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# The Reaction of Sulfenyl Chlorides with Thioethers. II. Kinetic Studies

Michinori ŌKI and Keiji KOBAYASHI

*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo*

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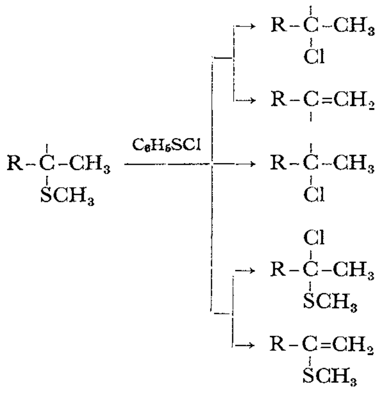
The rates of the reaction of methyl α-phenethyl sulfide with benzenesulfenyl chloride were measured by means of product analyses. It was found that the reaction was general-acid-catalyzed and autocatalyzed. The rate-determining step was suggested to be the formation of a sulfonium ion derived from the reactants. Mechanisms for the formations of the products are suggested.

In the preceding paper,[1] a general survey of the reactions of thioethers with sulfenyl chlorides has been presented. It has been established that three types of reactions occur, depending upon the structure of the thioethers: 1) the sulfur-carbon bond is cleaved to form a carbonium ion, which then undergoes nucleophilic substitution by chloride-ion and El-type elimination; 2) there is a cleavage of the C–S bond, with the simultaneous formation of a C–Cl bond, *i. e.*, an $S_N2$-type reaction takes place, and/or 3) there is oxidative chlorination at the alpha position, together with dehydrogenation, to form vinyl sulfide derivatives, probably *via* a common intermediate.



The purpose of this paper is to present kinetic data on the reaction between the thioether and the

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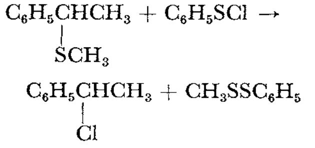
[1] M. Ōki and K. Kobayashi, This Bulletin, **43**, 1223 (1970).

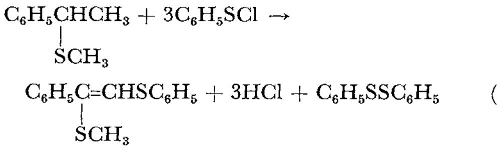
sulfenyl chloride, and also to propose reaction mechanisms for the formation of products.

## Results and Discussion

For the kinetic measurements, methyl α-phenethyl sulfide has been chosen as the sample because this compound has been shown to undergo two kinds of reactions of the possible three: the products are α-phenethyl chloride and a *cis-trans* mixture of α-methylthio-β-phenylthiostyrene. The stoichiometries of the formations of these compounds can be described as follows:[1]



$$\underset{\displaystyle SCH_3}{C_6H_5CHCH_3} + C_6H_5SCl \rightarrow \underset{\displaystyle Cl}{C_6H_5CHCH_3} + CH_3SSC_6H_5 \qquad (1)$$



$$\underset{\displaystyle SCH_3}{C_6H_5CHCH_3} + 3C_6H_5SCl \rightarrow \underset{\displaystyle SCH_3}{C_6H_5C}{=}CHSC_6H_5 + 3HCl + C_6H_5SSC_6H_5 \qquad (2)$$

The rates of the reaction of 0.199M methyl α-phenethyl sulfide with 0.525M benzenesulfenyl chloride in carbon tetrachloride at 25°C were followed by analyzing the starting thioether and the products by means of the NMR spectra, after quenching a fraction of the reaction mixture by dilute alkali, at various time intervals. It was not hard to find signals which were suitable for analytical purposes; the product distribution was then computed from the relative intensities of the signals.

Characteristic kinetic curves are shown in Fig. 1, where the yields of the respective products are calculated on the basis of the starting methyl α-phenethyl sulfide. The olefinic isomer which is predominant at the completion of the reaction is named A, while the less populated isomer as B. The configuration of A is *cis*, as will be shown in a subsequent paper.[2]

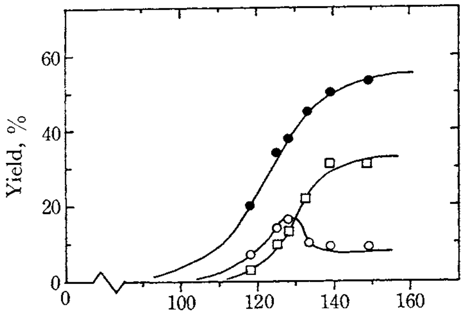


Fig. 1. Rate of the reaction of benzenesulfenyl chloride with methyl α-phenethyl sulfide at 25±0.1°C in carbon tetrachloride.
Initial concentration: benzenesulfenyl chloride 0.525M; methyl α-phenethyl sulfide 0.199M.

● : Yield of α-phenethyl chloride
□ : Yield of (A) ○ : Yield of (B)

The most remarkable feature of the kinetic curves is that each curve, not only of the olefin-forming reaction but of the chlorine-substitution reaction, shows the formation of the products with a definite induction period.

The addition of a small amount of trichloroacetic acid to the reaction mixture caused an increase in the rate of the formation of the products, whereas no decrease in the rate was observed upon the addition of a radical scavenger, 2,4,6-tri-*t*-butylphenol or *p*-benzoquinone, ruling out the possibility that these are radical reactions.

The appearance of the induction period, together with the rapid rise of the curve, suggests that some of the reaction products may be acting as catalysts; that is, these may be autocatalyzed reactions. None of the reaction products, except for the hydrogen chloride which was released by the reaction shown by Eq. (2), seemed to catalyze the reaction. Accordingly, a definite amount of trichloroacetic acid was added to the mixture, since, if this is a general acid-catalyzed reaction, the rate must be increased on the addition of this compound. The results, shown in Fig. 2, clearly indicate that the induction period, characterized by the half-life period of the starting material, decreases with the increase in the concentration of added trichloracetic acid, providing a firm basis for the idea that the reaction is general-acid-catalyzed. Further support is obtained from the facts that Lewis acids such as alu-

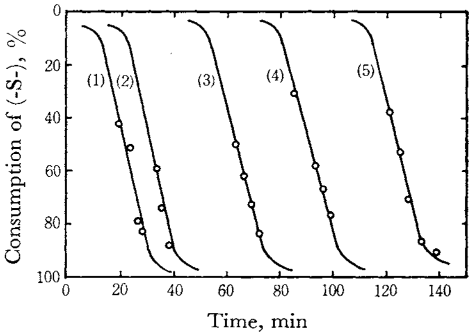


Fig. 2. The effect of added trichloroacetic acid on the rate of disappearance of methyl α-phenethyl sulfide.

Initial concentration of trichloroacetic acid:
(1) $4.11 \times 10^{-3}$M (2) $2.74 \times 10^{-3}$M
(3) $1.37 \times 10^{-3}$M (4) $0.69 \times 10^{-3}$M
(5) without trichloroacetic acid

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[2] M. Ōki and K. Kobayashi, This Bulletin **43**, 1234 (1970).

minum chloride and boron trifluoride also have the ability to catalyze the reaction.

Evidence that this reaction is autocatalyzed is obtained by plotting the logarithm of the initial concentration of acid *versus* the half-life period of methyl α-phenethyl sulfide. A good linear relation is obtained between these quantities, as is shown in Fig. 3. Since this behavior is characteristic of the autocatalyzed reactions, as will be discussed later, it is now established that the reaction between methyl α-phenethyl sulfide and benzenesulfenyl chloride is general-acid-catalyzed and autocatalyzed.

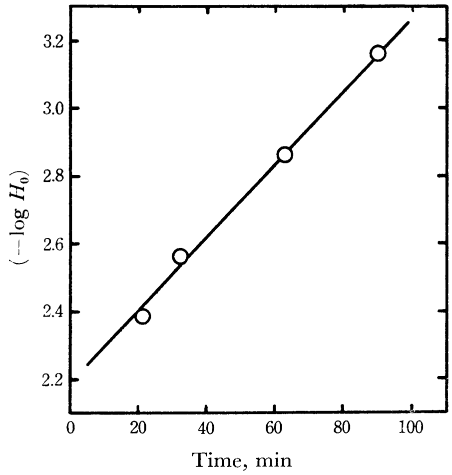

Fig. 3. Plot of the half-life period of methyl α-phenethyl sulfide *vs.* the logarithm of the concentration of added trichloroacetic acid ($H_0$).

Under the conditions of a pseudo-first order, *i. e.*, high concentrations of acid and one of the reactants, the reaction was too fast to follow by conventional methods. Therefore, the following discussion has to rely upon the results of the product analyses.

The rates of the disappearance of the sulfide are affected by the initial concentrations of itself and of benzenesulfenyl chloride. As is shown in Fig. 4, the change in the initial concentration of benzenesulfenyl chloride, with the concentration of the sulfide kept constant, modified both the shape of the kinetic curves and the half-life period of methyl α-phenethyl sulfide. A similar dependence of the features of the curves on the initial concentration of methyl α-phenethyl sulfide was also observed, using the constant concentration of the sulfenyl chloride.

These results suggest that at least three molecules participate in the rate-determining step of the reaction: one molecule each of the sulfide, the sulfenyl chloride, and acid.[*1] The existence of the induction period, not only in the formation of the olefins but also in the substitution reaction, suggests that there is a common intermediate from which two pathways are initiated to give chloride on the one hand and to give olefins on the other, and that the formation of the intermediate is the rate-determining step. Accordingly, the rates may be expressed by the following equation:

$$\text{rate} = k(\text{acid})(\text{sulfide})(\text{sulfenyl chloride})$$

A detailed observation of the rates of disappearance of *t*-butyl phenyl sulfide, on treatment with benzenesulfenyl chloride, shows the presence of the induction period here also. The same is true for the reactions of other sulfides, reported in the preceding paper, with benzenesulfenyl chloride. Thus, it is common for there to exist an induction period when sulfides are treated with sulfenyl chlorides.

The rates of the autocatalyzed three-molecular reaction can be expressed by,

$$\frac{dP}{dt} = k(R_0-P)(S_0-yP)(H_0+xP) \tag{3}$$

where $R$, $S$, and $P$ are the concentrations of methyl α-phenethyl sulfide, benzenesulfenyl chloride, and the products respectively, after $t$ minutes. $R_0$, $S_0$, and $H_0$ denote the initial concentrations of the reactants, whereas $x$ and $y$ are the constants as determined by stoichiometry and represent the amount of hydrogen chloride formed by the reaction and the sulfenyl chloride consumed per mole of the consumed sulfide. Here it is assumed that, during the reaction, the ratio of the products from the two reactions is constant throughout. This assumption seems fair judging from the experimental results: a 55 : 45 ratio is observed at all times during the reaction. It is also assumed that the efficiency of hydrogen chloride as the catalyst is the same as that of trichloroacetic acid. Thus, $H_0$ is null when no trichloroacetic acid is added.

By integrating Eq. (3) when $H_0$ is negligible compared with $R_0$, $S_0$, and $P_{1/2}$, which is the concentration of products at the half-life period of the sulfide ($t_{1/2}$), the following relation between $H_0$ and $t_{1/2}$ is obtained:

$$t_{1/2} = -\frac{\ln H_0}{kxR_0S_0} + \text{“constant”} \tag{4}$$

The term “constant” contains neither $H_0$ nor $t_{1/2}$. The observed relationship shown in Fig. 3 is in harmony with Eq. (4), since this equation shows that $t_{1/2}$ and $(-\log H_0)$ are related linearly. Equation (4) also implies that half-life period decreases with the increase in concentrations of either the sulfide or the sulfenyl chloride; it was found that this implication was really the case (for example, see Fig. 4).

Furthermore, it can be expected from Eq. (4) that $kxR_0S_0$ can be obtained as the slope in Fig. 3,

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[*1] It is not possible from these results to know how many molecules of the acid are participating. The authors assume that only one molecule of the acid is taking part in the reaction for the sake of convenience and simplicity of the analyses.

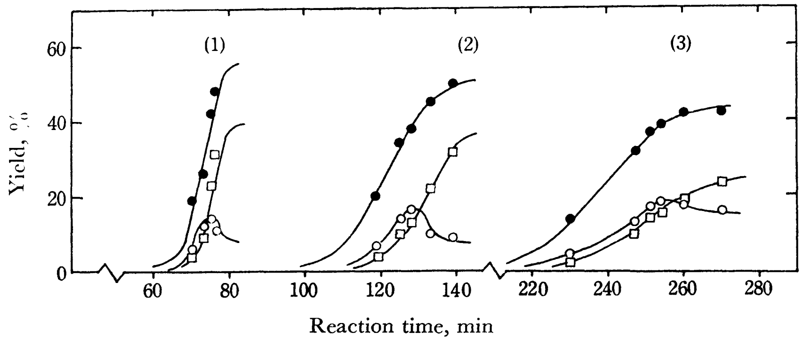


Fig. 4. The dependence of kinetic curves on the initial concentration of benzenesulfenyl chloride.
● : Yield of α-phenethyl chloride ○ : Yield of olefin (B)
□ : Yield of olefin (A)
Initial concentration; (1) (-S-): 0.199M, (PhSCl): 0.683M
(2) (-S-): 0.199M, (PhSCl): 0.525M
(3) (-S-): 0.199M, (PhSCl): 0.420M

since $t_{1/2}$ is now the abscissa and $(-\log H_0)$, the ordinate. Thus, various inclinations of the relationship between $(-\log H_0)$ and $t_{1/2}$ were obtained with various initial concentrations and plotted against $R_0S_0$. The good linear relation of these quantities implies that above treatment is fair (Fig. 5). These results also support the idea that the reaction is first-order in both the thioether and the sulfenyl chloride, since, if this were not the case, the linear relation would have been found between the slope and $(R_0S_0)^n$ instead of between the slope and $R_0S_0$.

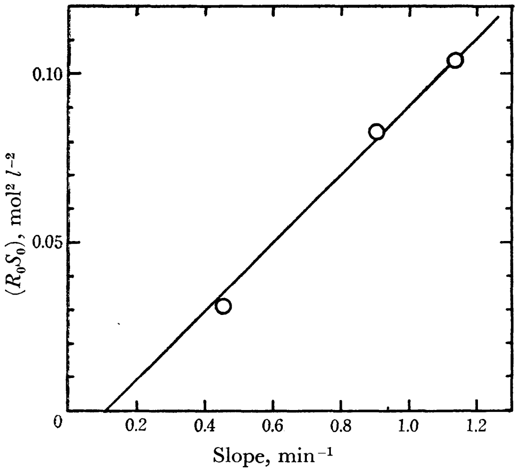
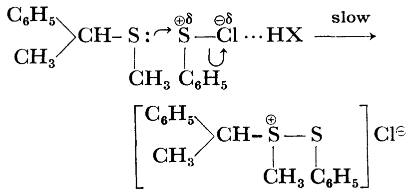


Fig. 5. Plot of the slope *vs.* $R_0S_0$.

From the discussions presented above, it appears that acid is necessary in order to promote the reaction of the thioether with the sulfenyl chloride, and that the formation of an intermediate from thioether, sulfenyl chloride, and acid is the rate-determining step. After the rate-determining step, there are several rapid reaction paths which could result in the formation of the products. A sulfonium ion resulting from the electrophilic attack by benzenesulfenyl chloride on the sulfur atom of the thioether is the most likely such intermediate, since the rate is proportional to the concentrations of both the thioether and the sulfenyl chloride.

Although there are many points to be clarified before we have a full understanding of the catalytic action of the acid, at present the authors choose to attribute it to the aid of acids in polarizing the sulfenyl chloride in an activated complex. That is, it is assumed that, although sulfenyl chlorides are polar enough to add to the olefinic bonds by second-order kinetics, they are too poorly electrophilic to attack the sulfur atom directly and that, subsequently, acids are necessary to assist the polarization. Thus, a kind of concerted mechanism can now be postulated:


$$\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\rangle CH\text{-}\underset{CH_3}{S}:\overset{\oplus\delta}{\underset{C_6H_5}{S}}\text{—}\overset{\ominus\delta}{Cl}\cdots HX \xrightarrow{\text{slow}} \left[\left.\begin{matrix}C_6H_5\\CH_3\end{matrix}\right\rangle CH\text{-}\overset{\oplus}{\underset{CH_3}{S}}\text{—}\underset{C_6H_5}{S}\right]Cl^{\ominus}$$

(I)

An analogy for this concerted reaction mechanism may be found in the electrophilic addition of hydrogen halide to olefins, which has been suggested3) to proceed *via* an activated complex which involves a few extra molecules of hydrogen halide in addition to the actually-adding molecule of HX. The paticipation of the extra molecule has been attributed to assistance in the polarization of the attacking hydrogen halide, thus facilitating the ionic cleavage of the molecule.

The reactions involving the electrophilic attack

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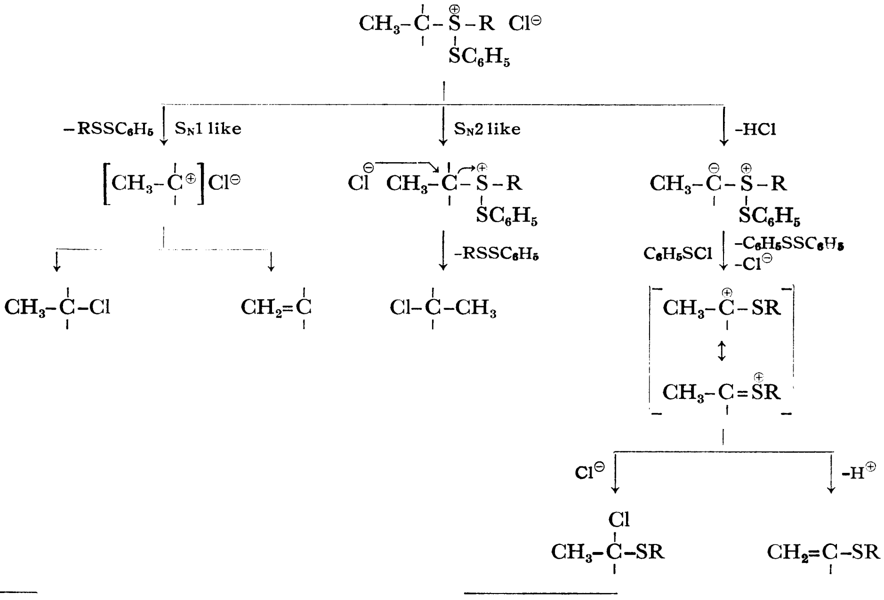
3) F. R. Mayo and J. J. Katz, *J. Amer. Chem. Soc.*, **69**, 1339 (1947).

by sulfenyl chloride are known to be accelerated by an acidic catalyst: the addition of sulfenyl chloride to the acetylenic bond[4] and electrophilic aromatic substitution[5] with arenesulfenyl chloride are catalyzed by Lewis acids. These examples, together with the results presented here, suggest that the sulfenium cation, $RS^+$, plays an important role in the electrophilic attack by the sulfenyl chlorides. Moreover, this idea is in conformity with the fact[6] that the solution of methanesulfenium 2,4,6-trinitrobenzenesulfonate generates dimethyl(methylthio)sulfonium salts in the presence of dimethyl sulfide.

It may be argued that the sulfonium ion (I) would be formed rather rapidly from the sulfenyl chloride and the sulfide, and that the decomposition of the sulfonium ion, I, would be the rate-determining step, because the data presented here are confined to product analyses and to the measurement of the half-life period, and because various $S_N2$ reactions of sulfonium ions are known. This argument can be worthwhile if it is assumed that the sulfonium ion from the disulfide gives back the starting sulfide upon the subsequent work-up. However, it is rather unlikely, since the measurements of the ultraviolet spectra ($\lambda_{max}=390$ m$\mu$, $\varepsilon=470$) of benzenesulfenyl chloride, when mixed with the thioether, show an induction period in the decrease in the absorption coefficient, indicating that the sulfenyl chloride is not used until some time later, even in the presence of the thioether. The decrease in intensity might have been observed immediately after mixing if I were formed rapidly. Furthermore, this induction period corresponds to that of the decrease in the thioether.

After the unstable sulfonium ion intermediate is formed, the reaction may now take three different courses, according to the structure of the intermediate. One reaction path is the loss of the disulfide molecule to form a carbonium ion, which then undergoes nucleophilic substitution or the elimination of a proton to form the olefin. This occurs when a stable carbonium ion is to be formed; *t*-butyl phenyl sulfide[1] is an example. The second path is the $S_N2$ reaction by the chloride ion, which is evident from the inversion of the configuration in the reaction of methyl 1-phenylpropyl sulfide.[1] The third path is the elimination of α-hydrogen and the alkylthio (or arylthio) group. The mechanism of this last case has not been studied well enough to present the details here, but, by analogy from other Pummerer-type reactions, it can tentatively be postulated that a sulfur ylide is formed first by the elimination of α-hydrogen as the proton, followed by the elimination of the phenylthio group. In the latter step, probably another molecule of benzenesulfenyl chloride assists the removal by forming diphenyl disulfide. The carbonium ion thus formed will give α-chloro sulfide if it is not too stable, whereas it will give α,β-unsaturated sulfide if it can survive long enough to eliminate a proton from the β-carbon.

Although α,β-unsaturated sulfide is sometimes obtained[7] in the original Pummerer reaction, *i.e.*, the reaction of sulfoxide and acetic anhydride,



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[4] N. Kharasch and S. J. Assony, *ibid.*, **75**, 1081 (1953).

[5] C. M. Buess and N. Kharasch, *J. Amer. Chem. Soc.*, **72**, 3529 (1950).

[6] G. K. Helmkamp, D. C. Owsley, W. M. Barnes and H. N. Cassey, *ibid.*, **90**, 1635 (1968).

[7] W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28**, 2686 (1963): R. B. Morin, D. O. Spry and R. A. Mueller, *Tetrahedron Lett.*, **1969** 849.

its formation can be explained if the thermal decomposition of an intermediate α-acetoxy sulfide is assumed. Therefore, there can be disagreement concerning the mechanism of the formation of α,β-unsaturated sulfide in the Pummerer reaction. The present authors feel that the discussions given above may throw light on the possibility of the presence of a carbonium ion intermediate in the formation of α,β-unsaturated sulfide.

## Experimental

**Starting Materials.** Methyl α-phenethyl sulfide was prepared from α-phenethyl chloride and methyl mercaptan and was freshly distilled immediately before making the solution for experiments in every case; bp 67°C/3 mmHg, $n_D^{20.5}$ 1.5491 (lit,[8]) $n_D^{20}$ 1.5497).

Benzenesulfenyl chloride was prepared from diphenyl disulfide and chlorine, as in the literature,[9]) and was always distilled prior to its use; bp 79°C/10 mmHg.

Carbon tetrachloride of a commercial source was purified by distillation.

Commercial trichloroacetic acid was distilled under reduced pressure in a dry atmosphere. Contact with moisture was carefully avoided.

**Rate Measurements.** Stock solutions of the sulfenyl chloride, methyl α-phenethyl sulfide, and trichloroacetic acid were prepared by weighing the proper amounts of the freshly-purified materials and by then making the solution up to the desired volume with dry carbon tetrachloride at 25°C. The solutions were then brought to a desired temperature (25±0.1°C) in a constant-temperature bath. The desired volume of each solution was pipeted and mixed. Although some change in volume may result from the mixing of three kinds of solutions, this effect was neglected in the calculation.

The reaction mixture was taken out with a pipet, *ca.* 20 m*l* at a time, and drained into a separately funnel containing 30 m*l* of aqueous sodium carbonate. The lower layer was dried over anhydrous sodium sulfate and then submitted to NMR analysis after filtration. In the NMR spectra of the reaction mixture, the signal of the methylthio protons of methyl α-phenethyl sulfide and the lower one of the doublet signal of methyl protons of α-phenethyl chloride coincided. However, the yields based on methyl α-phenethyl sulfide could be calculated by the integration of the other, non-overlapping signals.

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8) W. E. Bacon and W. M. LeSuer, *J. Amer. Chem. Soc.*, **76**, 670 (1954).

9) H. Lecher and F. Holschneider, *Chem. Ber.*, **57**, 755 (1924).