

under nitrogen and protected from moisture by a sodium hydroxide drying tube was added sodium metal (1.01 g., 0.44 g.-atom) until a permanent blue color remained for 45 min. The excess sodium was decomposed by adding a little ammonium chloride and the ammonia allowed to evaporate under nitrogen. The residue was dissolved in water and made acid with *p*-toluenesulfonic acid monohydrate. The water was separated from the products by freeze drying. The residue was extracted with hot isopropyl alcohol. The addition of ether to the extracts precipitated 5.9 g. of solid that was 67% pure by an *N*-ethylmaleimide sulfhydryl analysis. A number of recrystallizations from ethanol

and ether yielded 2 g. (31.2%) of 2-(2-carboxyethylamino)-ethanethiol *p*-toluenesulfonate salt, m.p. 118–121°, 95% pure by -SH analysis. A mixture melting point with the acid obtained from *N*-(2-carboxyethyl)-*N*-2-tritylthioethylamine occurred at 117–120°. The infrared spectra of the two compounds were identical.

Acknowledgment.—We are indebted to Dr. Richard G. Hiskey, University of North Carolina, for helpful discussions.

Reactions of Trichloromethanesulfonyl Bromide with Some Hydrocarbons

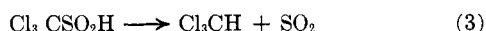
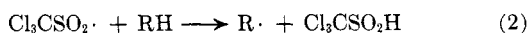
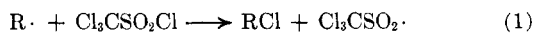
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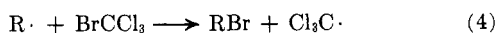
Trichloromethanesulfonyl bromide reacts with cyclohexane, cyclopentane, and toluene under the influence of light to yield the expected bromohydrocarbons, chloroform, and sulfur dioxide. The competitive bromination of cyclohexane and toluene strongly suggests that the $\text{Cl}_3\text{C}\cdot$ radical is involved in hydrogen abstraction from the hydrocarbons. This is in sharp contrast to the previously reported reactions of trichloromethanesulfonyl chloride with hydrocarbons, in which $\text{Cl}_3\text{CSO}_2\cdot$ is apparently the hydrogen abstractor. Peroxide- or light-induced decomposition of trichloromethanesulfonyl bromide into bromotrichloromethane and sulfur dioxide is proposed to account for the behavior of this material with hydrocarbons.

In a previous report from this laboratory,¹ trichloromethanesulfonyl chloride was found to chlorinate alkanes and alkyl aromatics in reactions induced by benzoyl peroxide or light. Mechanistic studies^{2,3} indicated that chloroform, sulfur dioxide, and alkyl halide were formed by the following free-radical chain sequence.



The ready decomposition of trichloromethanesulfonyl chloride into the products noted above was observed many years ago.⁴

It was found that the relative reactivities of hydrocarbons toward chlorination by $\text{Cl}_3\text{CSO}_2\text{Cl}$ were different from the relative reactivities toward bromination by bromotrichloromethane, a type of reaction which most likely involves the following chain sequence.⁵

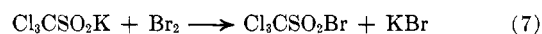
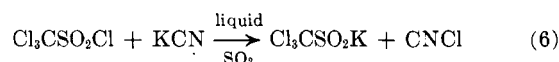


We felt that further support for the proposal that the $\text{Cl}_3\text{CSO}_2\cdot$ radical functions as the hydrogen abstractor in chlorination of hydrocarbons with $\text{Cl}_3\text{CSO}_2\text{Cl}$ could be obtained by studying the reactions of trichloromethanesulfonyl bromide. However, our investigation shows that the chemistry of trichloromethanesulfonyl bromide differs from that of the previously investigated chloride.

Results and Discussion

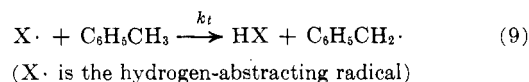
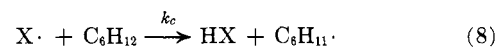
In contrast to trichloromethanesulfonyl chloride, which is readily available, the bromide cannot be obtained from commercial sources. Loew prepared the

bromide by reaction of bromine with sodium trichloromethanesulfinate.⁶ We, however, were unable to reproduce the preparation of this salt, but were able to make the potassium salt unequivocally by reaction between trichloromethanesulfonyl chloride and potassium cyanide in liquid sulfur dioxide. Treatment of an aqueous solution of this salt with bromine gave trichloromethanesulfonyl bromide.



The results of a study of the light-induced reactions of $\text{Cl}_3\text{CSO}_2\text{Br}$ with cyclohexane, cyclopentane, and toluene are shown in Table I. The observation that ring-brominated products were formed when toluene was used as substrate was unexpected. These products may well have resulted from rearrangement of benzyl bromide; indeed, the latter compound was shown to undergo partial rearrangement when subjected to illumination at 110–115°. The products formed with all three hydrocarbons and their distribution can be interpreted in terms of a chain sequence similar to that proposed previously for analogous reactions of $\text{Cl}_3\text{CSO}_2\text{Cl}$ with hydrocarbons. However, comparison of competition reactions between cyclohexane and toluene toward light-induced halogenation by $\text{Cl}_3\text{CSO}_2\text{Br}$ and toward halogenation by $\text{Cl}_3\text{CSO}_2\text{Cl}$ and BrCCl_3 would appear to eliminate this chain sequence.

Table II lists the relative reactivity ratios k_c/k_t , where k_c and k_t are the reaction rate constants for hydrogen abstraction from cyclohexane and toluene, respectively. Examination of the data certainly eliminates the possi-



(1) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 5246 (1960).
 (2) E. S. Huyser and B. Giddings, *J. Org. Chem.*, **27**, 3391 (1962).
 (3) E. S. Huyser, H. Schinke, and R. L. Burham, *ibid.*, **28**, 2141 (1963).
 (4) M. Battagay and W. Kern, *Bull. soc. chim. France*, **41**, 34 (1927).
 (5) (a) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958);
 (b) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960); (c) G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

(6) V. O. Loew, *Z. Chem.*, **82** (1869).

TABLE I
 LIGHT-INDUCED^a BROMINATION OF HYDROCARBONS WITH Cl₃CSO₂Br

Reactants, mmoles		Time, hr.	Temp., °C.	Products, mmoles			
Hydrocarbon	Cl ₃ CSO ₂ Br			CHCl ₃	SO ₂	Brominated products	% conversion
Cyclohexane, 250	10.02	5	60-65	7.0	7.2	Cyclohexyl bromide, 6.8	68
Cyclopentane, 10	2.00	4	48-51	b	1.5	Cyclopentyl bromide, 1.1	79
						Bromotrichloromethane, 0.5	
Toluene, 10	2.01	4	110-115	b	1.6	Benzyl bromide, 1.3	85
						Ring-brominated toluene, 0.46	

^a Light source: 275-w. Sylvania sunlamp. ^b Identified qualitatively.

 TABLE II
 RELATIVE REACTIVITIES OF CYCLOHEXANE AND TOLUENE TOWARD Cl₃CSO₂Br, ClCSO₂Cl, AND BrCCl₃

Halogenating agent	Temp., °C.	Initiation	k _c /k _t	No. of runs	Av. dev.	Ref.
Cl ₃ CSO ₂ Br	78	hν	0.21	3	0.02	a
Cl ₃ CSO ₂ Br	78	Bz ₂ O ₂	0.36	10	0.03	a
Cl ₃ CSO ₂ Cl	80	Bz ₂ O ₂	1.2 ^b	3	0.1	c
	80	Bz ₂ O ₂	1.86 ^d	2	0.03	a
BrCCl ₃	78	hν	0.20	3	0.03	c

^a Present work. ^b A minimum value. ^c E. S. Huyser and B. Giddings, *J. Org. Chem.*, **27**, 3391 (1961). ^d This value was determined from relative rates of formation of the corresponding chloro hydrocarbons; the value 1.2, previously reported, was determined by the rates of disappearance of the hydrocarbons.

 TABLE III
 RATES OF BENZOYL PEROXIDE-INDUCED DECOMPOSITIONS OF Cl₃CSO₂Br IN Cl₄C AT 78°

[Cl ₃ CSO ₂ Br], mmoles/l.	[Bz ₂ O ₂], mmoles/l.	Rate × 10 ³ mmoles/min.	
		Obsd.	Calcd.
35.1	20.4	3.25	3.16 ^a
39.5	4.0	1.40	...
39.0	0.8	0.58	0.63 ^b

^a Determined by multiplying 1.40 by (20.4/4.0)^{1/2}. ^b Determined by dividing 1.40 by (4.0/0.8)^{1/2}.

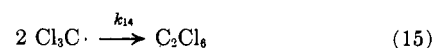
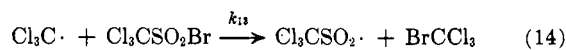
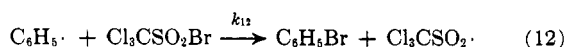
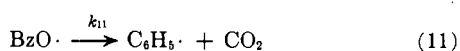
bility that the hydrogen-abstracting species involved in halogenation with the chloride is the same as that obtained from the bromide. It would appear that Cl₃CSO₂Br and BrCCl₃ give rise to the same hydrogen-abstracting species, namely the Cl₃C· radical.

One possible mode by which brominations with Cl₃CSO₂Br could involve the Cl₃C· radical as the hydrogen-abstracting agent would be through the decomposition of Cl₃CSO₂Br to SO₂ and BrCCl₃. Indeed, in carbon tetrachloride at 78° under the influence of light, Cl₃CSO₂Br does undergo an extremely rapid decomposition into the products cited. In the dark, decomposition at the same temperature is negligible. However, the decomposition can be induced in the dark by benzoyl peroxide. These observations are illustrated in Figure 1.

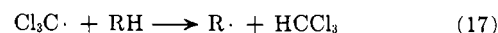
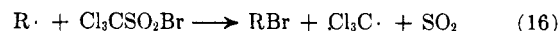
The requirement of light or benzoyl peroxide suggests that the decomposition of Cl₃CSO₂Br is a free-radical chain reaction. The data of Table III show that the rate of decomposition is proportional to the square root of the benzoyl peroxide concentration. This half-order dependence on the benzoyl peroxide concentration is consistent with the following rate expression derived through the use of steady-state kinetics applied to the mechanism outlined in eq. 10-15.

$$\text{rate} = k_{13} \left(\frac{k_{10}}{2k_{13}} \right)^{1/2} [\text{Cl}_3\text{CSO}_2\text{Br}] [\text{Bz}_2\text{O}_2]^{1/2}$$

$$\text{Bz}_2\text{O}_2 \xrightarrow{k_{10}} 2 \text{BzO}\cdot \quad (10)$$



An alternative explanation for the observation that the Cl₃C· radical is apparently the hydrogen abstractor in brominations with Cl₃CSO₂Br is that abstraction of the bromine atom could result in a concurrent scission of the carbon-sulfur bond as shown below. Such a



mechanism is unlikely as an important path since it is not apparent why changing the sulfur-bonded halogen should change the course of reaction of the trichloromethanesulfonyl halide with an alkyl radical. It certainly cannot be regarded as the only route for the reaction. The isolation of considerable quantities of bromotrichloromethane, particularly in the cyclopentane reaction, strongly supports a mechanism in which this polyhalomethane is an intermediate.

Trichloromethanesulfonyl chloride does not decompose in carbon tetrachloride to sulfur dioxide and the polyhalomethane under conditions analogous to those which cause such decomposition of the bromide. It is of interest also that carbon tetrachloride has never been found as a product in the reactions of Cl₃CSO₂Cl with hydrocarbons.

Experimental

Trichloromethanesulfonyl chloride (Eastman) was sublimed before using. Toluene, cyclohexane, cyclopentane and carbon tetrachloride were commercial materials and purified by distillation, when necessary, until they gave a single gas chromatographic peak. Bromotrichloromethane (Dow Chemical Co.) was distilled under vacuum to remove trace amounts of carbon tetrachloride. Potassium cyanide (Baker analyzed reagent) was dried in a vacuum over phosphorus(V) oxide before use. Other commercial reagents used without further purification were benzoyl peroxide (Lucidol), bromine (Mallinckrodt), benzyl bromide (Eastman), sulfur dioxide (Matheson Corp.), and cyclohexyl bromide (Dow Chemical Co.). The authentic sample of cyclopentyl bromide was prepared by the reaction of cyclopentanol with hydrogen bromide.

The gas chromatographic analyses were performed on an Aerograph A-90-P and recorded on a Sargent recorder (Model SR). The infrared spectra were obtained on a Beckman IR-8.

Potassium Trichloromethanesulfinate.—A mixture of potassium cyanide (6.52 g., 0.10 mole) and trichloromethanesulfonyl chloride (43.52 g., 0.20 mole) was placed in a flame-dried flask. After the flask was flushed with dry nitrogen, about 100 ml. of sulfur dioxide was condensed onto the solid reactants with a Dry Ice–Cellosolve mixture as a coolant. Before the introduction of the sulfur dioxide was completed, a slow stream of nitrogen was introduced into the reaction mixture. This flow of nitrogen was maintained throughout the 5-hr. reaction period during which time the mixture was held at the temperature of refluxing sulfur dioxide. At the end of this period, the sulfur dioxide was evaporated and the resulting residue, handled at all times in an atmosphere of dry nitrogen, was extracted with three 30-ml. portions of dry benzene. The crude potassium trichloromethanesulfinate at this point was over 90% pure and amounted to 20.3 g. (91% yield based on potassium cyanide). The material was further purified by extraction with liquid sulfur dioxide until the extracting liquid was pale yellow or colorless. The resulting pale tan solid at this point amounted to 15.5 g. (70% of theory) and was analytically pure.

Potassium was determined as $K_2Na[Co(NO_2)_6]H_2O$; chlorine was determined as silver chloride after decomposition of the sample by the method outlined by Dains.⁸ The sulfur was determined by oxidation of a sample of the compound with alkaline potassium permanganate.

Anal. Calcd. for CCl_3KO_2S : Cl, 48.01; K, 17.65; S oxidation state change, 2. Found: Cl, 48.04, 47.96; K, 17.70, 17.82; S oxidation state change, 1.96, 1.97.

Trichloromethanesulfonyl Bromide.—Potassium trichloromethanesulfinate (10.2 g., 0.041 mole) was dissolved in about 50 ml. of oxygen-free water and the solution was covered with 20 ml. of benzene. A solution of bromine (8.5 g., 0.053 mole) in 50 ml. of benzene was added and the resulting mixture was stirred for about 15 min. until the bromine had reacted. The organic layer was separated and washed with three 40-ml. portions of 10% $NaHSO_3$, and with three 40-ml. portions of water. After drying over anhydrous magnesium sulfate, the benzene was evaporated, leaving a slurry from which trichloromethanesulfonyl bromide was sublimed. After several sublimations, 5.88 g. (48.6% yield based on Cl_3CSO_2K) of trichloromethanesulfonyl bromide was obtained as colorless crystals which melted at 138.5–139°.

*Anal.*⁹ Calcd. for $CBrCl_3O_2S$: C, 4.58; Br, 30.46; Cl, 40.54; S, 12.22. Found: C, 4.62; Br, 30.36; Cl, 40.57; S, 12.01.

The infrared spectrum of this material showed two strong absorptions, one at 1398 and the other at 1177 cm^{-1} , due, respectively, to the unsymmetrical and symmetrical sulfur oxygen stretching modes.¹⁰

Reactions of Toluene, Cyclohexane, and Cyclopentane with Trichloromethanesulfonyl Bromide.—Trichloromethanesulfonyl bromide was dissolved in the hydrocarbon and the resulting solution was illuminated with a 275-w. Sylvania sunlamp for the period of time and at the temperature indicated in Table I. During the illumination, a stream of dry nitrogen was passed through the reaction mixture and carried the sulfur dioxide produced into a standardized sodium hydroxide solution. The sulfur dioxide formed in the reaction was determined by titration of an aliquot of this solution with standard acid. The chloroform and the bromination product produced in each reaction were identified by comparison of their gas chromatographic retention times with those of authentic samples on two or more columns. The quantitative determinations were made from the relationship of the peak areas of these components with that of an internal standard which was added in known quantity to a weighed sample of the reaction mixture.

Competitive Brominations of Toluene and Cyclohexane with Trichloromethanesulfonyl Bromide. Light-Induced.—A portion of a sample containing about equivalent quantities of trichloromethanesulfonyl bromide, toluene, cyclohexane, and chlorobenzene (which served as an internal standard for the gas chromatographic analysis) was subjected to gas chromatographic analysis

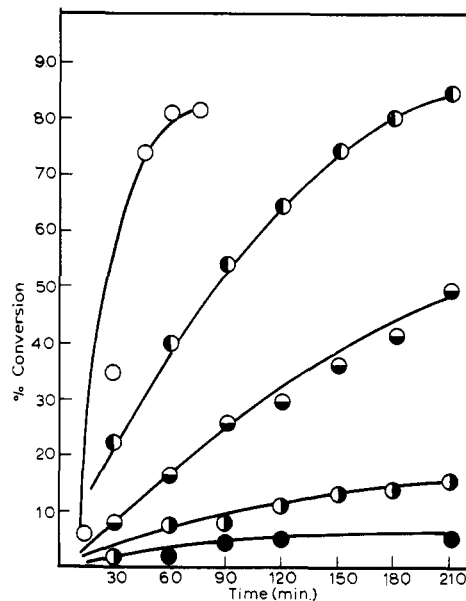


Figure 1.—Decomposition rates of Cl_3CSO_2Br (II) at 78°: O, light-induced reaction of 2.00 mmoles of II in 15 ml. of CCl_4 ; ●, 0.255 mole of Bz_2O_2 and 0.44 mmole of II in 25 ml. of CCl_4 ; ◐, 0.05 mole of Bz_2O_2 and of 0.48 mmole of II in 25 ml. of CCl_4 ; ◑, 0.001 mmole of Bz_2O_2 and 0.48 mmole of II in 25 ml. of CCl_4 ; ◒, 0.50 mmole of II in 25 ml. of CCl_4 .

and the initial peak heights of the toluene, cyclohexane, and chlorobenzene were determined. Another portion of the mixture was sealed in a Pyrex tube and illuminated with a 275-w. sunlamp for about 30 hr. at 78° in an ethanol vapor bath. At the end of this reaction period, the contents of the tube were chromatographed on the same column and the peak heights of toluene, cyclohexane, and chlorobenzene were found. The amounts of toluene and cyclohexane that remained were determined by comparison of the initial peak heights with those found after reaction, using the observed peak heights of the internal standard to correct for any differences in the size of the samples used in the analysis. In each case, about 25–50% conversion of the halogenating agent had occurred as determined by gas chromatographic analysis of the amount of chloroform produced. The relative reactivity ratio of the cyclohexane with respect to toluene, k_c/k_t , was determined from the data obtained, using the following equation

$$k_c/k_t = \log \frac{(C_6H_{12})_o}{(C_6H_{12})_f} / \log \frac{(C_6H_5CH_3)_o}{(C_6H_5CH_3)_f}$$

where the subscripts "o" and "f" refer to original and final amounts of the substrates.

Peroxide-Induced.—Equivalent quantities of toluene and cyclohexane were weighed into a Pyrex tube along with about 0.01 equiv. of trichloromethanesulfonyl bromide. About 10 mole % of benzoyl peroxide based on the brominating agent was added. The resulting solution, along with the gas chromatographic internal standard *o*-dichlorobenzene in amount about equivalent to trichloromethanesulfonyl bromide was sealed in the tube and heated at 78°. Samples were periodically withdrawn from the reaction mixture during the first 2 hr. of reaction and the amounts of cyclohexyl bromide and benzyl bromide were determined by gas chromatographic analysis. Since the changes in the hydrocarbon concentrations were negligible in such reactions, the relative reactivity ratio k_c/k_t was determined simply by dividing the amount of cyclohexyl bromide by that of benzyl bromide. The data given in Table II are the determinations on ten samples withdrawn during the initial 2-hr. reaction period from two different reaction mixtures.

Competitive Chlorinations of Toluene and Cyclohexane with Trichloromethanesulfonyl Chloride.—In the previously reported competition studies,² the ratio k_c/k_t was determined by the relative rates of disappearance of the two hydrocarbons in the manner described above for the light-induced competition studies with Cl_3CSO_2Br . In the present work, the relative reactivity ratio was determined by the appearance of the substrate chlorides in

(7) A. I. Vogel, "Quantitative Inorganic Analysis," 2nd Ed., Longmans, Green and Co., New York, N. Y., 1951, p. 488.

(8) "Scott's Standard Methods of Analysis," 5th Ed., N. H. Furman, Ed., Van Nostrand and Co., Inc., New York, N. Y., 1939, p. 266.

(9) Analysis performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(10) E. A. Robinson. *Can. J. Chem.*, **39**, 247 (1961).

benzoyl peroxide induced reactions in the manner described above for the peroxide-induced competition reactions with $\text{Cl}_3\text{CSO}_2\text{Br}$.

Rate Determinations.—The rates of the peroxide- and light-induced decompositions of $\text{Cl}_3\text{CSO}_2\text{Br}$ were determined either by measuring the rate of sulfur dioxide evolution or by infrared analysis of the reaction mixture.

In the sulfur dioxide evolution experiments, the sulfur dioxide produced was carried from the reaction in a stream of nitrogen into a standard sodium hydroxide solution. At specified time intervals, 5-ml. aliquots of the resulting solution were withdrawn and allowed to react with a known volume of standard potassium triiodide solution in 30 ml. of water containing 1 ml. of glacial acetic acid. The sulfite content in the aliquot was determined by titrating the iodine liberated with standard sodium thiosulfate solution.

The infrared method made use of the very strong and distinct absorptions at 1398 and 1177 cm^{-1} due, respectively, to the unsymmetrical and symmetrical sulfur-oxygen stretching modes.

Beer's law plots at both absorptions were obtained from standard solutions of $\text{Cl}_3\text{CSO}_2\text{Br}$ varying from 6×10^{-4} to $2.5 \times 10^{-1} M$ in carbon tetrachloride. Measurement of the absorption intensities of samples withdrawn from a reaction mixture allowed for the determination of the unreacted $\text{Cl}_3\text{CSO}_2\text{Br}$ in the sample.

All of the peroxide-induced reaction rates were determined by the infrared method and the photochemically induced reaction rates by the sulfur dioxide evaluation technique.

Heating trichloromethanesulfonyl chloride in carbon tetrachloride at 78° in the presence of 10 mole % benzoyl peroxide or illumination with a 275-w. sunlamp for 2 hr. in the absence of peroxide failed to cause any change in the intensities of the symmetrical and unsymmetrical sulfur-oxygen stretching frequencies at 1404 and 1183 cm^{-1} , respectively.

Acknowledgment.—We are indebted to the National Science Foundation for a grant in support of this research.

The Favorskiĭ Rearrangement of Pulegone Dibromide

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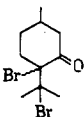



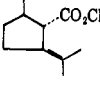
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Pulegone dibromide is converted by sodium methoxide in anhydrous methanol or sodium ethoxide in ethanol into equilibrium mixtures of 26% *cis* and 74% *trans* methyl and ethyl pulegenates, respectively. Hydrolysis of the *cis*- and *trans*-methyl and -ethyl pulegenates leads predominantly or exclusively to *trans*-pulegenic acid. The predominant or exclusive formation of *trans*-pulegenic acid is due to the rapid base-catalyzed equilibration of the *cis* and *trans* esters and the retarded rate of hydrolysis of the sterically hindered *cis* isomers.

Pulegone dibromide, produced by the addition of bromine to (+)-pulegone, is converted by heating with aqueous alkali to a mixture of *cis*- and *trans*-pulegenic acids,¹⁻³ whereas, with sodium in methanol^{2,4} or sodium ethoxide in ethanol,^{3,5} *trans*-pulegenic acid is the predominant or only product. It was suggested² that the course of the Favorskiĭ rearrangement reflects the likelihood that pulegone dibromide is a mixture of isomers and that stereospecific rearrangement with aqueous alkali affords a kinetically controlled mixture of acids, whereas, with sodium methoxide, methyl esters result and epimerize to the more thermodynamically stable *trans* ester which is converted to the *trans* acid during the reaction work-up (Table I). A contrary view was expressed by Cavill³; pulegone dibromide is considered to be a single isomer and rearranges stereospecifically with sodium ethoxide, whereas aqueous alkali produces a resonance-stabilized intermediate which equilibrates and leads ultimately to the observed mixture of *cis* and *trans* acids. We have re-examined this matter and wish to report evidence which confirms a modified version of our original interpretation.

When pulegone dibromide is heated with sodium methoxide in *anhydrous* methanol and the reaction mixture is poured rapidly into dilute acid in order to avoid basic hydrolysis, there is obtained, in 67% yield, a mixture of esters comprised of 26% methyl *cis*-pulegenate and 74% methyl *trans*-pulegenate. The same ratio of *cis*- and *trans*-ethyl pulegenates results when sodium ethoxide in dry ethanol is employed. Equilibration of pure methyl *trans*-pulegenate with sodium

Reactant	Base	Product	% <i>cis</i> ^a	% <i>trans</i>
	NaOH-H ₂ O		45-60	40-55
	NaOCH ₃ -CH ₃ OH H ₂ O		8	92
	NaOEt-EtOH H ₂ O		0	100
	NaOEt-EtOH		26	74
	NaOCH ₃ -CH ₂ OH		26	74
	NaOCH ₃ -CH ₃ OH		23	77

^a Analyses were conducted by vapor phase chromatography of the methyl (or ethyl) esters obtained directly or prepared from the acids by the action of diazomethane.

methoxide affords a mixture of 23% *cis* and 77% *trans*-methyl pulegenates. These observations establish the fact that the first isolable product of the reaction of pulegone dibromide with alkoxides is the thermody-

(1) O. Wallach, *Ann.*, **414**, 233 (1918).

(2) J. Wolinsky, H. Wolf, and T. Gibson, *J. Org. Chem.*, **28**, 274 (1963).

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