and ten 100-ml. portions of ether yielded 0.5 g. of IV; and (C) five 10-ml. portions of 10% methanol–ether yielded no product.

The picrate of I melted at 218–220°, lit.[5] m.p. 225°. The picrate of IV melted at 188–189°, lit.[5] m.p. 186°.

Hexahydrojulolidine (I) from the Palladium Reduction.—A solution of 3.0 g. of cyclohexanone-2,6-dipropionitrile in 25 ml. of glacial acetic acid was hydrogenated in the presence of 1.0 g. of palladium on charcoal for 20 hr. at an initial pressure of 60 p.s.i. A drop in pressure equivalent to 0.069 mole (theoretical 0.074 mole) occurred. The catalyst was filtered off and the acetic acid removed *in vacuo*. The resulting material was diluted with 5 ml. of water and made basic to a pH of 12 with 15% sodium carbonate solution and concentrated sodium hydroxide solution. The basic solution was extracted with five 20-ml. portions of ether. The ether extracts were dried over magnesium sulfate and concentrated *in vacuo* giving 2.44 g. (93%) of material. Infrared analysis indicated that the product was approximately 90% *cis*-hexahydrojulolidine.

2-Oxocyclohexaneacetonitrile.—1-Pyrrolidinocyclohexene was prepared by refluxing 129 g. (1.32 moles) of cyclohexanone and 115 g. (1.6 moles) of pyrrolidine in 150 ml. of benzene under an azeotropic receiver for 8 hr. The benzene and excess pyrrolidine were removed by distillation, finally *in vacuo*, and the product used without further purification.

To this enamine in 100 ml. of acetonitrile was added over a period of 30 min. a solution of 100 g. (1.32 moles) of chloroacetonitrile in 100 ml. of acetonitrile. The resulting solution was stirred at room temperature overnight, refluxed for 1 hr., and concentrated *in vacuo*. After cooling, 150 ml. of 5% hydrochloric acid was added and the resulting mixture stirred at room temperature for 1 hr. The organic layer was separated and the aqueous layer extracted with three 75-ml. portions of ether. The combined organic layers were washed three times with 5% hydrochloric acid, twice with 5% sodium bicarbonate solution, and once with water. The ether solution was dried over magnesium sulfate and concentrated *in vacuo*. Distillation of the residue gave a forerun of starting materials and 64–80 g. (35–45%) of 2-oxocyclohexaneacetonitrile, b.p. 96–99° (1 mm.), lit.[11] b.p. 143–145° (12 mm.). The 2,4-dinitrophenylhydrazone derivative melted at 168–169°, lit.[11] m.p. 166.5–167°.

2-Cyanomethyl-6β-cyanoethylcyclohexanone (VIIb).—The pyrrolidine enamine of 2-oxocyclohexaneacetonitrile was prepared by refluxing 60.5 g. (0.44 mole) of the keto nitrile and 40 g. (0.56 mole) of pyrrolidine in 100 ml. of benzene under an azeotropic receiver for 12 hr. The benzene and excess pyrrolidine were removed by distillation, finally *in vacuo*, and the resulting product used without further purification.

A solution of this enamine in 100 ml. of absolute ethanol was cooled in an ice bath and a solution of 24 g. (0.45 mole) of acrylonitrile in 50 ml. of absolute ethanol was added. The ice bath was removed and the solution stirred at room temperature for 12 hr. The solution was then refluxed for 1 hr., cooled, 75 ml. of 5% hydrochloric acid added, and this mixture stirred for 1 hr. at room temperature. The product was isolated as for 2-oxocyclohexaneacetonitrile. Distillation gave 15.9 g. of the starting keto nitrile and 32.2 g. (38%) of the desired product as a light yellow oil, b.p. 174–176° (0.7 mm.).

Hydrolysis of a sample of the keto dinitrile with concentrated hydrochloric acid gave quantitatively the keto diacid, m.p. 166–168°, lit.[12] m.p. 167–168°.

2,6-Dicyanomethylcyclohexanone (VIIc).—A solution of 21.0 g. (0.28 mole) of chloroacetonitrile in 50 ml. of acetonitrile was added to a solution of the enamine of 2-oxocyclohexaneacetonitrile (from 41.6 g. of keto nitrile converted to enamine in the usual way) in 75 ml. of acetonitrile, and this was refluxed for 6 hr. After cooling, 100 ml. of 5% hydrochloric acid was added, and the mixture was stirred for 2 hr. The product was isolated as for 2-oxocyclohexaneacetonitrile. Distillation gave 26.0 g. of the starting keto nitrile and 5.0 g. (9.5%) of the desired product as a light yellow oil, b.p. 173–175° (1 mm.). The yellow liquid crystallized from ethanol to give a white solid, m.p. 66.0–66.5°.

Hydrolysis of a sample of the keto dinitrile with concentrated hydrochloric acid gave quantitatively the keto diacid, m.p. 186–187°, lit.[12] m.p. 188°.

Hexahydrolilolidine (XIb).—A solution of 10 g. of VIIb in 75 ml. of absolute ethanol was hydrogenated in the presence of 4 g. of W-7 Raney nickel catalyst at 145–155° and an initial pressure of 2300 p.s.i. for 10 hr. The apparatus was allowed to cool overnight, the catalyst filtered off, and the ethanol removed *in vacuo* leaving 8.5 g. of crude material. This was chromatographed on 60 g. of neutral alumina. Elution with 400 ml. of petroleum ether gave 5 g. of material, distillation of which gave two fractions boiling at 44–45° (0.2 mm.), 2.0 g., and 90–100° (0.2 mm.), 1.5 g.

The lower boiling fraction, contrary to the other, gave a crystalline picrate, m.p. 226–228° dec.

Anal. Calcd. for $C_{17}H_{23}N_4O_7$: C, 51.77; H, 5.62; N, 14.21. Found: C, 51.85; H, 5.94; N, 14.05.

1-Azatricyclo[6.2.1.0^{4,11}]hendecane (XIc).—A solution of 10 g. of VIIc was hydrogenated in the presence of Raney nickel as in the preparation of VI. Removal of the ethanol left 8.5 g. of crude product which was chromatographed on 60 g. of neutral alumina. Elution with 300 ml. of petroleum ether gave 4.8 g. of material which on distillation at 1 mm. gave three fractions: 0.5 g., b.p. 35°; 1.5 g., b.p. 76–77°; and 2 g., b.p. greater than 150°. The first fraction gave a crystalline picrate, m.p. 250–252° dec.

Anal. Calcd. for $C_{16}H_{21}N_4O_7$: C, 50.52; H, 5.30; N, 14.73. Found: C, 50.73; H, 5.41; N, 14.60.

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(11) A. Dornow and E. Fleishmann, *Ber.*, **88**, 1340 (1955).

(12) G. Opitz, H. Mildenberger, and H. Suhr, *Ann.*, **649**, 47 (1961).

Free-Radical Additions to 2-Cyclopropylpropene[1]

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The peroxide- and light-induced additions of bromotrichloromethane and carbon tetrachloride to 2-cyclopropylpropene yield the 1,1,1-trichloro-3-methyl-6-halohex-3-enes as products. Addition of thiophenol to 2-cyclopropylpropene yields the unrearranged addition product, 1-thiophenoxy-2-cyclopropylpropane, whereas methyl mercaptan yields a mixture of the unrearranged and rearranged addition products, methyl 2-cyclopropylpropyl sulfide and methyl 2-methylpent-2-enyl sulfide, respectively. A mechanism is suggested to account for the products of these reactions. Competition reactions involving addition of thiyl radicals and trichloromethyl radicals to 2-cyclopropylpropene and 2,3-dimethyl-1-butene show that the cyclopropyl group enhances the reactivity of a double bond toward addition of these free radicals by a factor of about five.

The cyclopropylcarbinyl cation has received a considerable amount of attention from organic chemists because of its apparent ease of formation and its ability to undergo rearrangements.[3] The somewhat general parallel stabilities of carbonium ions and alkyl free radicals suggests that an unusual degree of stability might be found in the cyclopropylcarbinyl radical.

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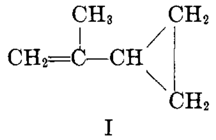
[1] This work was supported by Grant No. 512-A from the Petroleum Research Fund.

[2] Taken in part from the thesis submitted by J. D. T. in partial fulfillment of the requirements for the Ph.D. degree, University of Kansas.

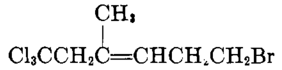
[3] For a discussion of some of the chemistry concerning this system, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp. 588–590.

Previous reports in the literature indicate that this radical has been formed by the hydrogen abstraction encountered in chlorination of alkyl cyclopropanes[4] and by thermal decomposition of appropriate peroxides[5] and azonitriles.[6] In the latter two cases, rate studies do suggest that the cyclopropylcarbinyl radical may have an unexpected degree of stability. Our approach to this problem was to seek products of a rearrangement in the free-radical additions of polyhalomethanes and mercaptans to 2-cyclopropylpropene (I) and to determine the effect of the cyclopropyl group on the reactivity of its double bond toward addition by free radicals.



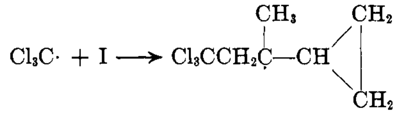
I

The photochemically induced reaction of bromotrichloromethane with I at 5° yielded a 1:1 addition product in 68% yield which was identified as 1,1,1-trichloro-3-methyl-6-bromohex-3-ene (II). Thus, the compound reacted with one equivalent of hydrogen. Its n.m.r. spectrum indicated the presence of a single vinyl hydrogen (5.65 p.p.m.), the absence of any cyclopropyl hydrogens, and contained other features consistent with II. (See Experimental). A free-radical chain reaction that accounts for the formation of this product is the following.



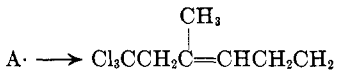
$$Cl_3CCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_2Br$$

II



(1)

A·

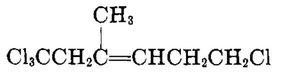


$$A\cdot \longrightarrow Cl_3CCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2\dot{C}H_2 \quad (2)$$

B·

$$B\cdot + BrCCl_3 \longrightarrow II + Cl_3C\cdot \quad (3)$$

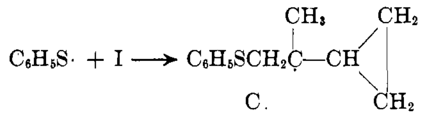
Carbon tetrachloride added to I in a benzoyl peroxide-induced reaction at 80° yielding a 1:1 addition product in 12% yield. The n.m.r. spectrum of the addition product was consistent with the assignment of structure III. It was probably formed in a chain sequence similar to that shown for the addition of bromotrichloromethane.



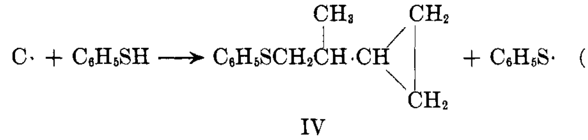
$$Cl_3CCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_2Cl$$

III

The addition of thiophenol to I under photochemical conditions at 5° yielded a 1:1 addition product in 57% yield. The n.m.r. spectrum of this addition product showed not only the absence of any vinyl hydrogen but also the presence of cyclopropyl group. In this case, there apparently is no rearrangement of the carbon skeleton and the simple addition product, 1-thiophenoxy-2-cyclopropylpropane (IV), is formed by a free chain sequence which involves no rearrangement of the adduct radical C·.



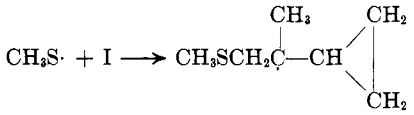
C. (4)



(5)

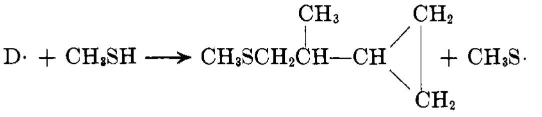
IV

Methyl mercaptan added to I in a light-induced reaction and yielded a mixture of both a simple and a rearranged addition product as evidenced by the appearance of both cyclopropyl hydrogens and a vinyl hydrogen in the n.m.r. spectra of the addition product. These products, methyl 2-cyclopropylpropyl sulfide (V) and methyl 2-methylpent-2-enyl sulfide (VI) very likely result by the following mechanism.



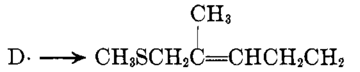
(6)

D



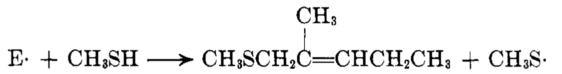
(7)

V



$$D\cdot \longrightarrow CH_3SCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2\dot{C}H_2 \quad (8)$$

E·



$$E\cdot + CH_3SH \longrightarrow CH_3SCH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_3 + CH_3S\cdot \quad (9)$$

VI

Evidence that the rearranged products are formed by a chain transfer reaction which occurs after rearrangement of the intermediate radical was obtained by varying the ratio of I to methyl mercaptan. Table I shows that at high concentrations of the mercaptan, less rearranged product is formed. This observation is consistent with a reaction scheme that yields an unrearranged product in a process that is first order in both the adduct radical and transfer agent, and a rearranged product in a reaction that is independent of the mercaptan concentration.[7] In the addition of bromotrichloromethane, the rate of rearrangement of the simple adduct radical A· to B· is apparently much faster than bromine abstraction by A·. The ability of thiophenol to transfer its hydrogen must be very facile since no rearrangement of the adduct radical C· is observed.

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[4] H. C. Brown and M. Barkowshi, *J. Am. Chem. Soc.*, **74**, 1894 (1952); J. D. Roberts and R. H. Mazur, *ibid.*, **78**, 2509 (1953).

[5] H. Hart and R. A. Cipriani, *ibid.*, **84**, 3697 (1962); H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).

[6] C. G. Overberger and A. Lebovits, *ibid.*, **76**, 2722 (1954).

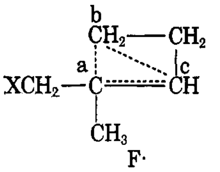
[7] This argument is valid only if the rate of formation of rearranged product is dependent on the rate of reaction 8 and not on the rate of the transfer reaction 9 which also involves mercaptan. A situation where this might occur would be one in which the reverse reaction of 8 would occur (E· → D·) at a rate fast enough to compete with reaction 7. The data appear to eliminate this possibility as an important factor to consider in these reactions since the ratio of the two products is dependent on the concentration of methyl mercaptan.

TABLE I

EFFECT OF $[CH_3SH]:[I]$ RATIO ON PRODUCT DISTRIBUTION

$[CH_3SH]:[I]$	% rearranged product
10.8	38
5.5	51
1.7	74
0.6	82
0.2	88

The preceding study discredits the possibility of a single adduct radical such as F· being formed as a discreet intermediate which might give rise to both the simple and rearranged addition products. One might postulate that a species such as F· reacts with thiophenol only at carbon a yielding a simple product, with the polyhalomethanes only at carbon b, and with methyl mercaptan at both a and b yielding a mixture of the simple and rearranged products. If this were the case, changing the mercaptan concentration should have no effect on the distribution of the products in the methyl mercaptan reactions. Furthermore, F· also might be expected to react at carbon c yielding cyclobutane derivatives and no cyclobutane derivatives were found in our reaction mixtures.


F·

The reactivity of the double bond in I toward addition by a free radical is influenced to some degree by the cyclopropyl group. Competition reactions involving addition of bromotrichloromethane, thiophenol, and *n*-amyl mercaptan to mixtures of I and 2,3-dimethyl-1-butene (VII), an olefin structurally very similar to I from a steric standpoint, show that I is more reactive than VII toward addition by both trichloromethyl radicals and thiyl radicals (Table II).

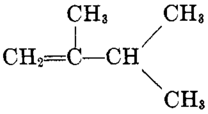
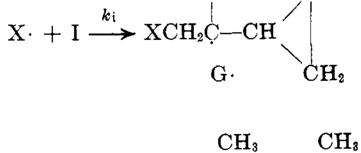
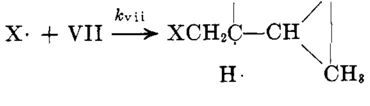

VII

TABLE II

COMPETITION REACTIONS BETWEEN 2-CYCLOPROPYLPROPENE AND 2,3-DIMETHYL-1-BUTENE TOWARD RADICAL ADDITION AT 5°

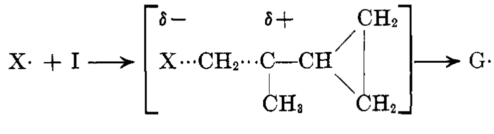
Adding reagent	X·	k_i/k_{vii}	No of runs	Av. deviation
$BrCCl_3$	$Cl_3C\cdot$	4.4	6	0.2
C_6H_5SH	$C_6H_5S\cdot$	6.6	6	1.2
n-$C_5H_{11}SH$	n-$C_5H_{11}S\cdot$	5.3	7	0.4





The increased reactivity of I with respect to VII toward addition may be the result of either a resonance factor or polar factor (or both) that lowers the activation energy requirement for the addition of a radical to I. If it is a resonance factor, the nature of the stabilizing effect of the cyclopropyl group is certainly open for speculation. In view of the product studies outlined previously, a radical involving extensive delocalization of several carbon–carbon bonds in G· analogous to the cyclopropyl carbinyl cation seems unlikely.[8] However some degree of delocalization of the unpaired electron into the cyclopropyl group, admittedly small in view of the rather small degree of rate enhancement, may exist.

A polar contribution resulting from the presence of the cyclopropyl group might explain the enhanced rate of addition of these particular free radicals to I. Both trichloromethyl and thiyl radicals are good electron-acceptor radicals and a polar contribution to the transition state of the addition reaction may play a significant role in lowering the activation energy requirement. The role the cyclopropyl group plays in stabilizing the cyclopropyl carbinyl cation may be invoked in causing the olefin to act as a good electron donor in the transition state of the reaction when an electron-acceptor radical is involved. Low yields in the reactions of aldehydes prevented us from getting reliable data in competition reactions of I and VII with these reagents. This reaction would involve addition of the electron-donating acyl radical and, if the polar factor were involved, the rate enhancement of I with respect to VII would not be observed.



Certain aspects of this work, namely the stereochemistry of the rearrangement of the cyclopropyl carbinyl radical and the nature of the rate enhancement caused by the cyclopropyl group, are currently under further investigation.

Experimental[9]

Reagents.—Carbon tetrachloride, Spectro quality reagent, was obtained from Matheson Coleman and Bell. Bromotrichloromethane, obtained from the Dow Chemical Company, was redistilled under vacuum to remove carbon tetrachloride and was better than 99% pure by gas chromatographic analysis. Methyl mercaptan was obtained from Matheson Coleman and Bell, *n*-amylmercaptan from Aldrich Chemical Co., thiophenol from Eastman Organic Chemicals, and 2,3-dimethyl-1-butene from Sinclair Research Inc.

2-Cyclopropylpropene (b.p. 71°) was prepared by dehydration of dimethylcyclopropylcarbinol as described by Boord, *et al.*[10] The alcohol was prepared by the Grignard reaction of methylmagnesium iodide with methyl cyclopropyl ketone.

The gas chromatographic analyses were performed on a 10 ft. by 0.25 in. column packed with 12% Oronite 20 on Chromosorb

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[8] See also J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3543 (1951).

[9] Molecular weights were determined on a Mechrolab vapor pressure osmometer. The n.m.r. spectra were made on a Varian analytical n.m.r. spectrometer, Model A-60. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, 37th Ave., Woodside 77, N. Y. All boiling points are uncorrected.

[10] R. VonVokennburg, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 172 (1949).

P. Column temperature was maintained at 80° and helium (head pressure, 10 p.s.i.g.) was used as carrier gas.

A 275-w. Sylvania sun lamp was used as a source of ultraviolet light for the photochemically induced reactions.

Addition of Bromotrichloromethane to 2-Cyclopropylpropene.—Bromotrichloromethane (7.5 g., 0.038 mole) and 2-cyclopropylpropene (3 g., 0.037 mole) were sealed in a tube and illuminated at 5° in a water bath for 460 min. with a sun lamp. The reaction mixture was distilled and 7.0 g. (68% based on olefin used) of 1:1 adduct was collected, b.p. 88° (0.09 mm.).

Anal. Calcd. for $C_7H_{10}Cl_3Br$: C, 29.98; H, 3.59; halogen, 2.210 g. of AgX per gram of sample; mol. wt., 281. Found: C, 30.27; H, 3.54; halogen, 2.220 g. of AgX per gram of sample; mol. wt., 272.

The compound absorbed 98% of the theoretical amount of hydrogen based on one olefinic linkage per molecule.

The n.m.r. spectrum of this material had a triplet centered at 5.60 p.p.m. due to the single vinyl hydrogen but no absorption in 0.5-p.p.m. region which would be present if cyclopropyl hydrogens were present in the molecule. Other characteristic features of the n.m.r. spectrum of this material were two singlets, one at 1.95 p.p.m. due to the protons of the 3-methyl group and the other at 3.40 p.p.m. due to the protons of the 2-methylene, a quartet centered at 2.80 p.p.m. due to the 5-methylene group, and a triplet centered at 3.40 p.p.m. due to the 6-methylene group. The integrated peak areas were consistent with these assignments.

Addition of Carbon Tetrachloride to 2-Cyclopropylpropene.—Carbon tetrachloride (6.0 g., 0.0039 mole) and 2-cyclopropylpropene (3.0 g., 0.037 mole) were combined and sealed in a tube with benzoyl peroxide (0.01 g.). After 14 hr. of heating in an oil bath at 80°, more benzoyl peroxide (0.01 g.) was added and the tube heated for another 12 hr. The reaction mixture was distilled and 1.0 g. (12% yield based on the olefin) of the 1:1 addition product was isolated, b.p. 76° (0.04 mm.)

Anal. Calcd.: mol. wt., 236. Found: mol. wt., 232.

The n.m.r. spectrum of this material was identical in all respects with that of the addition product obtained from the bromotrichloromethane reaction with the exception that the triplet peak due to the hydrogens of the 6-methylene were centered at 3.50 p.p.m.

Addition of Thiophenol to 2-Cyclopropylpropene.—Thiophenol (4.0 g., 0.037 mole) and 2-cyclopropylpropene (3.0 g., 0.037 mole) were sealed in a glass tube and illuminated with a sun lamp for 8 hr. at 5° in a water bath. The reaction mixture was distilled and 4.0 g. (57% yield based on olefin) of the 1:1 addition product was collected, b.p. 74–75° (0.04 mm.).

Anal. Calcd. for $C_{12}H_{16}S$: C, 71.06; H, 12.29; S, 17.48; mol. wt., 192. Found: C, 70.89; H, 11.90; S, 17.20; mol. wt., 188.

The n.m.r. spectrum of this material showed an absorption in the region of 7–7.5 p.p.m. which can be assigned to the protons of the aryl group and an absorption in the region of 0.5 p.p.m. due to the cyclopropyl protons. There was no evidence of any absorption in the vinyl proton region. The integrated absorptions at 1.15, 1.82, and 3.08 p.p.m. account for the other protons in the molecule.

Addition of Methyl Mercaptan to 2-Cyclopropylpropene.—Mixtures of methyl mercaptan and 2-cyclopropylpropene in the mole ratios shown in Table I were sealed in Pyrex tubes. The tubes were placed in a water bath set at 5° and illuminated for 2 hr. with a sun lamp. The unchanged methyl mercaptan and olefin were distilled from the reaction mixture and the remaining material analyzed by means of n.m.r. The per cent rearranged material was determined from the integrated resonance peak of the single vinyl proton of the rearranged addition product (5.6) compared with that of the methyl thiol protons (2.05 p.p.m.).

Addition of Bromotrichloromethane to 2,3-Dimethyl-1-butene.—Bromotrichloromethane (15.0 g., 0.071 mole) and 2,3-dimethyl-1-butene (7.5 g., 0.09 mole) were sealed in a tube and illuminated with a sun lamp for 5 hr. in a water bath set at 5°. The reaction mixture was distilled and 9.0 g. (42% based on $BrCCl_3$) of a 1:1 addition product was collected, b.p. 78° (0.06 mm.).

Anal. Calcd. for $C_7H_{12}Cl_3Br$: C, 29.71; H, 4.28; mol. wt., 282. Found: C, 30.02; H, 4.60; mol. wt., 292.

Addition of Thiophenol to 2,3-Dimethyl-1-butene.—Thiophenol (8.5 g., 0.077 mole) and 2,3-dimethyl-1-butene (7.5 g., 0.09 mole) were combined and sealed in a glass tube. The mixture was illuminated with a sun lamp for 7 hr. in a 5° water bath. The reaction mixture was distilled and 10 g. (66% yield based on thiophenol) of the 1:1 addition product was isolated, b.p. 68° (0.04 mm.).

Anal. Calcd. for $C_{13}H_{18}S$: C, 74.25; H, 9.27; S, 16.43; mol. wt., 194. Found: C, 74.25; H, 9.34; S, 16.50; mol. wt., 197.

Relative Reactivities of 2-Cyclopropylpropene and 2,3-Dimethyl-1-butene.—The relative reactivities of 2-cyclopropylpropene and 2,3-dimethyl-1-butene toward trichloromethyl and thiyl radicals were determined in the following manner: A mixture consisting of 0.04 to 0.09 g. (0.5 to 1.1 mmoles) of the two olefins and benzene, which served as an internal standard for the gas chromatographic method used, the amount of each accurately determined on an analytical balance, was diluted with an excess of the adding reagent. In the case of the mercaptan additions (thiophenol and *n*-amyl mercaptan), the initial mole ratio of the adding reagent to the total amount of olefins was about 2:1 in all cases. A sample of the mixture (0.01 ml.) was removed by means of a pipet and injected on the gas chromatographic column through a Fisher sample injection valve. The areas of the two olefin and benzene peaks were determined. The reaction mixtures were sealed in Pyrex tubes and the tubes immersed in a constant temperature water bath set at 5°. The sun lamp used for illumination was placed six inches from the side of the bath to avoid heating of the bath. The reactions were stopped in all cases before either of the two olefins was completely consumed. The tubes were removed from the bath and brought to room temperature and another 0.01-ml. sample was removed by means of a pipet and subjected to gas chromatographic analysis under the same conditions used for the first sample. Determination of the amounts of each of the olefins remaining in the reaction mixture was made by comparison of the olefin peak areas (corrected for sample size variations by means of the internal standard) with those obtained before the reaction. The amounts of the two olefins before and after the reaction were substituted in equation

$$\frac{k_{\text{I}}}{k_{\text{vii}}} = \frac{\log \frac{[\text{I}]_0}{[\text{I}]}}{\log \frac{[\text{VII}]_0}{[\text{VII}]}}$$

where $[\text{I}]_0$ and $[\text{VII}]_0$ refer to the initial amounts of the two olefins and [I] and [VII] to the amounts of the olefins after reaction.