) and III (29%). To indicate the reaction specificity, no IIt, the *trans*-geometrical isomer of IIc (t or c denotes such products in which the fluorine-containing groups are *trans* or *cis* to each other), was formed in any of the above reactions.



(1)

2-Methylpropene is the only olefin studied that gave a 3:1 product. It (1 mol) with hexafluoroacetone (4.52 mol) at 209° for 150 hr gave 3% IIc, 3% III, and 91% IV. A ketone/olefin ratio of 3.1 at 200° for 60 hr gave 13% IIc, 11% III, and 76% IV.



IV

Other 2-methyl-1-alkenes give these sequential reactions with ease to give 2:1 products. However, 3:1 products were not observed since in general large groups on the terminal olefinic carbon atoms of the allylic systems [C_2H_5– in V, $CH_3(CH_2)_6CH_2$– in VII, and indeed –$C(CF_3)_2OH$ in IIc, VIc, and VIIIc] in-

---

(1) D. C. England, *J. Amer. Chem. Soc.*, **83**, 2205 (1961).

(2) H. R. Davis. Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept, 1961, p 25M.

(3) I. L. Knunyants and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **2**, 355 (Engl. ed, 329) (1962).

(4) M. H. Litt and G. J. Schmitt, U. S. Patent 3,324,187 (June 6, 1967); British Patent 964,755 (July 22, 1964).

(5) N. P. Gambarjan, E. M. Rolshlina, and Y. V. Zeifman, *Izv. Akad. Nauk SSSR*, **8**, 1466 (Engl. ed, 1425) (1965).

(6) H. R. Davis, U. S. Patent 3,284,516 (Nov 8, 1966).

(7) K. Alder, F. Pascher, and A. Schmitz, *Chem. Ber.*, **76**, 27 (1943).

(8) R. T. Arnold and J. S. Showell, *J. Amer. Chem. Soc.*, **79**, 419 (1957).

(9) R. T. Arnold and P. Veeravagu, *ibid.*, **82**, 5411 (1960).