Nucleophilic Substitution at Dicoordinated Sulfur. Effect of the Leaving Group on the Reaction between Triphenylmethyl Sulfenyl Derivatives and *n*-Butylamine

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Received September 8, 1969

The rates of reaction between trityl sulfenyl chloride, bromide, iodide, thiocyanate, and *n*-butylamine have been measured in benzene and in benzene–ethanol (1:1) at 25° by a spectrophotometric technique. In solvent benzene, for all substrates the rate depends on the square of the amine concentration, while in benzene–ethanol the reactions are first order in amine. The change in leaving group does not cause large variations in the reaction rates. The relative rates for nucleophilic displacement at dicoordinated sulfur with I, SCN, Br, and Cl, respectively, as leaving groups are the following: (a) in benzene, 1, 3, 190, and 140; (b) in benzene–ethanol, 1, 2.2, 191, and 400. Such an order of relative rates is discussed in terms of sulfur d-orbital participation in the transition state.

The question of d-orbital participation in nucleophilic substitution at sulfenyl sulfur was discussed by Parker and Kharasch in 1959.[1] Since then only a few articles have appeared dealing with the same subject. The view originally expressed by Fava and Iliceto[2] that there is little if any d-orbital participation to the transition state is supported by more recent papers[3] and by some unpublished data.[4] However, evidence for the formation of pentacoordinate sulfur compounds as intermediates in organic reactions has been reported by Kwart[3a] for the chlorination of sulfenyl chlorides and by Trost[6] in the reaction of sulfonium salts with organolithium compounds.

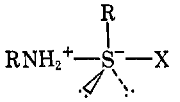
In a recent paper[7] we have already taken up this problem by studying the reaction between triphenylmethyl sulfenyl chloride (RSCl) and *n*-butylamine ($BuNH_2$) to form N-(*n*-butyl)-triphenylmethyl sulfenamide (RSNHBu) and *n*-butylamine hydrochloride (eq 1, X = Cl).

$$RSX + 2BuNH_2 \longrightarrow RSNHBu + BuNH_3X \qquad (1)$$

In benzene the reaction is cleanly second order in amine while in the presence of several additives a term which is first order in amine is also important and in some cases predominates. Consideration of the effect of the additives led to the conclusion that the reaction is subject to general base catalysis. A two-step mechanism (2a,b), where hydrogen abstraction occurs after formation of an intermediate, has been postulated. Although we were inclined to consider more likely the formation of a pentacovalent intermediate (I), formed through the use of sulfur d orbitals, we could not rule out an ion-pair intermediate (II). We felt that a more conclusive answer about which of the two intermediates is formed and about the general problem of d-orbital participation in nucleophilic substitution at divalent sulfur could be offered by a study of the leaving group effect on reaction 1 since such an effect is related to the amount of bond breaking at the transition state.

$$RSX + BuNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{intermediate} \qquad (2a)$$

$$\text{intermediate} \xrightarrow{k_B[B]} \text{products} \qquad (2b)$$



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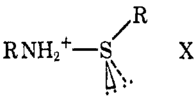

II

Results

The rates of reaction of triphenylmethyl sulfenyl bromide, RSBr, triphenylmethyl sulfenyl iodide, RSI, and triphenylmethyl sulfenyl thiocyanate, RSSCN, with $BuNH_2$ have been measured in benzene at 25°. In all cases the sulfenamide and the corresponding *n*-butylammonium salt were formed (eq 1) in quantitative yield. The data are collected in Table I. The general behavior of these substrates is very similar to that already found for RSCl.[7] The pseudo-second-order rate coefficient, $k_2 = k'/[BuNH_2]$, where k' is the pseudo-first-order rate coefficient, varies linearly with the amine concentration (eq 3) and vanishes at zero amine concentration, as shown in Figure 1. Thus for all substrates in benzene the reaction is second order in amine. Since the salt formed in the reaction is a good catalyst, at low amine concentration autocatalysis was observed; thus initial rates have been measured. As the concentration of amine is increased, the catalytic effect of the salt becomes negligible and the pseudo-first-order plots appear to be linear within experimental error. This phenomenon has been considered in detail in the preceding paper[7] for RSCl and we shall not discuss it further. The close similarity of behavior between RSCl and the substrates considered in this paper is also shown by their response to additions of salts, polar solvents, or tertiary amines.[8] It is this similarity between the various substrates, which implies an identity of mechanism under various experimental conditions, which will allow us to draw meaningful conclusions from their relative rates of reaction.

$$k_2 = k_3[BuNH_2] \qquad (3)$$

As seen for RSCl,[7] one of the important consequences of the presence of additives is that in their presence the second-order rate constant, k_2, still varies linearly with

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[1] A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

[2] A. Fava and A. Iliceto, *J. Amer. Chem. Soc.*, **80**, 3478 (1958).

[3] (a) E. N. Givens and H. Kwart, *ibid.*, **90**, 378, 386 (1968); (b) J. L. Kice and J. M. Anderson, *J. Org. Chem.*, **33**, 3331 (1968); (c) C. Brown and D. R. Hogg, *Chem. Commun.*, 38 (1967).

[4] (a) A. Ceccon and A. Fava, unpublished data cited in ref 3b and 5; (b) L. Senatore, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, in press.

[5] E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968).

[6] B. M. Trost, R. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969).

[7] E. Ciuffarin and G. Guaraldi, *ibid.*, **91**, 1745 (1969).

[8] E. Ciuffarin and G. Guaraldi, unpublished results.

TABLE I

KINETIC DATA FOR THE REACTION BETWEEN RSX AND $BuNH_2$ IN BENZENE AT 25°

RSX[a]	$[BuNH_2] \times 10^2\ M$	$k' \times 10^4\ sec^{-1}$	$k_2 \times 10^3\ M^{-1}\ sec^{-1}$
X = Br	0.256	0.26[b]	10.1
	0.508	1.1[b]	22
	0.566	1.1[b,c]	20
	0.968	3.6[b]	37
	1.00	3.7[b]	37
	1.13	4.3[b,c]	38
	2.26	18[c]	79
	2.31	19	82
	2.56	26	100
	4.29	59	140
	5.08	91	180
X = I	4.52[d]	0.44[b,d]	0.98
	5.08	≤0.48[b,e]	≤0.95
	5.08	0.41[b]	0.81
	6.71	0.63[b]	0.94
	9.05	1.7[b,d]	1.9
	10.0	1.9[b]	1.9
	16.6	5.6[b]	3.4
	18.1[d]	5.7[b,d]	3.1
	19.4	5.8	3.0
	32.7	24	7.3
X = SCN	5.08	1.3	2.6
	13.2	8.6[b]	6.5
	33.1	61	18

[a] The concentration of the substrate ranged between 1 and 2 × $10^{-4}\ M$. [b] Initial rate. [c] In the presence of 73 mg/l. of decomposition products (see Results). [d] In the presence of 79 mg/l. of decomposition products (see Results). [e] [RSI] = 2.9 × $10^{-2}\ M$; followed by titration with iodate (see Experimental Section).

the amine concentration but a term which is first-order in amine emerges (eq 4). The form of eq 4 shows that

$$k_2 = k_0 + k_3'[BuNH_2] \tag{4}$$

the effect of the leaving group cannot be drawn directly from a comparison of the second-order rate constant, k_2, which is not independent of the amine concentration. The effect of the leaving group can be measured on k_0 and/or k_3 which are both independent of the amine concentration. The data in benzene are perfectly suited to measure the effect of the leaving group on k_3 since in such a solvent eq 3 applies. To determine the leaving-group effect on k_0 a solvent medium has to be found where the third-order term ($k_3'[BuNH_2]$) is negligible and thus $k_2 = k_0$. A suitable solvent is a 50% benzene–alcohol mixture,[9] where k_2 is in fact independent of the amine concentration. The data are collected in Table II.

Although ethyl alcohol reacts with sulfenyl halides,[10] experiments showed that the reaction is very much slower than that which occurs upon further addition of $BuNH_2$. Moreover, the only product recovered in quantitative yield from the sulfenyl derivatives (0.2 *M*) and $BuNH_2$ (0.4 *M*) in 50% benzene–ethanol was the sulfenamide. Although product identification could not be performed under the highly diluted kinetic conditions, the possibility of ethanolysis in the kinetic runs was excluded on mechanistic grounds. Ethanolysis is in fact very slow also in the presence of a large excess of triethylamine (3.36 × $10^{-2}\ M$), while 2.58 × $10^{-3}\ M$ butylamine is sufficient to cause fast reaction. Thus, addition of ethyl alcohol does affect the reaction rate without changing the products. The rates and their relative values in pure benzene and in 50% benzene–ethanol are summarized in Table III.

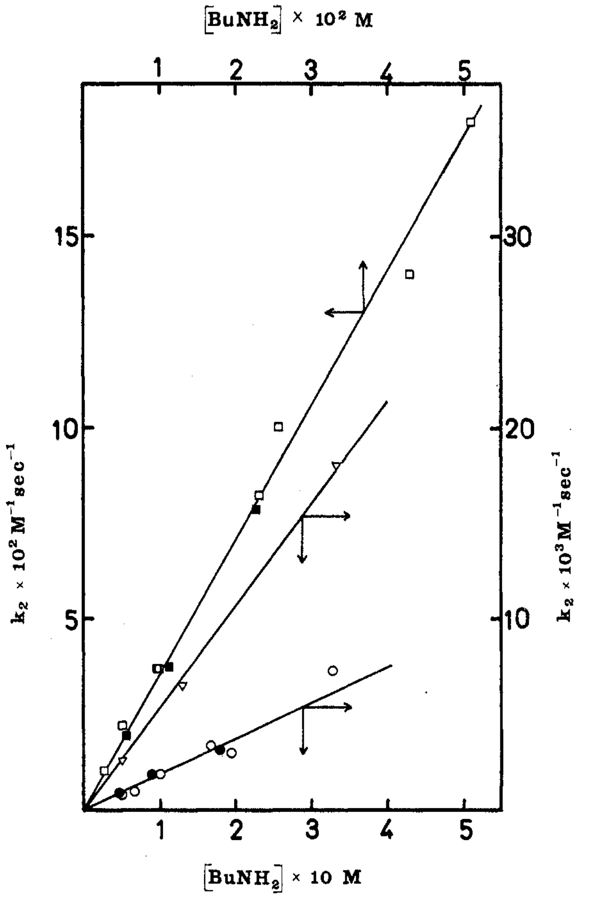

Figure 1.—Plots of the second-order rate constant for the reaction of n-$BuNH_2$ with RSX in benzene at 25° *vs.* the amine concentration: □ = RSBr, ▽ = RSSCN, ○ = RSI, ■ = RSBr in the presence of decomposition products, ● = RSI in the presence of decomposition products.

TABLE II

KINETIC DATA FOR THE REACTION BETWEEN RSX AND $BuNH_2$ IN 50% BENZENE–ETHANOL AT 25°

RSX[a]	$[BuNH_2] \times 10^3\ M$	$k' \times 10^4\ sec^{-1}$	$k_2,\ M^{-1}\ sec^{-1}$
X = Cl	2.76	190	6.9
	4.32	290	6.7
	2.58[b]	180	7.0
X = Br	2.76	91	3.3
	5.66[c]	180	3.2
X = SCN	1.44	0.56	0.039
	4.32	1.6	0.037
	27.6	10.5	0.038
X = I	27.6	4.7	0.017
	45.2[d]	7.7	0.017

[a] The substrates' concentration ranged between 1 and 2 × $10^{-4}\ M$. [b] With added Et_3N, 3.36 × $10^{-2}\ M$. [c] In the presence of 70 mg/l. of decomposition products (see Results). [d] In the presence of 85 mg/l. of decomposition products (see Results).

Owing to their thermal lability RSBr and RSI could not be thoroughly purified and their elemental analysis was less than satisfactory. A purity of 96% could be approximately assessed for the two products. One could argue that the presence of impurities might affect in some way the kinetics and thus impair the results

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[9] In pure ethyl alcohol the reaction is too fast to be measured with standard techniques for RSCl and RSBr.

[10] L. Goodman and N. Kharasch, *J. Amer. Chem. Soc.*, **77**, 6541 (1955).

TABLE III
SUMMARY OF THE LEAVING-GROUP EFFECT IN BENZENE AND 50% BENZENE–ETHANOL

X	k_3, M^{-2} sec^{-1}	Benzene, relative rates	50% benzene–ethanol k_2, M^{-1} sec^{-1}	50% benzene–ethanol Relative rates
Cl	2.6[a]	140	6.8[c]	400
Br	3.6[b]	190	3.25[c]	191
SCN	.057[b]	3	0.038[c]	2.2
I	.019[b]	1	0.017	1

[a] From ref 7. [b] Calculated from the slope of Figure 1. [c] Average value.

and the mechanistic conclusions resting on them. Hence, a number of experiments has been performed in the presence of a relatively large amount (about the same weight of the substrate) of their own decomposition products (see Experimental Section). The data thus obtained are identical within experimental error with those found without addition of decomposition products.

Discussion

The effect of the leaving group on the rate of reaction has long been recognized as a useful criterion for distinguishing whether or not bond breaking has made significant progress in the transition state.[11–13] If the leaving group is still almost fully bonded in the transition state, its electronegativity is the most important factor regulating the reactivity of the substrate;[11,14] on the contrary, when bond breaking is important, basicity of the leaving group and strength of the bond which is broken are responsible for the mobility of the group to be displaced,[15,16] bond strength being the more important factor.

Examples of reactions occurring with or without significant bond breaking in the transition state are well known for substitution at aliphatic, aromatic, or carbonyl carbon. When bond breaking is important, the halogen mobility follows the order I > Br > Cl with a Br/Cl ratio of about 400.[17] On the contrary, when bond breaking is unimportant, the difference in mobility is usually small[12,18] and mostly in the reverse order.

The effect of the leaving group has also been measured in nucleophilic substitutions at silicon[19] and sulfur.[4b,20] However, the difference in leaving group was obtained by a *para* substitution while maintaining constant the element displaced. Clearly in such cases the mobility of the leaving group parallels its basicity.

This is the first example of a study of the leaving group effect on sulfur obtained by a change of the displaced element.

Although to our knowledge no bond dissociation energies for the S–X bond of sulfenyl derivatives are available, data from organic and inorganic halides and sulfides[21] allow us to reasonably assess the following order of decreasing bond strength: S–Cl $\simeq$ S–SCN > S–Br > S–I.

Were bond breaking important in nucleophilic displacement at divalent sulfur, we would expect the mobility of the leaving group to follow the order I > Br > SCN $\simeq$ Cl. This order does not resemble the leaving group mobilities summarized in Table III. Chlorine is in fact at least 100 times more easily displaced than iodine; *i.e.*, the substrate with the weaker S–X bond reacts more slowly. Thus we do not expect appreciable S–X bond fission at the transition state.

In order to explain the second order in amine found in benzene, the mechanism involving the intermediate (eq 2) seems the most likely explanation.[7] The present results rule out an attack by an amine dimer even though such a possibility is sometimes offered as an explanation of the order 2 in amine.[22] A one-step nucleophilic displacement by an amine dimer would in fact assume appreciable S–X bond fission at the transition state and iodine should be much more easily displaced than chlorine. On the same grounds we can also exclude the possibility of an ionization mechanism *via* sulfenium ions (eq 5) which have been postulated for many reactions of sulfenyl derivatives.[23]

$$\mathrm{RSX} \overset{\substack{\text{assisted}\\ \text{by}\\ \text{additives}}}{\rightleftarrows} \mathrm{RS}^{+} + \mathrm{X}^{-} \xrightarrow{\mathrm{B}} \text{products} \qquad (5)$$

Steady-state treatment of eq 2 gives

$$k_2 = \frac{k_1 k_{\mathrm{B}}[\mathrm{B}]}{k_{-1} + k_{\mathrm{B}}[\mathrm{B}]} \qquad (6)$$

where k_2 is the observed second-order rate coefficient. If we assume that in benzene $k_{-1} \gg k_{\mathrm{B}}[\mathrm{B}]$, eq 6 simplifies to

$$k_2 = \frac{k_1 k_{\mathrm{B}}[\mathrm{B}]}{k_{-1}} \qquad (7)$$

which is equivalent to the observed rate expression (eq 3). On the other hand in 50% benzene–ethanol overall second-order kinetics is observed which is consistent with the suggested mechanism, if in that medium $k_{\mathrm{B}}[\mathrm{B}] > k_{-1}$. This is reasonable in view of the consideration that the solvent itself may operate as the base.[7] Thus in 50% benzene–ethanol k_2 measures the rate of formation of the intermediate (eq 8).

$$k_2 = k_1 \qquad (8)$$

Table III shows that the relative mobility in 50% benzene–ethanol is Cl > Br > SCN > I. This order parallels nicely the order of decreasing electronegativity of the group to be displaced. It seems that the major "effect" of the leaving group is that of creating a positive charge on the reaction center facilitating the rate of formation of the intermediate without extensive bond breaking. A very similar situation can be found in aromatic nucleophilic substitutions where the second

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(11) J. F. Bunnett, E. W. Garbish, Jr., and K. M. Pruitt, *J. Amer. Chem. Soc.*, **79**, 385 (1957).

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(13) W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **90** 2622 (1968).

(14) H. Suhr, *Chem. Ber.*, **97**, 3268 (1964).

(15) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1962, pp 185–392.

(16) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., New York, N. Y., 1962, p 29.

(17) (a) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Amer. Chem. Soc.*, **86**, 1553 (1964); (b) Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760 (1965); (c) A. Y. Parker, *J. Chem. Soc.*, 1328 (1961).

(18) J. F. Bunnett and C. Bernasconi, *J. Amer. Chem. Soc.*, **87**, 5209 (1965).

(19) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., New York, N. Y., 1965, p 146.

(20) J. L. Kice and G. Guaraldi, *J. Org. Chem.*, **31**, 3568 (1966).

(21) T. L. Cottrell, "The Strength of Chemical Bonds," Butterworths, London, 1954.

(22) (a) F. M. Menger, *J. Amer. Chem. Soc.*, **88**, 3081 (1966); (b) R. F. Hudson and I. Stelzer, *J. Chem. Soc., B*, 775 (1966).

(23) N. Kharasch, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, Oxford, 1961, pp 375–396.

step of the intermediate complex mechanism[11,18] is not rate determining. In these cases the maximum variation for different leaving groups goes from 5 to 100.[11,18]

In benzene a similar order of reactivity obtains even though the comparison involves third-order rate coefficients resulting from a combination of no less than three rate constants, $k_3 = k_1k_B/k_{-1}$ (eq 7). This may be taken to imply that the factor controlling the relative rate is again the formation of the intermediate.

Since in both solvent media bond breaking seems unlikely to occur to an appreciable extent, the only way to account for this is to assume that sulfur expands its valence shell and that the leaving group is still almost fully bonded in the transition state. In benzene–ethanol, once the transition state is passed, formation of products is very fast and no intermediate can be kinetically detected. In benzene, where hydrogen abstraction is the slow step, an intermediate is formed. This intermediate could either be an ion pair (II) or a complex where both entering and leaving groups are bonded to a pentacovalent sulfur (I). The formation of an ion pair has been suggested by Kharasch and Goodman[10] in the base-catalyzed methanolysis of sulfenyl halides and by Savige and Fava[24] in the base-catalyzed racemization of thiolsulfinates.

Although we cannot rule out the formation of an ion pair, we prefer the pentacovalent complex since the very labile intermediate is likely to be very close in energy and structure[25] to the pentacovalent transition state, from which it would differ only slightly in bond lengths. Its geometry is likely to be a trigonal bipyramid with the two electron pairs in radial position, as the most electropositive substituents, and with the amino and leaving groups in the apical positions as the more electronegative ligands[26] (I).

Very recently Kice and Anderson[3b] have taken a position against d-orbital participation in nucleophilic substitutions at sulfur. They support their view with other reported data[3a,c,4a] besides their own. Although we also tend to believe[4b] that in many instances there is no d-orbital participation, we would like to add a word of caution against generalizations. Even silicon, which is usually presented as an element which can easily expand its valence shell, does not always do so. There are data[3a,6] besides those presented in this paper that are certainly in favor of d-orbital participation. It might be the case that different charge distributions in the transition state could bring about structurally different transition states. As a matter of fact while d-orbital participation can be safely excluded with negatively charged nucleophiles, evidence in favor of d-orbital participation has been obtained when neutral reagents have been used.

Experimental Section

Materials.—Preparation and/or purification of benzene, *n*-butylamine, triphenylmethyl sulfenyl chloride, and N-(*n*-butyl)triphenylmethylsulfenamide have been already described.[7] Reagent grade absolute ethanol was used without further purification.

Triphenylmethyl Sulfenyl Bromide.—A suspension of 1 g of RSCl and 0.7 g of NaBr in acetone is vigorously stirred for about 1 hr.[27] The mixture is filtered and, after evaporation of the solvent in a rotary evaporator at room temperature, 0.9 g of crude RSBr is obtained. The crude bromide is dissolved in benzene, dried over anhydrous sodium sulfate, and filtered; the solution is concentrated in a rotary evaporator. Upon addition of petroleum ether (bp 40–60°) a precipitate obtains which is further recrystallized from benzene–petroleum ether, yield 50%, orange crystals which slowly decompose at room temperature or faster upon heating. The product can be kept for extended periods at temperatures below 0°.

Anal. Calcd for $C_{19}H_{15}SBr$: C, 64.25; H, 4.22; S, 9.04; Br, 22.5. Found: C, 63.3; H, 4.3; S, 9.8; Br, 22.4.

Triphenylmethyl Sulfenyl Iodide.—A suspension of 400 mg of RSCl in 35 ml of petroleum ether is shaken for about 1 min[27] with 550 mg of NaI in 5 ml of acetonitrile. The mixture is washed twice with water, once with 10 ml of 0.05 *N* thiosulfate, and three times with water. After the ethereal layer cools to about −80° a precipitate is obtained which is filtered off at −80°. The precipitate is washed twice with cold petroleum ether and dried with a current of dry air. The apparatus used in the preparation must be rapidly disassembled and the product used up within a few minutes since at room temperature decomposition is complete in about 30 min, yield 40%, deep orange powder. The product can be kept for extended periods under nitrogen in sealed vials at Dry Ice temperature. In the 5–6 min necessary to disassemble the apparatus used in the preparation and to make up a solution, no decomposition occurs (the product is probably still cold). However, as soon as decomposition starts with liberation of iodine, it progresses very rapidly. In solution the product is much more stable even at room temperature, in the absence of light. The presence of iodine catalyzes the decomposition.

Anal. Calcd for $C_{19}H_{15}SI$: S, 7.97; I, 31.55. Found: S, 8.58; I, 30.[28]

The decomposed product consists mostly of iodine, sulfur, and trityl sulfide with a trace of disulfide[29] even though mechanistic analysis of the decomposition[29] shows that the products initially formed are probably iodine and disulfide.

Anal. (of a decomposed sample). Calcd for $C_{19}H_{15}SI$: C, 56.7; H, 3.73; S, 7.97; I, 31.55. Found: C, 57.6; H, 3.8; S, 8.45; I, 30.3.[30]

Triphenylmethyl Sulfenyl Thiocyanate.—A suspension of 0.453 g of RSCl and 0.3 g of NaSCN in 25 ml of acetone is stirred for about 30 min. The mixture is filtered and evaporated in a rotary evaporator. An oil is obtained which yields white crystals upon addition of petroleum ether. The product is recrystallized from benzene–petroleum ether: yield after recrystallization, 50%; mp 101–102°.

Anal. Calcd for $C_{20}H_{15}S_2N$: C, 72.03; H, 4.53; S, 19.22; N, 4.20. Found: C, 72.1; H, 4.5; S, 19.1; N, 4.25.

Kinetics.—Kinetic measurements were carried out by the general technique described earlier[7] at the following wavelengths for RSSCN, RSCl, RSBr, and RSI, respectively: 280, 280, 380, and 440 mμ. A single run with RSI (2.9×10^{-2} *M*) was followed by titration with 0.01 *N* iodate of the iodide formed in the reaction and extracted with water from the benzene solution. At such a high concentration of substrate autocatalysis was so strong that the initial rate could not be measured accurately.

While RSCl and RSSCN could be thoroughly purified, RSBr gives only a fair analysis and RSI has a purity of about 96%. However, the concentration of the substrates was never higher than $^1/_{20}$ of butylamine and thus a small per cent impurity should not change the kinetics. Although the most likely impurities are sulfur, trityl disulfide, and sulfide, which are not likely to affect the kinetics, several runs were followed in the presence of decomposition products.

The decomposition products of RSBr have been obtained from a sample of the product which had been left for about a week at room temperature. The orange crystals yielded a yellow powder.

The decomposition products of RSI were prepared from a sample of the product left at room temperature for about 2 hr. The mixture, by analogy with the preparation of RSI, was dis-

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[24] W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965).

[25] G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

[26] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1967, p 402.

[27] A check of the rate of reaction in similar experimental conditions but in homogeneous phase shows that the reaction is over in less than 10 sec.

[28] By titration with iodate after reaction with excess butylamine.

[29] Unpublished data by M. Tentori, E. Ciuffarin, and A. Fava.

[30] By titration with thiosulfate.

solved in petroleum ether and freed from iodine by washing once with 0.05 N thiosulfate and twice with water. The solvent was then stripped at room temperature with a rotary evaporator.

Although RSI and to a lesser degree RSBr are thermally unstable, in solution and in the absence of light they can be kept 1 day or more at room temperature without any detectable decomposition. The uv spectrum is a very good probe for decomposition since in each case the spectrum of the decomposed product is quite different from that of the starting material. The stability depends on the concentration. For example, solutions 10^{-2} M of RSI are stable for about 24 hr in the dark before decomposition starts. At the concentrations used in this paper ($1\text{-}2 \times 10^{-4}$ M) the solutions are stable 1 week or more and the limited exposure to light in the spectrophotometer is not sufficient to initiate the decomposition. Solutions of RSBr present an even greater stability.

Products.—N-(n-Butyl)triphenylmethylsulfenamide is the only product recovered in the reaction of RSI, RSBr, and RSSCN with n-butylamine. To about 1 g of RSI, RSBr, and RSSCN in 20 ml of benzene, n-butylamine was added (5% excess) while stirring. The mixture was washed three times with 1 N HCl and three times with water and dried over anhydrous sodium sulfate. The solution was filtered and the solvent stripped in a rotary evaporator. In order to remove all traces of benzene, about 10 ml of petroleum ether was added and evaporated as before. The weight of the oil thus obtained was within 95 and 102% of the stoichiometric yield in sulfenamide. Moreover, the ir spectrum of the oil was identical with that of an authentic sample. After recrystallization from petroleum ether[7] yields of pure, crystalline product ranging from 75 to 85% were obtained.

Registry No.—butylamine, 109-73-9; trityl sulfenyl chloride, 24165-03-5; trityl sulfenyl bromide, 24165-04-6; trityl sulfenyl iodide, 24215-85-8; trityl sulfenyl thiocyanate, 24165-05-7.

Acknowledgment.—This investigation was supported by CNR, Rome, under Contract No. 69.01531 115.-3357.0.

The Synthesis of *cis*-Pulegol and Its Allylomerization Products, 3-*p*-Menthen-8-ol and 3-*p*-Menthen-8-yl Ethers

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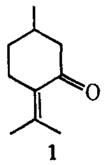
Received June 10, 1969

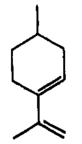
(−)-*cis*-Pulegol (6) allylomerizes readily to (+)-3-*p*-menthen-8-ol (5), $n^{20}\text{D}$ 1.4750, $\alpha^{25}\text{D}$ +80°, under mildly acidic conditions. In the presence of alcohols, 3-*p*-menthen-8-yl ethers (4) are also formed, while, in the presence of aluminum isopropoxide (AIP), at temperatures above 100°, both 5 and 6 dehydrate, affording a mixture of 3,8-*p*-menthadiene (2) and 2,4(8)-*p*-menthadiene (3), a fact that may account for the failure of previous workers to isolate pulegols from pulegone (1) by a Meerwein–Pondorff–Verley reduction. *trans*-Pulegol (6a), because of its greater instability, could not be detected from reduction products of 1 under kinetically or thermally controlled conditions.

In the course of an investigation on the nature of some alcohols related to pulegols, we reviewed the possible synthetic routes for *cis*- and *trans*-pulegol (6 and 6a). The AIP reduction of (+)-pulegone (1) at 120–170° according to Short and Read[1] yielded, instead of the desired alcohols, mainly 3,8- and 2,4(8) *p*-menthadiene (2 and 3) and minute amounts (5%) of an alcohol to which they assigned the structure of neoisopulegol.

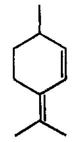
Lithium aluminum hydride reduction of (+)-pulegone (1) proceeded smoothly and yielded (−)-*cis*-pulegol (6), mp 35.5, $\alpha^{25}\text{D}$ −80°, in over 99% yield. Similar results were reported by Porsch, *et al.*,[2] with $NaBH_4$. However, in an attempt to synthesize *trans*-pulegol (6a) by treating excess triisobutylaluminum (TIBAL) with (+)-pulegone (1), under conditions[3] reported to favor kinetically controlled backside attack leading to an axial OH, we obtained none of the expected *trans*-pulegol (6a) but, instead, (−)-*cis*-pulegol (6), in over 85% yield, together with a small amount (8–10%) of its allylomer, (+)-3-*p*-menthen-8-ol (5). When we carried out the reduction of 1, in isopropyl alcohol (IPA) in the presence of 0.5–1 equiv of AIP at 85° for 4–5 hr, we obtained the following reaction mixture (vpc by order of elution on 20M 1/8-in. column at 200°).



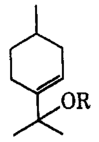
1
(23.5%)



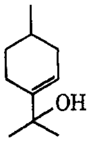
2
(12.5%)



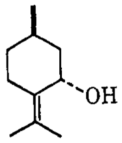
3
(8.5%)



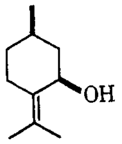
4, R = Ip
(6%)



5
(28%)

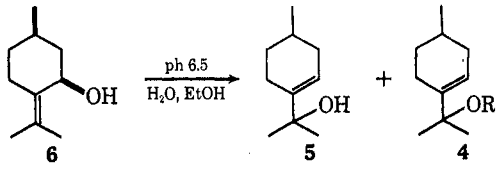


6a
(0%)



6
(21%)

An extension of the reaction time, to complete the conversion of the unreacted pulegone (1), resulted only in larger amounts of 2 and 3 being formed. Unreacted pulegone (1), which made the separation of 3-*p*-menthen-8-ol (5) very difficult, was easily converted into *cis*-pulegol (6) by reduction with $LiAlH_4$. If, on the other hand, the unreacted pulegone (1) was oximated, with a mixture of $NH_2OH \cdot HCl$, and sodium acetate in aqueous ethanol (pH 6.5), most of the *cis*-pulegol (6) was



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[1] A. G. Short and J. Read, *J. Chem. Soc.* 1306 (1939); see also Read and Grubb, *ibid.* 242 (1934).

[2] F. Porsch, H. Farnow, and H. Winkler, *Dragoco Rept.*, **4**, 75 (1964).

[3] H. Haubenstock and E. G. Davidson, *J. Org. Chem.*, **28**, 2772 (1963).