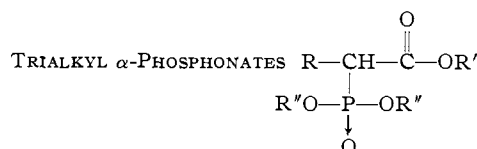


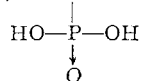
TABLE II



R	Compound R'	R''	Yield, %	B.p. °C.	Mm.	Phosphorus, % Calcd.	Phosphorus, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	n_D^{20}	d_4^{20}	Molecular refraction Calcd.	Molecular refraction Found
CH ₃ (CH ₂) ₈	C ₂ H ₅	<i>n</i> -C ₄ H ₉	73	210	0.18	7.37	7.18					1.4413	0.9547	116.4	116.5
CH ₃ (CH ₂) ₉	C ₂ H ₅	<i>n</i> -C ₅ H ₁₁	53	173	.25	6.50	6.37	65.5	65.1	11.2	11.3	1.4440	.9394	134.8	134.7
CH ₃ (CH ₂) ₉	R' = R'' = <i>n</i> -C ₄ H ₉		75	182	.6	6.91	7.15	64.3	64.3	11.0	10.7	1.4420	.9462	125.6	125.6
CH ₃ (CH ₂) ₈	R' = R'' = <i>n</i> -C ₅ H ₁₁		40	139	.15	6.91	7.45	64.3	63.6	11.0	11.1	1.4405	.9344	125.6	126.6
CH ₃ (CH ₂) ₉	R' = R'' = CH ₃		61	156	.7	9.61	9.06	55.9	55.4	9.69	9.71	1.4440	1.0203	84.02	83.9
CH ₃ (CH ₂) ₉	<i>n</i> -C ₄ H ₉	C ₂ H ₅	89	186	.3	7.89	7.79	61.2	60.5	10.5	10.5	1.4416	0.9644	107.1	107.6
CH ₃ (CH ₂) ₁₀	2-Ethylhexyl	C ₂ H ₅	73	215	.4	5.82	5.26	67.6	67.3	11.5	11.8	1.4507	.9326	153.3	153.7
CH ₃ (CH ₂) ₁₀	<i>n</i> -C ₄ H ₉	C ₂ H ₅	79	195	.4	6.50	6.23	65.5	65.0	11.2	11.1	1.4466	.9402	134.8	135.4
CH ₃ (CH ₂) ₈	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₅ H ₁₁	30	163-171	.3	6.91	6.68	64.3	63.9	11.0	11.2	1.4427	.9438	125.6	125.9

Trialkyl α -phosphonates were prepared by heating the alkyl α -bromo ester with a 100% molar excess of trialkyl phosphite at 160-190° in an atmosphere of nitrogen. The alkyl bromide formed was swept out and collected in a Dry Ice trap. The reaction was stopped when the weight of alkyl bromide became constant (usually 4-5 hr.). Generally, 90% of the calculated amount of alkyl bromide was obtained. The entire reaction mixture was then fractionally distilled to obtain the pure α -phosphonates (Tables I and II).

Hydrolysis Studies. (a) **Dilute Acid.**—The procedure described previously for the hydrolysis of acyloxyethylphosphonates was employed.⁶ The trialkyl α -phosphonates were extremely resistant to hydrolysis under conditions which gave complete hydrolysis of the acyloxyethylphosphonates (or ethyl laurate) at the carboxylic ester. (b) **Concentrated Acid.**—Three triethyl α -phosphonates were refluxed for 18-24 hr. with a large excess of 20-35% hydrochloric acid. The reaction mixture was transferred to an evaporating dish and evaporated to dryness. The crude residues from the hydrolysis of triethyl α -phosphonostearate and -laurate were hard, brittle solids, m.p. 125-130°; the residue from triethyl α -phosphonobutyrate was a hygroscopic semi-solid. The neutralization equivalents found (thymolphthalein indicator) were, respectively, 129, 101 and 58 (calculated for the tribasic acids, R-CH-CO₂H,



122, 94 and 56). Thus, essentially complete hydrolysis occurred. (c) **Dilute Alkali.**—In a kinetic study it was shown that one equivalent of base was consumed in about 1 hr. The following hydrolysis-isolation procedure was, therefore, employed to obtain the α -diethylphosphonocarboxylic acid: approximately 0.5-1 g. of triethyl α -phosphon-

ate (accurately weighed) was refluxed for 1 hr. with exactly 25 ml. of 0.2 *N* KOH in aldehyde-free 95% ethanol. The excess alkali was back titrated with 0.1 *N* HCl (phenolphthalein indicator) which permitted calculation of the saponification equivalent of the α -phosphonate, if desired. A few ml. of concentrated HCl was then added and the reaction mixture was evaporated to dryness. The residue was washed several times with ethyl ether and the combined ether solutions were filtered. Evaporation of the ether from the filtrate yielded the α -diethylphosphonocarboxylic acid, on which the neutralization equivalent was then determined. The saponification equivalents of the triethyl α -phosphonates and the neutralization equivalents of the α -diethylphosphonocarboxylic acids prepared from them are given in Table III.

TABLE III

SAPONIFICATION EQUIVALENT OF TRIETHYL α -PHOSPHONATES AND NEUTRALIZATION EQUIVALENT OF α -DIETHYLPHOSPHONOMONOCARBOXYLIC ACIDS ISOLATED

α -Phosphonate	Sapon. equiv.		Neut. equiv. of isolated acid	
	Calcd.	Found	Calcd.	Found
Butyrate			228	247
Caproate	280	290 ^a	252	230-240
Pelargonate			294	297
Laurate	364	356-362	336	344
Myristate			364	366
Palmitate	421	413-426	392	396
Stearate	449	428-437	420	417

^a 0.1 *N* KOH in 80% aldehyde-free ethanol was used.

PHILADELPHIA, PENNA.

[CONTRIBUTION NO. 425 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Sulfenyl Carboxylates

BY ROBERT E. PUTNAM AND WILLIAM H. SHARKEY

RECEIVED JUNE 27, 1957

The synthesis of a number of sulfenyl carboxylates is described. These compounds are, in general, quite unstable, and preliminary evidence indicates that they decompose to give free radicals in a manner similar to peroxides.

Although amides, esters and acid halides of sulfenic acids have been known for a number of years,¹ the only example of a sulfenyl carboxylate that has been reported is 2,4-dinitrobenzenesul-

(1) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

fenyl acetate. This compound recently has been described by Havlik and Kharasch² and found to add to cyclohexene in the same fashion as sulfenyl halides. The reaction of 2,4-dinitrobenzenesulfenyl acetate with the sodium salt of 2-nitropro-

(2) A. J. Havlik and N. Kharasch, *THIS JOURNAL*, **78**, 1207 (1956).

TABLE I
 SULFENYL CARBOXYLATES

Carboxylate	Yield, %	M.p., °C.	Analyses, %		Carbonyl band in infrared, cm. ⁻¹
			Calcd.	Found	
2,4-Dinitrobenzenesulfonyl acetate	86	85-90 d.	C 37.21 H 2.34	37.40 2.60	1780
2,4-Dinitrobenzenesulfonyl benzoate	75	82 d.	C 47.75 H 2.52 N 8.73	48.13 2.68 8.66	1720
Trichloromethanesulfonyl benzoate	92	28-30°	C 35.38 H 1.85	35.01 2.04	1770
1-Anthraquinonesulfonyl acetate	52 ^a	139-145 d. ^b	1710
2-Nitrobenzenesulfonyl acetate	61 ^c	95-100 d. ^b	1775
4-Nitrobenzenesulfonyl acetate	63 ^c	90-95 d. ^b	1775
Benzenesulfonyl benzoate	.. ^d ^d ^b	1775
Pentachlorobenzenesulfonyl benzoate	.. ^d ^d ^b	1725

^a 47% yield of disulfide as by-product. ^b Decomposed too rapidly for analysis. ^c Disulfide obtained as by-product. ^d Could not be determined because of rapid decomposition. ^e After recrystallization from ether at -80°.

pane to form 2,4-dinitrophenyl 2'-nitro-2'-propyl sulfide also has been disclosed.³

Since sulfonyl carboxylates may be considered to be mixed anhydrides of sulfenic and carboxylic acids, they might be expected to undergo many of the reactions of anhydrides. In addition, the presence of a sulfur-oxygen bond suggests that these compounds may undergo radical reactions in a fashion similar to peroxides and disulfides. Accordingly, a study of the preparation and properties of a number of sulfonyl carboxylates was made in this Laboratory.

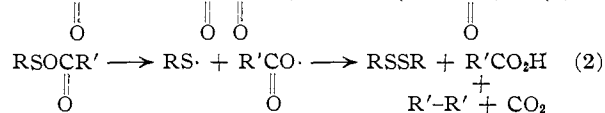
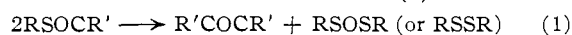
The carboxylates investigated (see Table I) were prepared by a modification of the method employed by Havlik and Kharasch² in the synthesis of 2,4-dinitrobenzenesulfonyl acetate. A finely divided silver carboxylate was stirred at room temperature with a solution of the appropriate sulfonyl halide in methylene or ethylene chloride. The sulfonyl carboxylates formed rapidly and, in the most favorable examples, were obtained in yields of 75-92% (compounds 1, 2 and 3, Table I).

The most striking property of this class of compounds is the tendency of its members to undergo spontaneous decomposition. Of the compounds prepared, only 2,4-dinitrobenzenesulfonyl benzoate proved to be stable indefinitely at room temperature. The thermal stability of the carboxylates seemed to be proportional to the electron-withdrawing ability of the groups attached to sulfur. Thus, 2,4-dinitrobenzenesulfonyl acetate and benzoate and trichloromethanesulfonyl benzoate were all stable enough to allow purification and identification. On the other hand, 1-anthraquinone-, 2-nitrobenzene- and 4-nitrobenzenesulfonyl acetates, although stable at -20°, decomposed so rapidly at room temperature that elemental analyses could not be obtained. Benzenesulfonyl and pentachlorobenzenesulfonyl benzoates were the least stable of the carboxylates prepared. These compounds decomposed at an appreciable rate even at -20°. The carboxylates were found to exhibit a characteristic infrared absorption band in the region 1710-1780 cm.⁻¹, and this band was used to identify those compounds for which analytical data could not be obtained. It is in-

(3) J. L. Cameron and N. Kharasch, U. S. Patent 2,671,113, March 2, 1954.

teresting that 1700-1800 cm.⁻¹ is the region in which carboxylic anhydrides exhibit strong carbonyl absorption in the infrared.

The nature of the decomposition of sulfonyl carboxylates is not known with certainty. The two most likely modes of decomposition are disproportionation to a sulfenic anhydride and a carboxylic anhydride (1) and homolytic cleavage of the -S-O- bond to form free radicals (2).



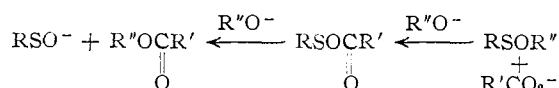
Preliminary evidence points to path 2 as the mechanism of decomposition. During the determination of the infrared spectra of benzenesulfonyl benzoate and pentachlorobenzenesulfonyl benzoate, it was noted that the carbonyl band of the carboxylate gradually disappeared and was replaced by a band characteristic of the carboxylic acid from which the carboxylate was derived. From the resulting mixtures it was possible to isolate the disulfides and carboxylic acids which would be expected according to path 2. In addition, pyrolysis of 1-anthraquinonesulfonyl acetate *in vacuo* at 150° led to bis-(1-anthraquinonyl) disulfide and acetic acid as the only identifiable products. It is probable that compounds of the type R-R and CO₂ were also produced but they were not identified.

As is the case with sulfonyl halides,^{1,4,5} sulfonyl carboxylates are rapidly decomposed by aqueous base giving complex mixtures of disulfides, sulfenic anhydrides and salts of sulfenic acids. Sulfonyl carboxylates have two potential sites for attack by nucleophilic reagents, at the sulfur atom and at the carbonyl group. Attack at either position by aqueous base would yield a sulfenic acid which would then undergo further reactions. Reaction with other nucleophilic agents, such as alcoholates, would be expected to give a sulfenic ester or a carboxylic ester, either of which would be sufficiently stable for isolation.

Investigation of this reaction has shown the primary site of attack to be the carbonyl group.

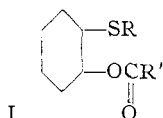
(4) A. Burawoy and A. Chadhuri, *J. Chem. Soc.*, 653 (1956).

(5) R. N. Haszeldine and J. M. Kidd, *ibid.*, 2901 (1955).



Thus, addition of a solution of 2,4-dinitrobenzenesulfonyl acetate in methylene chloride to methanolic potassium hydroxide at -80° gave as the major products methyl acetate and a deep violet solid, which is thought to be the potassium salt of the hitherto unknown 2,4-dinitrobenzenesulfenic acid. Because of its instability this salt could not be isolated in pure form but analytical data on the crude, dry material corresponded to an empirical formula of $2[(\text{NO}_2)_2\text{C}_6\text{H}_3\text{SO}_2\text{K}]\cdot\text{CH}_3\text{OK}\cdot 3\text{CH}_3\text{OH}$. The properties of the material support this structure. The deep violet color is similar to that of the previously described salts of 1-anthraquinonesulfenic and 2-nitrobenzenesulfenic acids.^{6,7} When dissolved in deoxygenated water and acidified, the material lost its deep violet color and bis-(2,4-dinitrophenyl) disulfide precipitated from the solution. A disulfide is one of the products to be expected from reactions in which sulfenic acids are intermediates.^{1,4,5}

As mentioned previously, Kharasch² has described the addition of 2,4-dinitrobenzenesulfonyl acetate to cyclohexene to give a product of type I.



This reaction has been confirmed in this Laboratory, and, in addition, 1-anthraquinonesulfonyl acetate was added to cyclohexene to give a product ($\text{R} = 1\text{-C}_{14}\text{H}_7\text{O}_2$, $\text{R}' = \text{CH}_3$) identical to that of Jenny⁸ who prepared it by reaction of silver acetate with 1-(2'-bromocyclohexylmercapto)-anthraquinone.

A brief study⁹ also was made of the behavior of sulfonyl carboxylates as photoinitiators for the polymerization of methyl methacrylate. As might be expected those carboxylates having nitro groups proved to be efficient polymerization inhibitors. However, both trichloromethanesulfonyl benzoate and benzenesulfonyl benzoate initiated the polymerization of methyl methacrylate when exposed to ultraviolet light, being considerably less active than 2-methoxy-2-phenylacetophenone¹⁰ and dibenzoyl disulfide.¹¹ It is interesting in this respect that esters of several sulfenic acids recently have been reported to be effective photoinitiators.¹²

Experimental¹³

2,4-Dinitrobenzenesulfonyl Acetate.—The following procedure is typical of that employed in the preparation of sulfonyl carboxylates. Temperatures as low as -20° were used successfully in the case of less stable members of the series.

To a solution of 11.8 g. (0.05 mole) of 2,4-dinitrobenzenesulfonyl chloride in 200 ml. of methylene chloride was added 16.7 g. (0.1 mole) of silver acetate. The slurry was stirred at 28° in the dark for 18 hr. The silver salts were removed by filtration and the filtrate was evaporated to dryness *in vacuo* (without heating). In this way there was obtained 11.1 g. (86%) of 2,4-dinitrobenzenesulfonyl acetate as a bright yellow solid which decomposed without melting at $85\text{--}90^\circ$. An infrared spectrum of the compound showed an "anhydride" carbonyl absorption band at 1780 cm^{-1} .

Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_2\text{O}_6\text{S}$: C, 37.21; H, 2.34. Found: C, 37.40; H, 2.60.

Pentachlorobenzenesulfonyl Chloride.—A slow stream of chlorine (dried by H_2SO_4) was passed through a solution of 25 g. (0.09 mole) of pentachlorobenzenethiol in 500 ml. of refluxing carbon tetrachloride containing a few crystals of iodine for 5 hr. During this time a bright red color developed. Evaporation of the solvent *in vacuo* gave 26 g. (92%) of pentachlorobenzenesulfonyl chloride as a bright orange solid, m.p. $99\text{--}101^\circ$. One recrystallization from carbon tetrachloride gave long orange needles, m.p. $103\text{--}104^\circ$.

Anal. Calcd. for $\text{C}_6\text{Cl}_5\text{S}$: S, 10.12. Found: S, 10.07.

This compound was used in the preparation of pentachlorobenzenesulfonyl benzoate (Table I).

1-(2'-Acetoxycyclohexylmercapto)-anthraquinone.—To a solution of 1 g. of 1-anthraquinone sulfonyl acetate in 30 ml. of glacial acetic acid was added 5 ml. of cyclohexene. The mixture was refluxed for 10 minutes and poured onto 200 g. of ice. The orange-yellow precipitate was removed by filtration. Recrystallization from absolute ethyl alcohol gave 1-(2'-acetoxycyclohexylmercapto)-anthraquinone as orange-yellow needles, m.p. $162\text{--}163^\circ$. A mixed melting point with an authentic sample prepared by the method of Jenny⁸ (m.p. $163\text{--}165^\circ$) showed no depression ($162\text{--}163^\circ$).

Decomposition of 1-Anthraquinonesulfonyl Acetate by Heat.—In a flask equipped with a thermometer extending nearly to the bottom was placed 5 g. of 1-anthraquinonesulfonyl acetate. The flask was evacuated and heated gradually to 150° . At about 130° a distinct color change from orange to yellow-green occurred. Volatile products were collected in a trap cooled to -70° . The reaction vessel was heated at 150° for 3 hr. The residue in the flask weighed 4.25 g. and proved to be mainly bis-(1-anthraquinonyl) disulfide as shown by identity of its infrared spectrum with that of an authentic sample. From the -70° trap there was obtained 0.6 g. of a liquid which was chiefly acetic acid (neutralization equivalent calculated 60, found 63.5).

Methanolysis of 2,4-Dinitrobenzenesulfonyl Acetate.—To a solution of 7.8 g. (0.03 mole) of 2,4-dinitrobenzenesulfonyl acetate in 300 ml. of methylene chloride, cooled to -70° and kept under a blanket of nitrogen, was added dropwise a solution of 1.6 g. (0.03 mole) of potassium hydroxide in 15 ml. of anhydrous methanol. During the addition (about 15 minutes) the mixture was stirred vigorously and stirring was continued for 30 minutes longer. By this time a large quantity of deep violet solid had precipitated. The mixture was filtered carefully under nitrogen at -50° . After washing with ether and vacuum drying, there was obtained 6.3 g. of a deep violet powder. The filtrate had a strong odor of methyl acetate, and an infrared spectrum confirmed the presence of appreciable quantities of this ester. No attempt was made to isolate the ester quantitatively because of the large volume of methylene chloride present.

Analysis of the violet solid after drying showed it to have an empirical formula of $2\text{C}_6\text{H}_3\text{N}_2\text{SO}_2\text{K}\cdot\text{CH}_3\text{OK}\cdot 3\text{CH}_3\text{OH}$.

Anal. Calcd. for $2\text{C}_6\text{H}_3\text{N}_2\text{SO}_2\text{K}\cdot\text{CH}_3\text{OK}\cdot 3\text{CH}_3\text{OH}$: C, 28.48; H, 3.14; N, 8.30; S, 9.50. Found: C, 28.12; H, 2.66; N, 8.26; S, 9.55.

When the salt was allowed to stand in air it rapidly decomposed, losing its violet color in the process. Similarly, it proved to be quite unstable in ordinary distilled water. However, a solution in deoxygenated water was stable for several hours. For this reason an attempt was made to isolate the free sulfenic acid by acidification of its salt in a completely deoxygenated system.

To 1 g. of crude potassium salt dissolved in 200 ml. of deoxygenated water was added 0.5 *N* HCl (made up in deoxygenated water) until no further color change was appar-

(6) K. Fries, *Ber.*, **45**, 2965 (1912).

(7) T. Zincke and F. Baeumer, *Ann.*, **391**, 57 (1912).

(8) W. Jenny, *Helv. Chim. Acta*, **36**, 1278 (1953).

(9) We are indebted to Dr. H. B. Stevenson of this Laboratory for examining sulfonyl carboxylates as photoinitiators.

(10) M. M. Renfrew, U. S. Patent 2,448,828, Sept. 7, 1948.

(11) L. M. Richards, U. S. Patent 2,460,105, Jan. 25, 1949.

(12) G. H. Birum and R. J. Kern, U. S. Patent 2,769,777, Nov. 6, 1956.

(13) All melting points are uncorrected.

ent. The cloudy, orange-yellow solution was cooled to 0° and filtered. In this way there was obtained 0.3 g. of bis-(2,4-dinitrophenyl) disulfide as a yellow powder (structure shown by identity of its infrared spectrum with that of an authentic sample). The filtrate was extracted with ether, and the ether layer dried over anhydrous sodium sulfate.

Evaporation of the solvent yielded 0.24 g. of a brownish acidic solid that could not be identified positively. No evidence for the presence of 2,4-dinitrobenzenesulfenic acid was obtained.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXXIX. The Reaction of α,α -Dimethylallyl Chloride and γ,γ -Dimethylallyl Chloride with Thiourea and Substituted Thioureas¹

BY J. M. RULE, I. J. WILK, T. I. WRIGLEY AND WILLIAM G. YOUNG

RECEIVED JULY 19, 1957

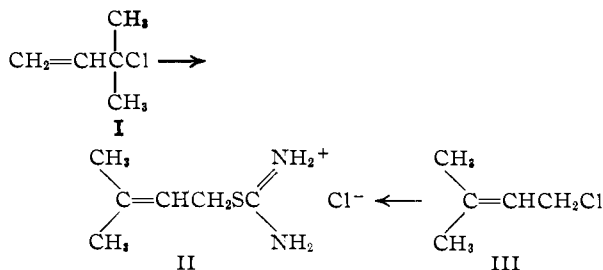
The reactions of α,α -dimethylallyl chloride and γ,γ -dimethylallyl chloride with thiourea in acetone both follow second-order kinetics. The tertiary allylic chloride undergoes an abnormal SN2' displacement while the primary chloride undergoes a normal SN2 displacement. The same product γ,γ -dimethylallylthiouronium chloride, was obtained in both cases. *sym*-Diphenylthiourea behaved similarly, but fully substituted thioureas did not undergo reaction with either the primary or the tertiary allylic chloride.

Introduction

Two mechanisms of bimolecular nucleophilic substitution are available to allylic compounds, the normal displacement, SN2, and the abnormal displacement SN2'. Several examples of the latter process are known and have been reviewed recently in detail.² For example, it has been shown by de la Mare³ that nucleophilic attack on α,α -dimethylallyl chloride (I) by thiophenolate ion yielded only the product due to an abnormal SN2' displacement. Allylic halides are known⁴ to react with thiourea to form thiouronium halide salts which can be hydrolyzed to thiols by aqueous alkali. The purpose of the present work was to examine the reaction of pentenylallylic chlorides with various thioureas.

Results

When α,α -dimethylallyl chloride (I) was treated with thiourea in acetone at 25° an abnormal SN2' displacement resulted and γ,γ -dimethylallylthiouronium chloride (II) was obtained in 80% yield. This salt was also the sole product from the reaction of γ,γ -dimethylallyl chloride (III) with thiourea, and after ozonization and suitable decomposition of the resulting ozonide it afforded acetone in high yield.



Similarly, treatment of α,α -dimethylallyl chloride (I) with *N,N'*-diphenylthiourea (IV) gave only the abnormal product γ,γ -dimethylallyl-*N,N'*-

diphenylthiouronium chloride (V) which was also isolated from the reaction of the primary chloride III with IV. No reaction was detected between *N,N'*-dibutylethylenethiourea and α,α -dimethylallyl chloride (I). In order to lower the activation energy the primary chloride III was substituted for I, but still no reaction was observed. Similarly, neither *N,N,N',N'*-tetramethylthiourea (VI) nor *N,N'*-dibenzoylthiocarbamide (VII) would react with γ,γ -dimethylallyl chloride (III) in acetone.

A kinetic study of the reaction of the primary and tertiary allylic halides I and III with thiourea, followed by alcoholic base titration of the acidic components present, indicated both reactions to be second order. Rate constants were calculated from the integrated form of the usual second-order rate expression,⁵ as given in equation 1.

$$k_2 = \frac{2.303}{t(b-a)} \log \frac{(b-x)a}{(a-x)b} \quad (1)$$

Where x is the amount of allylic halide reacted in moles/l., b is the initial concentration of thiourea in moles/l., a is the initial concentration of allylic halide in moles/l. and t is the time, in minutes, elapsed from zero time. The rate was followed by titration with alcoholic sodium methoxide of the acidic isothiuronium salts formed. Rate constants are listed in Table I.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF α,α -DIMETHYLALLYL CHLORIDE AND γ,γ -DIMETHYLALLYL CHLORIDE WITH THIOUREA IN ACETONE

Isomer	RCl ^a	Thiourea ^a	Temp., °C.	k_2^b
Tertiary	0.03341	0.06595	44.96	$1.54 \pm 0.03 \times 10^{-3}$
Tertiary	.00341	.06595	74.70	$1.93 \pm .18 \times 10^{-2}$
Primary	.01995	.07030	44.96	$3.18 \pm .15 \times 10^{-2}$
Primary	.01995	.07030	74.70	$2.01 \pm .17 \times 10^{-1}$

^a Units of concentration are moles/l. ^b Units of k_2 are (mole/l.)⁻¹ (min.)⁻¹.

As the second-order rate constants are known at two different temperatures, it is now possible to calculate the experimental energy of activation, E^{\ddagger} ,

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(1) This work was supported in part by a grant from the National Science Foundation.

(2) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

(3) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3555 (1953).

(4) A. Luttringhaus, H. B. Konig and B. Bottcher, *Ann.*, **560**, 201 (1947).