benzoyl peroxide induced reactions in the manner described above for the peroxide-induced competition reactions with Cl_3CSO_2Br.

Rate Determinations.—The rates of the peroxide- and light-induced decompositions of Cl_3CSO_2Br 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 aliquots of the resulting solution were withdrawn and allowed to react with a known volume of standard potassium triiodide solution in 30 ml.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 Cl_3CSO_2Br varying from 6×10^{-4} to 2.5×10^{-1} M in carbon tetrachloride. Measurement of the absorption intensities of samples withdrawn from a reaction mixture allowed for the determination of the unreacted Cl_3CSO_2Br in the sample.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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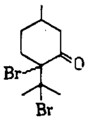
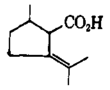
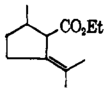
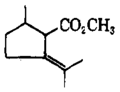
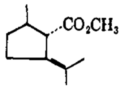
Pulegone dibromide is converted by sodium methoxide in anhydrous methanol or sodium ethoxide in ethanol into equilibrium mixtures of 26% *cis* and 74% *trans* methyl and ethyl pulegenates, respectively. Hydrolysis of the *cis*- and *trans*-methyl and -ethyl pulegenates leads predominantly or exclusively 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 suggested[2] 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 Cavill[3]; 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.

TABLE I

FAVORSKIĬ REARRANGEMENT OF PULEGONE DIBROMIDE

Reactant	Base	Product	% *cis*[a]	% *trans*
	NaOH–H_2O		45–60	40–55
	NaOCH$_3$–CH$_3$OH H_2O		8	92
	NaOEt–EtOH H_2O		0	100
	NaOEt–EtOH		26	74
	NaOCH$_3$–CH$_3$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.

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 hydrolyis, 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 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-

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

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

(3) S. A. Achmad and G. W. K. Cavill, *Australian J. Chem.*, **16**, 858 (1963).

(4) O. Wallach, *Ann.*, **289**, 349 (1895).

(5) H. Rupe and K. Schafer, *Helv. Chim. Acta*, **11**, 463 (1928).

TABLE 2

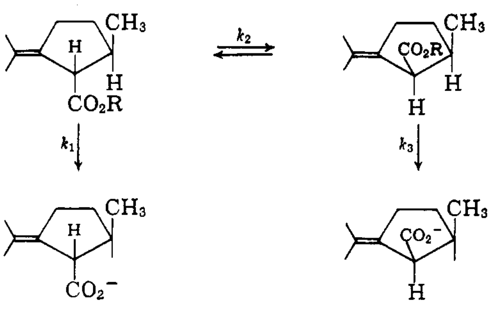
HYDROLYSIS OF ETHYL AND METHYL PULEGENATES

Reactant	Equivalents of KOH in EtOH-H_2O	—Neutral fraction, %— *cis*	*trans*	—Acidic fraction, %— *cis*	*trans*
Ethyl pulegenate, 24% *cis*–76% *trans*	0.31	33	67	0	100
	0.59	47	53	0	100
	0.84	53	47	0	100
	ca. 1.0	67	33	0	100
	2.0	0	0	0	100
Ethyl pulegenate, 100% *trans*	0.58	17	83	0	100
Methyl pulegenate, 24% *cis*–76% *trans*	0.24	29	71	12	88
	0.79	50	50	6	94
	2.0	0	0	4	96
Methyl pulegenate, 100% *cis*	2.28	0	0	5	95
Pulegenic acid, 46% *cis*–54% *trans*	2.0–3.0 (3 hr.)	...	...	48	52
	2.0–3.0 (41 hr.)	...	...	48	52

namically controlled mixture of *cis*- and *trans*-pulegenates with the *trans* esters predominating.

There now remains to be considered the divergence in isomeric composition between the esters isolated when water is excluded from the reaction mixture and the acids isolated when water is added during the reaction work-up. The reason for this anomaly becomes apparent when the hydrolyses of the ethyl and methyl pulegenates are examined. Hydrolysis of each pure ester or mixtures of the *cis* and *trans* isomers leads in every instance to the predominant or exclusive formation of *trans* pulegenic acid depending on whether one initiates with the methyl or ethyl esters, respectively. Equilibration of the *cis* and *trans* esters must obviously compete with their saponification. This is not surprising in view of the relatively high acidity of the methine group at C-2 which is flanked by activating carboalkoxy and isopropylidene groups. Moreover, the hydrolysis of the *trans* esters should proceed more rapidly than the sterically hindered *cis* esters, with the greatest rate differential expected for the bulkier ethyl esters.[6]

In order to determine whether epimerization competes with the hydrolysis of the *trans* esters, the equilibrium mixture of *cis* and *trans* esters was subjected to the action of limited amounts of alkali. If equilibration proceeds faster than the hydrolysis of the *trans* ester the composition of the recovered ester should remain unaltered. On the other hand, if the hydrolysis of the *trans* ester is the fastest step, then the recovered ester will be enriched in the *cis* isomer. Examination of Table II demonstrates that the latter situation prevails; that is, according to the equations below, k_1 is larger than k_2, which in turn is greater than k_3.



In summary, we have shown that the Favorskiĭ rearrangement of pulegone dibromide with alkoxides affords, as suggested earlier,[2] a thermodynamically controlled mixture of *cis*- and *trans*-pulegenates. The stereospecific formation of *trans*-pulegenic acid is a consequence of the facile epimerization of the *cis* and *trans* esters and the retarded rate of hydrolysis of the *cis* isomers. Earlier statements regarding stereospecificity at the initial stages of the Favorskiĭ rearrangement are naive. In view of the lack of information regarding the composition of the relatively unstable pulegone dibromide[7] and the present uncertainty regarding predictions relative to the steric course of the Favorskiĭ rearrangement,[8] it cannot presently be decided whether the initial ring contraction involves an intramolecular nucleophilic displacement of bromide ion or a unimolecular solvolysis of bromide ion from pulegone dibromide enolate anion.[3]

Experimental[9]

Pulegone Dibromide.—To a stirred and cooled solution of 108.3 g. (0.71 mole) of (+)-pulegone in 150 ml. of glacial acetic acid was added dropwise 100 g. (0.626 mole) of bromine. After the addition was completed (*ca.* 0.5 hr.) the solution was stirred for another 30 min. and was then poured onto crushed ice. The resulting oily mixture was extracted with eight 100-ml. portions of petroleum ether (b.p. 35–37°). The combined petroleum ether extracts, 800 ml., were washed with dilute sodium bicarbonate solution and dried over anhydrous magnesium sulfate. No further attempt was made to purify the unstable dibromide.

Methyl *cis*- and *trans*-Pulegenates.—To a heated and stirred solution of sodium methoxide (prepared from 23 g. of sodium) in 500 ml. of dry methanol was added dropwise 400 ml. of the dried petroleum ether solution of pulegone dibromide obtained above. The petroleum ether was distilled from the reaction mixture as the addition proceeded. After the addition was complete and all the hydrocarbon had distilled, the mixture was heated to reflux for an additional 2 hr. Most of the methanol was distilled and the cooled mixture was poured rapidly into 10% hydrochloric acid. The mixture was extracted with ether and the ether extracts were dried over magnesium sulfate. Distillation gave 38.20 g. (67%) of a mixture of methyl *cis*- and *trans*-pulegenates, b.p. 52–58° (0.70 mm.), $n^{25}\text{D}$ 1.4694. Gas chromatographic analysis of this product indicated the presence of 26% of the *cis* isomer and 74% of the *trans* isomer.

Methyl *cis*-pulegenate, isolated by v.p.c., displayed $n^{24.5}\text{D}$ 1.4630; λ_{max} 3.42, 5.80, 6.90, 7.02, 7.32, 7.45, 7.60, 7.78, 8.00, 8.20, 8.45, 8.60, 8.75, 9.00, 9.54, 10.00, 11.10, 11.28, 11.75, 12.45, and 13.30 μ; and n.m.r. signals at 0.94, 1.04 (CH_3CH—),

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(6) T. L. Jacobs and W. H. Florsheim, *J. Am. Chem. Soc.*, **72**, 261 (1950).

(7) In view of the fact that a mixture of stereoisomeric epoxides is produced by the action of peracids on (+)-pulegone [W. Reusch and C. K. Johnson, *J. Org. Chem.*, **28**, 2557 (1963)], it appears most likely that pulegone dibromide is also a mixture of stereoisomers.

(8) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3980 (1961).

(9) All boiling and melting points are uncorrected. Gas chromatographic analyses and separations were conducted with a Carbowax 20M column. Nuclear magnetic resonance spectra were measured with the Varian Associates A-60 spectrometer. Chemical shifts were measured with reference to tetramethylsilane as an internal standard. The microanalyses were performed by Dr. C. S. Yeh and associates.

1.62 $[(CH_3)_2C{=}C]$, 1.80 (—CH—), a multiplet centered at 2.27 (—CH_2— and —$CH_2C{=}C$—), 3.30, 3.40 (C=C—CH—CO—), and 3.60 p.p.m. (—OCH_3).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.20; H, 10.15.

Methyl *trans*-pulegenate, isolated by v.p.c., showed $n^{22}D$ 1.4636; λ_{max} 3.42, 5.80, 6.93, 7.02, 7.32, 7.50, 7.70, 8.00, 8.13, 8.72, 9.20, 9.90, and 13.50 μ; and n.m.r. signals at 0.98, 1.08 (CH_3—CH—), 1.58, 1.66 $[(CH_3)_2C{=}C$—], 1.92 (—CH—), a multiplet centered at 2.30 (—CH_2— and —C=C—CH_2—), 2.90 (—C=C—CH—CO—), and 3.60 p.p.m. (—OCH_3).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.93; H, 10.32.

cis- **and *trans*-Pulegenic Acids.**—To a heated and well-stirred solution of 60 g. of potassium hydroxide in 700 ml. of water was added dropwise 400 ml. of the petroleum ether solution of pulegone dibromide obtained above. The petroleum ether was distilled from the reaction as the addition proceeded. After the addition was complete and the hydrocarbon had distilled, the mixture was heated for 4–5 hr. The undissolved organic material floated to the top of the mixture after 2.5 hr. After cooling and extracting the mixture with ether, the alkaline solution was acidified with dilute hydrochloric acid and extracted with ether. The ether solution was dried and distilled to give 13.86 g. (26%) of the pulegenic acids, b.p. 80–104° (0.70 mm.), $n^{25}D$ 1.4776. Ethereal diazomethane converted the acids into the corresponding methyl esters; gas chromatographic analysis of the esters indicated the presence of 47% of the *cis* isomer and 53% of the *trans* isomer.

In another experiment the pulegone dibromide was freed of solvent before its addition to aqueous alkali. In this instance a 36% yield of pulegenic acids was obtained. The composition of the acid was essentially identical with that of the acid described above.

Ethyl *cis*- and *trans*-Pulegenates.—A dried petroleum ether solution of pulegone dibromide, prepared from 20.0 g. of (+)-pulegone, was added dropwise to a heated and stirred solution of sodium ethoxide (from 9.5 g. of sodium) in 200 ml. of carefully dried ethanol. As the addition proceeded the petroleum ether was distilled from the reaction mixture. After the addition was complete and the hydrocarbon had been distilled, the mixture was kept at reflux for 2 hr. The mixture was cooled and poured rapidly into 300 ml. of 10% hydrochloric acid. The heavy oil which separated was taken up with ether and the aqueous phase was thoroughly extracted with ether. The combined ether extracts were washed successively with water, sodium bicarbonate solution, and water and finally dried. Distillation gave after a forerun of pulegone, b.p. 54–56° (0.60–0.65 mm.), 13.74 g. (64%) of the ethyl pulegenates, b.p. 56–62° (0.60–0.65 mm.), $n^{23.5}D$ 1.4674. Gas chromatographic analysis indicated the presence of 26% of the *cis* isomer and 74% of the *trans* isomer.

Ethyl *cis*-pulegenate, isolated by v.p.c., displayed $n^{23}D$ 1.4634; λ_{max} 3.42, 5.82, 6.91, 7.35, 7.51, 7.79, 8.02, 8.55, 8.80, 9.00, 9.18, 9.55, 9.75, 10.55, and 11.25 μ; and n.m.r. signals at 0.96, 1.06 (CH_3—CH—), 1.15, 1.25, 1.35 ($\mathit{CH_3}$—CH_2—), 1.68 ($(CH_3)_2$-C=C—), a multiplet centered at 1.86 (—CH—) and 2.28 (—CH_2—, —C=C—CH_2—), a doublet centered at 3.35 (—C=C—CH—CO), and a quartet centered at 4.15 (O—$\mathit{CH_2}$—CH_3) p.p.m.

Ethyl *trans*-pulegenate, isolated by v.p.c., exhibited $n^{23}D$ 1.4594; λ_{max} 3.42, 5.82, 6.95, 7.38, 7.55, 7.72, 8.02, 8.15, 8.58, 8.90, 9.20, 9.70 μ; and n.m.r. signals at 0.98, 1.09 (CH_3—CH—), a triplet centered at 1.22 ($\mathit{CH_3}$—CH_2—), 1.62, 1.70 ($(CH_3)_2C{=}$C—), multiplets at 1.96 (—CH—CH_3), 2.39 (—CH_2—, —CH_2—C=C—), 2.93 (—C=C—CH—CO—), and a quartet centered at 4.16 p.p.m. (O—CH_2—CH_3).

Hydrolysis of Ethyl *cis*- and *trans*-Pulegenates.—The following describes the typical conditions employed for the hydrolysis of methyl and ethyl pulegenates. To a solution of 1.00 g. (5.1 mmole) of the ethyl esters in 5 ml. of absolute ethanol was added 0.241 g. (4.3 mmoles) of potassium hydroxide in 2 ml. of water. The resulting solution was kept at reflux for 3 hr. After dilution with water the solution was extracted with ether to remove neutral products. The alkaline solution was acidified with dilute hydrochloric acid and the mixture was extracted with ether. The acid was converted into the corresponding methyl ester with ethereal diazomethane. Gas chromatographic analysis indicated the exclusive presence of methyl *trans*-pulegenate.

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Basic Cleavages of Arylsulfonamides[1]

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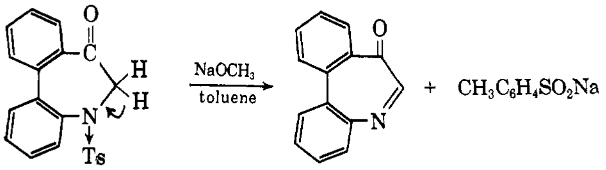
A novel, indirect, basic cleavage of arylsulfonamides of secondary amines has been studied. It appears to take place quite generally if the base which is used is strong enough to remove α-hydrogen. The reaction mechanism involves the formation of a >C=N— linkage and an arylsulfinate anion.

The basic cleavage of sulfonamides, in contrast with carboxamides, is a difficult reaction. Only in recent years have a few moderately useful methods of basic cleavage been devised.[3] Arylsulfonamides of some secondary amines have been successfully cleaved with sodium isoamoxide at 150–200°.[3b] The proposed mechanism involved a direct attack of the base at the sulfur atom with the replacement of the amino group.

No example of basic cleavage using metal amides has been reported but aminolysis of sulfonamides at 150–220° has been studied and successfully applied in some cases.[3c]

More recently several examples of a new type of basic cleavage of sulfonamides has been reported.[4] Proctor[4a] prepared a dibenzo derivative of azatropone in the following manner. Pyrrole derivatives have been prepared by similar cleavages of tosyl derivatives of dihydropyrroles.[4b,c]



The objectives of the present investigation were (1) to determine the nature and applicability of this

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[1] This work is part of a thesis submitted by E. Negishi in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[2] Harrison Fellow, 1962–1963.

[3] (a) Y. Takata, *J. Pharm. Soc. Japan*, **71**, 1471 (1951); D. Klamann and H. Bertsch, *Ber.*, **91**, 1688 (1958). (b) D. Klamann and H. Bertsch, *ibid.*, **212**, 1427 (1958). (c) D. Klamann and G. Hofbauer, *Ann.*, **581**, 182 (1953); D. Klamann and E. Fabienke, *Ber.*, **92**, 712 (1959).

[4] (a) G. R. Proctor, *Chem. Ind.* (London), 408 (1960); (b) A. V. Robertson, J. E. Francis, and B. Witkop, *J. Am. Chem. Soc.*, **84**, 1079 (1962); (c) A. H. Jackson, G. W. Kenner, and W. G. Terry, *Tetrahedron Letters*, **No. 20**, 921 (1962).