Substitution at a Saturated Carbon Atom. XV. Investigations of Ion-Pair Phenomena in Selected Allylic Systems[1]

Richard A. Sneen*[2] and Peter S. Kay

Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907. *Received July 28, 1971*

Abstract: Kinetics and product distributions resulting from the competitive reactions of the primary γ,γ-dimethylallyl chloride and of the allylically isomeric tertiary α,α-dimethylallyl chloride with solvent and sodium azide in 80% aqueous acetone at 32.0° have been studied. Both substrates undergo a kinetically second-order reaction with sodium azide, the reaction with the tertiary substrate being either bimolecular attack at tertiary carbon or a rather extraordinarily facile SN2′ reaction. A comparison of the relative rates of bimolecular attack by azide ion on the primary γ,γ-dimethylallyl chloride and on the secondary α,γ-dimethylallyl chloride[8] establishes that the rates of these displacement reactions are rather remarkably insensitive to the extent of steric congestion at the site of attack. Kinetic and product distributions resulting from the competitive reactions of α-methyl-γ-phenylallyl 2,6-dichlorobenzoate with solvent and various nucleophiles have been studied. Solvents included methanol and aqueous dioxane and methanolic dioxane mixtures, and nucleophiles included sodium azide, sodium thiophenoxide, and thiophenol. In no instance, even with 1.0 *M* sodium thiophenoxide in 50% methanolic dioxane, could a kinetically second-order reaction be observed.

In the years 1960–1961 we published a series of three papers[3-5] dealing with the concurrent substitutions (solvent and azide ion) and rearrangements of α-aryl-γ-methyl- and of α-methyl-γ-arylallyl *p*-nitrobenzoate. More recently we have directed our attention to the competitive substitution characteristics (with solvent and phenoxide ion) displayed by the allylic α- and γ-methylallyl chlorides.[6] With each of these two basic substrate types we have sought, and vainly, evidence for "borderline" behavior, that is, reaction of substrates with nucleophiles at a rate intermediate between zeroth- and first-order in the concentration of nucleophile, since we had established with other substrates[7] that these were among the conditions necessary to distinguish experimentally between, on the one hand, traditional SN1 and/or SN2 reactions, and, alternatively, an ion-pair mechanism.

Although borderline behavior could not be induced with either substrate type, these studies did in fact delineate the structural limitations of allylic systems necessary for "limiting SN1 and SN2 behavior"; thus the methylallyl chlorides[6] underwent reactions with nucleophile at a rate cleanly first-order in the concentration of nucleophile in all solvent systems studied ("SN2") while the phenylmethylallyl systems reacted cleanly at a rate independent of the concentration of nucleophile ("SN1") (*vide infra*).

While these experiments failed in their primary objective, that of providing a substrate appropriate for a test of the ion-pair mechanism, they did suggest, correctly, that a substituted allylic system, intermediate in reactivity between the monomethyl- and phenylmethylallyl substrates, would permit us to achieve our primary aim. Accordingly, we initiated a study of competitive substitutions into allylic substrates of intermediate reactivity, the various dimethylallyl chlorides, where in fact the desired "borderline" kinetic behavior was observed.[8] Experiments with the symmetrically substituted α,γ-dimethylallyl chloride were particularly simple and rewarding and provided just that behavior predicted by the ion-pair mechanism of substitution for this substrate. These experiments have been reported in the preceding paper (XIV).[8]

In the course of our investigations into the substitution reactions of the unsymmetric dimethylallyl systems, α,α- and γ,γ-dimethylallyl chloride, as well as of extended studies with the phenylmethylallyl substrates, a number of interesting observations were made and these observations, together with a discussion of their implications, will provide the subject matter of this paper.

α,α- and γ,γ-Dimethylallyl Chloride

Although our results with these substrates are somewhat fragmentary they do lead inescapably to certain conclusions of considerable interest and for that reason we publish them here.

Each of these substrates was allowed to react competitively with solvent and varying concentrations of sodium azide, the solvent system being 80 vol % aqueous acetone, the temperature 32.0°. Rates of acid production were followed by titration of liberated acid as a function of time while product distributions (total alkyl azide:total alcohol) could be determined from infinity titers since alkyl azide formation is not accompanied by liberation of acid. In several cases the distribution of solvolysis products, α,α- and γ,γ-dimethylallyl alcohol, was determined by vpc analysis; distributions of the allylic azides could not be determined in this manner since they are unstable to the reaction conditions, rearranging to their allylic isomers, *via* an intramolecular process involving a pseudo-six-membered ring transition state at rates comparable with their rates of formation.[9]

---

[1] Supported in part by the National Science Foundation.

[2] This author is indebted to the faculty, students, and staff of the Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, Zürich, Switzerland, for the use of their facilities and for their gracious hospitality during the writing of part of this manuscript.

[3] R. A. Sneen, *J. Amer. Chem. Soc.*, 82, 4261 (1960).

[4] R. A. Sneen and A. M. Rosenberg, *ibid.*, **83**, 895 (1961).

[5] R. A. Sneen and A. M. Rosenberg, *ibid.*, **83**, 900 (1961).

[6] R. A. Sneen and J. V. Carter, *ibid.*, **94**, 6990 (1972).

[7] R. A. Sneen and J. W. Larsen, *ibid.*, 91, 362 (1969).

[8] R. A. Sneen and W. A. Bradley, *ibid.*, **94**, 6975 (1972).

[9] A. Gagneux, S. Winstein, and W. G. Young, *ibid.*, **82**, 5956 (1960).

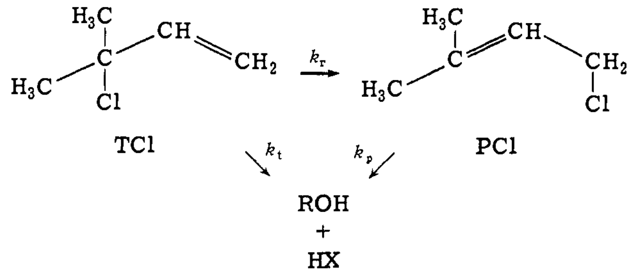
Although solvolysis (in the absence of azide ion) of the more stable primary isomer, γ,γ-dimethylallyl chloride, liberated acid at a steady first-order rate ($k_p = 1.32 \times 10^{-4}$ sec^{-1}), the isomeric tertiary isomer, α,α-dimethylallyl chloride, displayed a downward drifting rate constant (Table I). This of course reflects a competitive solvolysis and rearrangement to the less reactive primary isomer.[10] The integrated first-order rate constants can, by extrapolation to zero time, furnish an estimate of the rate of solvolysis of the tertiary isomer ($k_t = 4.81 \times 10^{-4}$ sec^{-1}).[11]

Table I. Rate and Product Distribution Data for the Competitive Reactions of α,α- and γ,γ-Dimethylallyl Chloride with Solvent and Sodium Azide in 80% Aqueous Acetone at 32.0°

Substrate[a]	$[\mathrm{NaN_3}] \times 10^2$	$k_{\mathrm{exptl}} \times 10^4$, sec^{-1}	% $\mathrm{RN_3}$
PCl		1.34 ± 0.03	
		1.31 ± 0.01	
	3.96	9.6 ± 0.3	88
TCl		4.81 → 2.19[b]	
	3.88	8.11 ± 0.15	53
	7.72	9.85 ± 0.11	63

[a] PCl = γ,γ-dimethylallyl chloride; TCl = α,α-dimethylallylchloride. [b] Downward drifting rate constant; see Table II.

Scheme I



Without regard to mechanistic details the various processes of interest can be defined by the rate constants of Scheme I.[12,13] For Scheme I one can derive[14] the following relationship for the concentration of liberated acid as a function of time on solvolysis of the tertiary α,α-dimethylallyl chloride.

$$[\mathrm{HCl}]_t = [\mathrm{HCl}]_\infty\left\{1 - \frac{(k_t - k_p)e^{-(k_r + k_t)t} + k_r e^{-k_p t}}{(k_t + k_r - k_p)}\right\} \quad (1)$$

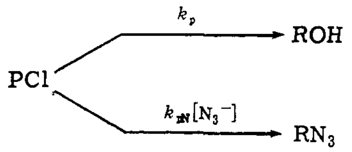
The ability of this equation (eq 1) to account for the rate of acid production, with $k_r = 1.75 \times 10^{-4}$ sec^{-1}, is then evidenced by a comparison of the observed (column 2) and calculated (column 4) acid titers as a function of time (Table II).

Table II. Kinetic Data for the Solvolysis of α,α-Dimethylallyl Chloride in 80% Aqueous Acetone at 32.0°[a]

Time, sec	Titrant (ml), exptl	k_1,[b] 10^4 sec^{-1}	Titrant (ml), calcd[c]
128	0.315		0.28
377	0.827	4.81	0.79
634	1.266	4.65	1.23
925	1.696	4.57	1.65
1325	2.229	4.58	2.13
1769	2.651	4.42	2.54
2276	3.028	4.25	2.92
2918	3.339	3.95	3.27
3699	3.618	3.66	3.57
4525	3.818	3.07	3.78
5528	3.985	2.73	3.98
7054	4.162	2.47	4.18
9088	4.352	2.19	4.34
12028	4.513		4.50

[a] $[\mathrm{TCl_i}] = 4.839 \times 10^{-2}$ M (initial concentration of TCl); titrant = 0.500 M HCl; theoretical infinity titer = 4.839 ml. [b] Calculated from the equation $k_1 = (1/t)\ln([\mathrm{HX}_\infty]/([\mathrm{HX}_\infty] - [\mathrm{HX}]))$. [c] Calculated from eq 1 with $k_t = 4.81 \times 10^{-4}$ sec^{-1}, $k_p = 1.32 \times 10^{-4}$ sec^{-1}, and $k_r = 1.75 \times 10^{-4}$ sec^{-1}.

When these kinetic studies were repeated, this time in the presence of externally added sodium azide (other conditions unchanged), some additional and interesting features of the systems came into focus (Table I). Thus the primary γ,γ-dimethylallyl chloride, in the presence of 0.0396 M sodium azide, now furnished some of the products of solvolysis (~12%) but mainly azide (~88%), the pseudo-first-order rate constant, $k_1 = 9.6 \pm 0.3 \times 10^{-4}$ sec^{-1}, being nearly that predicted from the product distribution for competitive SN2 reactions (1.32×10^{-4} sec^{-1} (([ROH] + [$\mathrm{RN_3}$])/[ROH] = 11.0×10^{-4} sec^{-1}). For the competitive reactions of solvent and azide ion with the primary chloride one can calculate, using the relationship, $[\mathrm{RN_3}]/[\mathrm{ROH}] = k_{pN}[\mathrm{N_3^-}]/k_p$, that the ratio, $k_{pN}/k_p = 200$.[15]



The competitive reactions of the tertiary isomer, α,α-dimethylallyl chloride, with solvent and azide ion were particularly instructive. Not only is there observed rate enhancement over and above that of the rate in the absence of added azide ion but the downward drifting of the rate constant with time observed on solvolysis is no longer evident (see Table I). Furthermore, the calculated pseudo-first-order rate constant increases with increasing azide ion concentration (see Table I).

Certain features of these observations become clear if one recognizes that, in the presence of azide ion (≥ 0.0388 M), the rearrangement product, PCl, is converted largely (>85%, see Table I) into $\mathrm{RN_3}$. This has two significant results: (1) it eliminates the source of the downward-drifting rate constant (the production of HCl from the slower solvolyzing PCl); and (2) the experimentally determined pseudo-first-order rate constant ($k_{\mathrm{exptl}} = \ln([\mathrm{HX}_\infty]/([\mathrm{HX}_\infty] - [\mathrm{HX}_t]))/(1/t)$)

---

(10) Parallel behavior in solvent acetic acid was first recognized and interpreted by W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1958 (1951).

(11) See ref 25.

(12) Throughout this section the symbol PCl will refer to the primary γ,γ-dimethylallyl chloride, TCl will refer to the tertiary α,α-dimethylallyl chloride and the symbol RCl will refer to both PCl and TCl: *i.e.*, RCl = PCl + TCl. Similarly POH will refer to the primary γ,γ-dimethylallyl alcohol, etc.

(13) The rearrangement of PCl to TCl (k_{-r}) is apparently sufficiently relatively slow that, in the first approximation, it can be neglected.

(14) J. V. Carter, Appendix B, Ph.D. Thesis, Purdue University, 1967.

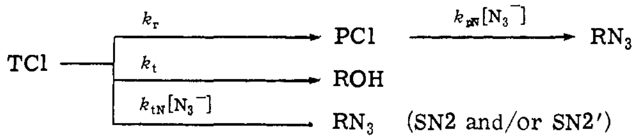
(15) The units of this quantity are, of course, properly mole^{-1}. However, we will not in general use this unit explicitly.

calculated using experimental infinity acid titers ($[HX_\infty]$) measures the *sum of all processes for the destruction of starting material,* including the rearrangement, k_r. The data make it apparent however that, since the sum of the constants, $k_t + k_r$ (4.81×10^{-4} sec^{-1} + 1.75×10^{-4} sec^{-1} = 6.56×10^{-4}) is less than k_{exptl} (8.11×10^{-4} sec^{-1} at 0.0388 *M* NaN_3 and 9.85×10^{-4} sec^{-1} at 0.077 *M* NaN_3), and, further, since k_{exptl} increases with increasing azide ion concentration, one or both of two conclusions must follow: (1) either the enhanced rates in the presence of azide ion over and above the sum of the constants, $k_t + k_r = 6.56 \times 10^{-4}$ sec^{-1}, result from a positive salt effect on their sum; or (2) a kinetically second-order process, $k_{tN}[N_3^-]$, on TCl must contribute to the total rate; *i.e.*, $k_{\text{exptl}} = k_t + k_r + k_{tN}[N]$.

If the first of these two possibilities, that NaN_3 exerts a positive salt effect on the sum, $k_t + k_r$, is adequately to account for all of the observed rate enhancement, the salt effect must be rather extraordinarily large. From the two appropriate azide runs of Table I, one calculates that a b[16] value of +7.2, on the combined sum, $k_t + k_r$, is required to rationalize, as a salt effect, the rate enhancement ($9.85/8.11 = (1 + b \cdot [0.077])/(1 + b[0.0388])$).[17] If one assumes that salt effects parallel solvent effects he can calculate that a $b = +7.2$ for the sum, $k_r + k_t$, for the α,α-dimethylallyl chloride system corresponds to a $b = +9.2$ for the dissected k_t process.[18]

All available comparisons indicate that a b value of this size is far too large reasonably to be expected of the k_t process in question.[20] These include: (1) diphenylmethyl chloride in 70% acetone (20°) (data of Kohnstam),[21] $b = 3.25$; (2) γ-methylallyl chloride in 60% dioxane[6] (50°), $b = 2.8$; (3) α-phenylethyl bromide in ethanol (50°),[22] $b = 4.0 \rightarrow 4.8$; (4) α-*p*-tolylethyl chloride in ethanol (50°),[22] $b = 2.84 \rightarrow 4.4$; (5) α,γ-dimethylallyl chloride in ethanol (36°),[8] $b = 3.0 \rightarrow 3.7$; and (6) α,γ-dimethylallyl chloride in 90% ethanol (27°),[8] $b = 3.1 \rightarrow 4.0$. Additional examples are given in the appendix to ref 22.

It will be apparent that, even in solvents of lower ionizing power ($Y_{\text{EtOH}} = -2.0$; $Y_{80\%\ \text{acetone}} = -0.53$),[23] salt effects on solvolysis do not exceed $b = 4.8$. We conclude that at least a portion of the enhanced rates of reaction of α,α-dimethylallyl chloride with azide ion must be ascribed to a second-order process, $k_{tN}[N]$, either directly at the tertiary carbon atom or, alternatively, at the γ positions (SN2′).[24]



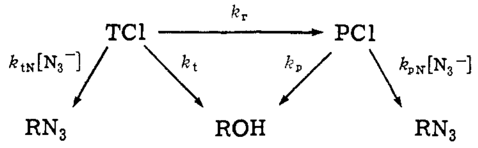
If one assigns the entire rate enhancement observed in the presence of azide ion to the bimolecular component, k_{tN} (a more realistic estimate might ascribe about one-third to one-half of it to salt effects), he can calculate its value since values of k_r and k_t are known (*vide supra*). From the pertinent data of Table I, $k_{tN} = 42 \pm 2\ M^{-1}$ sec^{-1}.[25]

Of greatest significance among these conclusions is that *this process labeled* k_{tN}, *bimolecular attack on tertiary chloride, is implicated.* It should be noted that the rate constant for this process, k_{tN}, is not too greatly different from the rate constant for bimolecular azide attack on the corresponding primary chloride, $k_{pN}/k_{tN} = \sim 6/1$ (or 9/1 to 12/1 if one-third or one-half of the rate enhancement is ascribed to salt effects).

Since the two possible products of azide attack, α,α- and γ,γ-dimethylallyl azide, are unstable under the conditions of their formation, equilibrating at rates comparable with their rates of formation,[9] it is not now possible to determine whether this process, k_{tN}, involves bimolecular attack at a tertiary carbon[26] or, alternatively, a very facile SN2′ reaction.

An attempt was made to determine whether the kinetic data, obtained as described above, could predict the product distributions (RN_3:ROH) obtained on solvolysis of the tertiary α,α-dimethylallyl chloride in the presence of varying concentrations of sodium azide. When all of the appropriate reactions studied in this work are summarized, Scheme II results. From

Scheme II



---

(16) Assuming the salt effect equation: $k = k^0(1 + b[\text{salt}])$. See, *e.g.*, ref 7, 8, and 22.

(17) Alternatively one can calculate the magnitude of the salt effect for each experimental point separately, assuming $k_t + k_r = 6.56 \times 10^{-4}$ sec^{-1}, wherein for 0.0388 *M* NaN_3, $b = 6.1$, and for 0.077 *M* NaN_3, $b = 6.5$. The chosen procedure avoids any ambiguity about the exact value of the sum $k_t + k_r$.

(18) There is of course ample precedent for the view that allylic rearrangement processes find it increasingly difficult to compete with solvolysis processes as the ionizing power of the solvent is increased.[8,19] The data of the preceding manuscript[8] allow a dissection of the relative solvent effects of the rearrangement (there racemization) and solvolysis processes for the substrate α,γ-dimethylallyl chloride as it is transferred from ethanol to 90% aqueous ethanol. One concludes from these data that, if salt effects parallel solvent effects, $b_{k_r}/b_{k_t} = 0.18$, and therefore for the α,α-dimethylallyl chloride system, that

$$\frac{b_{(k_r + k_t)}}{b_{k_t}} = \frac{1.75 \times 0.18 + 4.81 \times 1}{6.56} = 0.78$$

(19) See, for example, H. L. Goering and J. T. Doi, *J. Amer. Chem. Soc.*, **82**, 5850 (1960).

(20) Unfortunately the direct measurement of salt effects, with selected model salts, on the substrate in question, TCl, did not prove feasible because of complications arising from the concomitant rearrangement.

(21) G. Kohnstam, A. Queen, and B. Shillaker, *Proc. Chem. Soc.*, 157 (1959).

(22) R. A. Sneen and H. M. Robbins, *J. Amer. Chem. Soc.*, in press.

(23) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(24) For a recent evaluation of the SN2′ reaction, see F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

(25) Alternatively the value of k_{tN} can be evaluated without assumed values of k_t and k_r from the data of the two pertinents runs of Table I, since $(k_{\text{exptl}} - k_{tN}[N_3^-])_{\text{run 1}} = (k_{\text{exptl}} - k_{tN}[N_3^-])_{\text{run 2}}$. Determined in this way $k_{tN} = 46\ M^{-1}$ sec^{-1}. This observation incidentally provides a very convincing internal check on the purity of the α,α-dimethylallyl chloride used in the solvolysis studies of Table I. Had this tertiary chloride been contaminated with significant amounts of the more stable primary isomer, the calculated values of both k_t and k_r would have been lower than the true values. From the value for k_{tN} obtained as in this footnote, the sum, $k_t + k_r = k_{\text{exptl}} - k_{tN}[N_3^-]$, can be calculated independently and is found, from the azide runs of Table I, to be 6.31×10^{-4} sec^{-1}. This is to be compared with the sum obtained from solvolysis studies, $k_t + k_r = 6.56 \times 10^{-4}$ sec^{-1}.

(26) Independent investigators in three separate laboratories have recently communicated to us privately (N. Kornblum, Purdue) or indicated in lectures at Purdue (K. Servis, University of Southern California, and F. G. Bordwell, Northwestern) that they have observed bimolecular displacements at tertiary (benzylic and allylic) carbon atoms. We, of course, envisage these as rate-determining displacements on a preformed ion pair.

this follows the product relation

$$\frac{[RN_3]}{[ROH]} = \frac{k_{tN}[N_3^-] + k_r k_{pN}[N_3^-]/(k_p + k_{pN}[N_3^-])}{k_t + k_r k_p/(k_p + k_{pN}[N_3^-])} \quad (2)$$

The product distributions (per cent ROH) of Table III have been calculated from this equation and are then compared with experimental data. Although agreement is not excellent it is perhaps as good as can be expected, considering the number of independently measured parameters.

Table III. Product Distributions of the Competitive Reactions of α,α-Dimethylallyl Chloride (*ca.* 0.025 *M*) with Solvent and Added Sodium Azide in 80% Aqueous Acetone at 32.0°

$[NaN_3]$	% ROH exptl	% ROH calcd[a]	$\frac{[POH]}{[POH]+[TOH]} \times 100$
	100		21.8
0.050 LiOAc	100		24.2
0.0101			24.2
0.0250			23.6
0.0400	60.1	59	21.2
0.0603	59.4	54	21.1
0.0801	57.1	49	22.4
0.0999			20.3
0.199	38.9	33	22.9
0.301	33.8	26	25.4
0.400	26.7	21	
0.500	21.8	18	

[a] Calculated from eq 2 with $k_t = 4.81 \times 10^{-4}$ sec^{-1}, $k_p = 1.32 \times 10^{-4}$ sec^{-1}, $k_r = 1.75 \times 10^{-4}$ sec^{-1}, $k_{pN} = 264 \times 10^{-4}$ sec^{-1} mol^{-1}, $k_{tN} = 40 \times 10^{-4}$ mol^{-1}.

Table III also shows that, from TCl, the relative amounts of the isomeric solvolysis products cannot be altered by varying concentrations of added sodium azide, the tertiary α,α-dimethylallyl alcohol invariably comprising 78 ± 1% of the total solvolysis products. Solvolysis of the primary γ,γ-dimethylallyl chloride similarly gives solvolysis products at all concentrations of sodium azide in which the tertiary product comprises ~78% of the mixture (Table IV). There is no product spread.

Table IV. Product Distributions of the Competitive Reactions of γ,γ-Dimethylallyl Chloride (*ca.* 0.025 *M*) with Solvent and Added Sodium Azide in 80% Aqueous Acetone at 32.0°

$[NaN_3]$	% ROH, exptl	$\frac{[POH]}{[POH]+[TOH]} \times 100$
	100	25.7
0.0099		22.4
0.0250		25.6
0.0400	12.3	24.3
0.0602	8.8	20.6
0.0801	6.8	20.5
0.200	6.3	
0.400	4.4	

In the preceding manuscript[8] we established that the bimolecular component of the reaction rate for the reaction of azide ion with α,γ-dimethylallyl chloride was rather remarkably accelerated by an increase in the ionizing power of the solvent. Thus, whereas the observed rate of solvolysis of that secondary substrate is enhanced by a factor of 19 ($m_G \simeq 1.00$)[27,28] on passing from absolute ethanol as solvent to 90% aqueous ethanol, the bimolecular component of the rate (with azide ion) was enhanced by a factor of ~9.4 for the same change in solvent ($m_G = +0.73$). We pointed out there[8] that this rather extraordinary solvent sensitivity of a bimolecular displacement reaction resembled much more the behavior expected of carbonium ion (or ion-pair) reactions than that traditionally associated with "S$_N$2" displacements.[29] We concluded that these displacement transition states must have considerable ionic character, a conclusion in keeping with our view that these are in fact displacement reactions on ion-pair intermediates.

Completely independent but complementary evidence for the "carbonium-ion-like" character of these bimolecular substitutions into allylic chlorides can be gleaned from a consideration of the bimolecular rates of azide ion attack on primary (γ,γ-dimethylallyl chloride, Table I) and secondary allyl chlorides (α,γ-dimethylallyl chloride, Table VI of preceding paper[8]).[30] We choose to compare the available data for α,γ-dimethylallyl chloride in 90% ethanol ($Y = -0.73$)[23] with those for γ,γ-dimethylallyl chloride in 80% acetone ($Y = -0.53$),[23] since these are solvents of similar ionizing power. (Solvent nucleophilicity is not a factor here since product spreads do not exist.) Relative solvolysis rates can be estimated from the data of Vernon[31] ($k = 6.53 \times 10^{-5}$ sec^{-1} for γ,γ-dimethylallyl chloride, 44.6°, ethanol) and of Goering[32] ($k = 7.59 \times 10^{-5}$ sec^{-1} for α,γ-dimethylallyl chloride, 30°, ethanol) which corresponds to a rate ratio (at 44.6°)[33] of $k_{\alpha\gamma}/k_{\gamma\gamma} = 6.3$. From the rate data of Table I one calculates that $k_N/k_s = 156$ for γ,γ-dimethylallyl chloride in 80% acetone (32.0°) and from the data of Table VI of the preceding paper[8] one calculates that $k_N/k_s = 14.0$ for α,γ-dimethylallyl chloride in 90% aqueous ethanol (27.0°). One concludes that $k_{N\gamma\gamma}/k_{N\alpha\gamma} = 1.8$; that is, the bimolecular rate of attack by azide ion on the secondary substrate is within a factor of 2 of that on the primary substrate. It will be apparent that bimolecular rates of attack by azide ion on allylic chloride are remarkably insensitive to the steric congestion at the site of attack. These bimolecular rates of reaction at primary and secondary carbon are in fact more similar than are the corresponding solvolysis rates of these substrates. Again one must conclude that these substitution reaction transition states show characteristics, this time structure–reactivity relationships, considerably more reminiscent of carbonium ion reactions than of traditional S$_N$2 reactions.[34] And, yet, the bimolecular

---

(27) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, 56, 790 (1956).

(28) In this series of three papers[6,8] we have adopted the symbol, m_G (Grunwald), for the substituent constant of the Grunwald–Winstein equation;[23] then $\log (k_2/k_1) = m_G(Y_2 - Y_1)$. See ref 17 of ref 8.

(29) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter 7.

(30) Because of the ambiguities in interpretation of the bimolecular reaction of the tertiary α,α-dimethylallyl chloride (*i.e.*, what portion of the observed rate enhancement with azide ion results from a salt effect, and whether the bimolecular reaction is of the "S$_N$2" or "S$_N$2′" type), we elect not to reduce the forcefulness of this argument by including those data in our discussion.

(31) C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).

(32) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *J. Amer. Chem. Soc.*, 77, 5026 (1955).

(33) Assuming $\Delta H^{\ddagger} = 21.5$ kcal/mol. See ref 32.

(34) See ref 43 of ref 8.

kinetic component forces one to acknowledge the presence of azide ion in these transition states. The ramifications for the ion-pair mechanism are inescapable.

α-Methyl-γ-phenylallyl 2,6-Dichlorobenzoate

In earlier studies with α-methyl-γ-phenylallyl *p*-nitrobenzoate and its allylic isomer, our attempts to induce kinetically second-order nucleophilic displacement reactions were thwarted by the incursion of a quite facile acyl–oxygen cleavage reaction, catalyzed even by sodium azide.[5] These earlier studies were also hindered by the necessity, in the absence of vpc techniques, of developing a rather intricate product analysis procedure, using uv spectroscopy, which required the quantitative saponification (and subsequent quantitative basic extraction of *p*-nitrobenzoic acid) of unreacted ester.[4]

It accordingly seemed desirable, with the advent of vpc, to reinvestigate this system and thereby to validate certain of our earlier conclusions utilizing a different leaving group, in particular the hindered 2,6-dichlorobenzoate,[35] which could be expected to discourage attack at carbonyl carbon and thereby to permit a more thorough search for a second-order nucleophilic attack at alkyl carbon.

The desired α-methyl-γ-phenylallyl 2,6-dichlorobenzoate was readily prepared from the corresponding alcoholate and 2,6-dichlorobenzoyl chloride.[36] Rates of reaction and product distributions for selected reactions of α-methyl-γ-phenylallyl 2,6-dichlorobenzoate in various dioxane–water mixtures are given in Table V. Rates of reaction were in some cases followed both titrimetrically as well as by vpc techniques (see Experimental Section). Although considerably less precise, the rates followed by the latter technique, which also permits continual monitoring of the distribution of products, were within experimental error of the titrimetric runs. The product distribution, in the absence of buffer (α-methyl-γ-phenylallyl alcohol:α-phenyl-γ-methylallyl alcohol), changed with time due to an acid-catalyzed rearrangement of the α-phenyl isomer into its more stable α-methyl isomer.[4] Extrapolation of the product data to zero time indicates that the products are formed kinetically in an 85:15 α-methyl:α-phenyl ratio, a value in excellent agreement with the 84% α-methyl isomer obtained from α-methyl-γ-phenylallyl *p*-nitrobenzoate under similar conditions and determined by uv techniques in our earlier studies.[4]

Table V. Rates and Products of Solvolysis of α-Methyl-γ-phenylallyl 2,6-Dichlorobenzoate in Aqueous Dioxane

Solvent, % dioxane	Temp, °C	k, sec^{-1} × 10^{5}	Analytical method[a]	% α-methyl alcohol[b]
75	65.0	1.19 ± 0.04	T	
75	75.0	3.06 ± 0.06	T	
75	75.0	3.21 ± 0.04	T	
75	75.0	3.24 ± 0.04	T	
66.7	75.0	12.3 ± 0.2	T	
66.7	75.0	12.0 ± 0.1	T	
66.7	75.0	12.9 ± 1.0	Vpc	84[c]
66.7	75.0	13.5 ± 0.9	Vpc	86[c]

[a] T = titrimetric. [b] α-Methyl-γ-phenylallyl alcohol. [c] Percentage extrapolated to zero time; see text.

By interpolation of data from our earlier studies[3] for the solvolysis in 60 and 70% aqueous dioxane at 75° of α-methyl-γ-phenylallyl *p*-nitrobenzoate it can be estimated that this ester would solvolyze, at 75° in 66.7% aqueous dioxane, with $k = 3.9 \times 10^{-5}$ sec^{-1}; thus the corresponding 2,6-dichlorobenzoate ester, with $k = 1.21 \times 10^{-4}$ sec^{-1} at 75° in 66.7% aqueous dioxane (Table V), solvolyzes *ca.* 3.1 times more rapidly.

Selected product distribution and kinetic data for the methanolysis of α-methyl-γ-phenylallyl 2,6-dichlorobenzoate are given in Table VI. These data were obtained using vpc techniques. Among the more salient facts which emerge from Table VI are the following. (1) The ethereal solvolysis products, α-methyl-γ-phenyl-:α-phenyl-γ-methylallyl methyl ether, are formed, under kinetic conditions, in a ratio of 60:40%, virtually identical with the earlier reported distribution of 61:39% resulting from the methanolysis of the corresponding *p*-nitrobenzoate ester.[5] (2) Solvolysis in the presence of rather massive quantities of sodium azide (~0.75 *M*) diverts only *ca.* 38% of the starting material to allylic azide.[37] This result is to be contrasted with the earlier reported behavior of the corresponding α-methyl-γ-phenylallyl *p*-nitrobenzoate where only 0.077 *M* sodium azide was needed to divert 32% of the ester away from solvolysis products.[5] Most of this divergence with the *p*-nitrobenzoate ester was attributed (and apparently correctly) to the incursion of an acyl–oxygen cleavage reaction. Further confirmation that this side reaction does not here compete successfully with other reactions of the 2,6-dichlorobenzoate ester is furnished by our observation that its expected product, α-methyl-γ-phenylallyl alcohol, is absent from the product mixture. (3) Methanolysis in the presence of 0.39 *M* thiophenol (*ca.* 4.0 vol %) resulted in a somewhat decreased rate of reaction and a diversion of *ca.* one-third of the products to a mixture of the allylic sulfides, α-methyl-γ-phenyl-:α-phenyl-γ-methylallyl phenyl sulfide, in a ratio of 70:30.

Table VI. Rates and Products of Solvolysis of α-Methyl-γ-phenylallyl 2,6-Dichlorobenzoate in Methanol at 60.0°

[Salt]	k,[a] sec^{-1} × 10^{4}	% ethers[b]	α-Methyl:α-phenyl products[c] Ethers	Sulfides
	2.00 ± 0.13	100		
	2.01 ± 0.10	100		
1.0 *M* $NaOCH_3$[d]			60:40	
0.75 *M* NaN_3	2.24 ± 0.25	62	65:35	
0.39 *M* C_6H_5SH	0.887 ± 0.048	~67		70:30

[a] Followed by vpc. [b] α-Methyl-γ-phenyl- and α-phenyl-γ-methylallyl methyl ether. [c] Ratio of α-methyl-γ-phenylallyl to α-phenyl-γ-methylallyl ether or sulfide. [d] α-Methyl-γ-phenylallyl alcohol, the product of acyl–oxygen cleavage, identified among products.

Finally, attention is directed to Table VII where product distribution and rate data are reported for the

---

(35) G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4609 (1956).

(36) In contrast the allylically related α-phenyl-γ-methylallyl 2,6-dichlorobenzoate resisted all of our attempts at obtaining it in a pure crystalline form, rearranging on attempted crystallization to the more stable α-methyl-γ-phenylallyl 2,6-dichlorobenzoate.

(37) Only the more stable α-methyl-γ-phenylallyl azide is observed, its allylic and less stable isomer being isomerized nearly quantitatively under the reaction conditions *via* an intramolecular rearrangement.[9]

Table VII. Rates and Products of Selected Reactions of α-Methyl-γ-phenylallyl 2,6-Dichlorobenzoate

Solvent[a]	Temp, °C	[Salt],[b] M	k,[c] sec^{-1} × 10^5	% ethers	α-Methyl:α-phenyl product[d] Ethers	Sulfides
MeOH	50	0.480 PhSNa	11.9 ± 0.6[e]		65:35	80:20
MeOH	50	0.450 PhSNa		26	65:35	80:20
MeOH	50	0.885 PhSNa	17.0 ± 2.0	19		80:20
MeOH	50	0.484 $NaClO_4$	15.9 ± 1.9	100	[f]	
MeOH	40	1.01 PhSNa	6.41 ± 0.54	11	67:33	80:20
1:1 M:D	50	0.996 PhSNa	6.15 ± 0.31	<8	62:38	80:20
1:1 M:D	50	1.00 $LiClO_4$	3.31 ± 0.31	100	61:39[g]	
1:3 M:D	50	1.00 $LiClO_4$	1.74 ± 0.14	100	66:34[g]	

[a] M:D = methanol:dioxane. [b] PhSNa = sodium thiophenoxide. [c] Rates followed by vpc. [d] Ratio of α-methyl-γ-phenylallyl to α-phenyl-γ-methylallyl ether or sulfide. [e] No salt rate estimated to be 7.5 × 10^{-5} sec^{-1}. [f] No buffer added. [g] 0.31 M pyridine present; product distributions obtained by extrapolation to zero time.

competitive reactions of α-methyl-γ-phenylallyl 2,6-dichlorobenzoate with solvent and sodium thiophenoxide in various solvents (methanolic dioxane) of decreasing ionizing power. Of greatest interest are these observations. (1) Even in the rather poorly ionizing solvent system, 1:1 methanol–dioxane, in which the addition of 1.0 M sodium thiophenoxide diverts ~92% of products to thioethers, the observed rate constant is within a factor of 2 of that observed in this solvent system with 1.0 M lithium perchlorate. The reaction is obviously not kinetically second order. (2) Neither the dilution of the solvent methanol with dioxane nor the addition of salts, lithium or sodium perchlorate or sodium thiophenoxide, significantly affects the distribution of ethereal products. (3) The distribution of allylic sulfides (80:20 α-methyl-γ-phenyl-:α-phenyl-γ-methylallyl phenyl sulfide), effected by sodium thiophenoxide, is invariant with solvent and nucleophile concentration and, further, is identical with the distribution formed from its conjugate acid, thiophenol (Table VI).

In summary, it will be recognized that our objectives in this study of selected reactions of α-methyl-γ-phenylallyl 2,6-dichlorobenzoate have been met if, in one case, disappointingly. The reluctance of this substrate to undergo second-order nucleophilic displacement under any of the conditions or with any of the nucleophiles here studied is rather remarkable in view of the relative ease with which such a reaction could be induced with α,α-dimethylallyl chloride (*vide supra*). On the other hand, the choice of Stork's leaving group,[35] 2,6-dichlorobenzoate, to obviate competing reactions at carbonyl carbon proved to be a good one and in view of its solvolytic reactivity (~3.1 times that of *p*-nitrobenzoate, *vide supra*) is to be recommended as an attractive alternative to other carboxylate leaving groups where its greater steric requirements can be tolerated.

Experimental Section

Preparation and Purification of Chemicals. α,α-Dimethylallyl Chloride. This procedure was adapted from that of Ulteé.[38] A mixture of 50 g (0.734 mol) of isoprene and 8.4 ml of ether was placed in a 100-ml three-necked round-bottom flask fitted with a gas addition tube, a thermometer, and a calcium sulfate protected gas exit tube. The mixture was stirred magnetically and kept at −20° while hydrogen chloride gas was introduced through the gas inlet tube. Gas addition was continued until 28 g (0.77 mol) of hydrogen chloride had been taken up by the solution. Stirring was continued at −20° for 2 hr and the solution was then stored overnight at −5°. A 10-g portion of anhydrous potassium carbonate was added at 0° with stirring; after gas evolution had ceased a second 10-g portion of potassium carbonate was added. Stirring was continued until the solution was neutral to litmus paper. The mixture was filtered, followed by removal of unreacted isoprene and ether at water aspirator pressure. Distillation of the residue was always carried out just prior to kinetic runs and afforded a colorless liquid, bp 40–41° (200 mm), n^{20}D 1.4190 [lit.[10] n^{20}D 1.4188).

γ,γ-Dimethylallyl Chloride. The tertiary allylic isomer, α,α-dimethylallyl chloride, was prepared as above. After stirring at 0° for 8 hr, the reaction mixture was treated with hydrogen chloride gas until an additional gram of gas had been taken up. The mixture was kept at 0° overnight and work-up was carried out as in the case of the tertiary chloride. Distillation just prior to use afforded a colorless liquid, bp 67° (165 mm), n^{20}D 1.4495 (lit.[10] n^{20}D 1.4495).

α-Methyl-γ-phenylallyl 2,6-Dichlorobenzoate. A solution of 10.0 g (67.4 mol) of α-methyl-γ-phenylallyl alcohol[39] in 30 ml of dry ether was placed in a nitrogen-purged, magnetically stirred, 200-ml round-bottom flask fitted with a condenser (protected by a calcium sulfate drying tube) and a septum-covered side arm. The solution was cooled at −20°, and 45 ml (72 mmol) of a hexane solution of *n*-butyllithium (Foote Mineral Co.) was injected slowly through the septum. Gas evolution was observed, as well as formation of a deep red color, as the last drops of metalating agent were added. After 20 min, the solution was warmed to 0°, and a solution of 14.1 g (67.4 mmol) of 2,6-dichlorobenzoyl chloride[35] in 20 ml of ether was injected through the septum. After 30 min a yellow color began to develop, and a white precipitate began to form. The mixture was stirred at gentle reflux for 3 days. The solution was then poured into 200 ml of petroleum ether (bp 90–100°) and filtered. Ether was removed on the water aspirator and attempts at recrystallization were begun. The product is highly soluble in most organic solvents, particularly when impure. Purification was finally achieved by trituration in petroleum ether (bp 90–100°) at −78°, affording 9.22 g (43%) of product, mp 52.5–53°.

Anal. Calcd for $C_{17}H_{14}O_2Cl_2$: C, 63.57; H, 4.39; Cl, 22.08. Found: C, 63.74; H, 4.54; Cl, 22.00.

α-Methyl-γ-phenylallyl Phenyl Sulfide. Gaseous hydrogen chloride was passed through a stirred solution of 29.0 g (0.196 mol) of α-methyl-γ-phenylallyl alcohol[39] in 100 ml of ether for 24 hr. The solution was then cooled to 0°, and a solution of 26.0 g (0.196 mol) of sodium thiophenoxide in 40 ml of methanol was added slowly. The solution was allowed to warm to room temperature slowly, and stirring was continued for 24 hr. Solvents were removed at water aspirator pressure and micro distillation of the residue afforded small amounts of a pale yellow, clear liquid, bp 135° (0.50 mm), n^{20}D 1.6196. The infrared spectrum bears a strong resemblance to the spectrum of 3-phenyl-1-propyl phenyl sulfide,[40] except for a peak at 10.4 μ, indicative of a trans-disubstituted double bond. Mass spectral data showed a parent peak at 240, as well as fragment peaks at 130 (assigned to 1-phenyl-1,3-butadiene) and at 131 (phenylmethylallyl cation). Other peaks, such as those at 129 and 128, correspond to published spectra for vinylbenzenes.[41]

Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71; S, 13.34. Found: C, 79.28; H, 6.41; S, 13.22.

Acetone. Stockroom acetone (5 l.) was added to 50 g of potassium permanganate and 1 lb of calcium sulfate (Drierite). The

---

(38) A. J. Ulteé, *J. Chem. Soc.*, 530 (1948).

(39) J. Kenyon, S. M. Partridge, and H. Phillips, *ibid.*, 207 (1937).

(40) Sadtler Standard Spectra, No. 24831, Philadelphia, Pa.

(41) Private communication, F. McLafferty.

mixture was maintained at reflux temperature overnight and was then distilled through a Todd column, the first and last 500-ml portions being discarded. The purified solvent was stored under nitrogen and in the dark.

Dioxane. The procedure followed is essentially that of Fieser.[42] A mixture of 4 l. of dioxane, 54 ml of concentrated hydrochloric acid, and 400 ml of water was allowed to reflux overnight under nitrogen. The mixture was cooled and poured over Technical Grade potassium hydroxide to salt out the aqueous layer. The dioxane was decanted and treated again with potassium hydroxide and then refluxed overnight over 0.25 lb of sodium. The mixture was distilled through a Todd column, and the middle fraction of 2.5 l. was collected and stored under nitrogen in the dark.

Methanol. A 400-ml portion of stockroom absolute methanol was added to 50 g (2.1 g-atoms) of magnesium. After vigorous reaction had ceased, an additional 1500 ml of absolute methanol was added, and the mixture was allowed to reflux for 30 min. Pure methanol was obtained by distillation through a Todd column; the first and last 500-ml portions were discarded and the product was stored under nitrogen in the dark.

Water. Distilled water was passed through a mixed-bed Barnstead demineralizer. In runs made using sodium thiophenoxide as a nucleophile, this water was either passed through a Barnstead oxygen removal bed or distilled under nitrogen prior to use.

Salts. To prepare a methanolic solution of sodium methoxide, freshly cut sodium metal was consecutively dipped into four beakers of methanol and was then added to purified methanol in a nitrogen-flushed system. The resultant solution was titrated with standardized hydrochloric acid to determine molarity.

Solid sodium thiophenoxide was supplied by Mr. N. Holly;[43] its purity was found to be greater than 98% by titration. It was always weighed and handled in a nitrogen-flushed drybox. Reagent Grade lithium perchlorate (G. Frederick Smith Chemical Co.) was dried *in vacuo* at 160° for 72 hr prior to use. Commercial anhydrous sodium perchlorate (G. Frederick Smith Chemical Co.) was used without further purification. Commercial sodium azide (Fischer Scientific Co.) was recrystallized from water–ethanol mixtures.

Kinetic and Product Distribution Procedures. Glassware. All volumetric equipment and other glassware used in kinetic procedures were cleaned by immersion in hot sodium dichromate–sulfuric acid cleaning solution and then rinsed with copious amounts of water. The glassware was then dipped in methanolic potassium hydroxide solution, rinsed thoroughly in distilled water, and dried overnight in a 110° oven. Previously unused test tubes were used for sealed ampoule runs and were cleaned with hot soapy water, rinsed in distilled water, and dried in an oven before use. All kinetic glassware was kept in one drawer and was kept closed or covered to keep out dust particles.

Gas Chromatographs. Kinetic runs were made on an Aerograph Model A-600 Hy-FI flame ionization gas chromatograph, equipped with a Leeds and Northrup Speedomax H recorder (1-mV full-scale deflection) using a Model 207 Disc Integrator. Carrier gas was nitrogen, and hydrogen was supplied by an Aerograph Model 650 hydrogen generator. Some product studies were carried out on an F & M Scientific Corp. Model 609 flame ionization gas chromatograph, equipped with a Texas Instruments Model pws 956 recorder with integrator, 1-mV full-scale deflection. The column used in the dimethylallyl chloride studies was 34 ft × $^1/_8$ in., comprised of 6 ft of 10% FFAP on Chromosorb W, HMDS treated, 8-ft low-loaded (~2%) Carbowax 20M Chromosorb W, HMDS treated, and 20-ft low-loaded (~2%) FFAP on Chromosorb W, HMDS treated, and 20-ft low-loaded (~2%) FFAP on Chromosorb W, HMDS treated. Temperature programming was utilized to separate the alcohol.

Titrimetric Kinetics. Solvents were prepared by mixing the proper volume ratios of solvent components in an erlenmeyer flask. A 100-ml solution of ester, approximately 0.02 *M*, was then prepared and kept over ice. (Where salts or nucleophiles were used, it was general procedure to make up a solution of nucleophile in the solvent of choice and then to use this solution to make up the kinetic sample.) Ampoules made from 6-in. test tubes were then charged with ~6 ml of solution each, flushed for 10–15 sec with dry nitrogen, and sealed. Ampoules were maintained at 0° throughout the operation. All ampoules were placed in the rate bath simultaneously, and a "zero point" was removed after 10 min. Further ampoules were removed at appropriate time intervals and cooled in ice. Aliquots were then pipetted into a 10-ml acetone quench solution and titrated with standardized sodium hydroxide to the appropriate end point. (Various indicators were used: Bromocresol Green–Methyl Red mixed indicator for dichlorobenzoate runs, Phenolphthalein for base standardization, and Bromthymol Blue–Phenol Red mixed indicator for allyl chloride solvolyses.) Allyl chloride solvolyses were run in volumetric flasks, and samples for titration were taken directly from the reaction vessel.

Gas-Chromatographic Kinetics. The typical gas-chromatographic kinetic procedures for solvolysis of ester in aqueous dioxane were as follows. An aqueous dioxane solution (*ca.* 0.07 *M* ester and 0.02 *M* fluorene, the internal standard) was placed in a 5-ml volumetric flask and flushed with nitrogen. The flask was then sealed with a snug-fitting silicone rubber septum of the type used in Aerograph gas-chromatographic injector ports. The septum was held in place by wiring an inverted serum cap over the top of the flask. The flask was placed in the rate bath and, after 5 min, a 2-μl sample was removed with a Hamilton syringe and analyzed on the gas chromatograph. At appropriate time intervals further samples were removed for analysis. Carrier gas flow (nitrogen, dry, prepurified) was 20 ml/min, and hydrogen flow was 20 ml/min. The injector voltage setting was 50 V and the column temperature was approximately 140°. The column used was a 4 ft × $^1/_8$ in. stainless steel tube packed with 6% Carbowax 20M on silicone treated Chromosorb W. Peaks observed corresponded in retention times to unconjugated alcohol (6–7 min), conjugated alcohol (9–10 min), and fluorene (15–16 min). "Absolute values" for amounts of alcohols present in any given analysis were obtained by dividing alcohol peak areas (as given by the integrator) by the internal standard (fluorene) peak area. Isomer distributions were obtained from a direct comparison of peak areas. (It was rigorously shown that although equal amounts of the isomeric alcohols give differently shaped peaks, the areas are equal.) Kinetic data were obtained by substituting "absolute values" into the first-order kinetic equation.

For methanolysis runs, where products were methyl ethers, the same technique was used. The same column was used, but the temperature was lowered to 85–90° and a glass sleeve was inserted into the injector port to minimize solvent tailing. The internal standard was naphthalene. Retention times were 7–8 min for unconjugated ether, 9–10 min for naphthalene, and 14–15 min for conjugated ether.

For sulfide analyses, an extraction procedure was required to prevent reaction of ester with thiophenoxide ion in the injector port. Kinetic solutions were run in 10-ml volumetric flasks, sealed as described above. At appropriate time intervals, a 0.8-ml aliquot was withdrawn with a tuberculin syringe. The sample was then injected into the aqueous layer of a mixture of 2 ml of 20% sodium hydroxide solution and 6 ml of hexane in a 25-ml erlenmeyer flask equipped with a 0.5 in. Teflon-coated stirring bar. The mixture was vigorously stirred for 30–60 min (until the aqueous layer was clear), and the aqueous layer was then discarded. The organic layer was slowly flashed down to 0.25 ml or less in volume, using sharply pointed semimicro distilling receivers and a rotary flash evaporator. A 0.3-μl aliquot of the concentrate was then analyzed on the gas chromatograph. Internal standard for these analyses was fluoranthene. The column used was ~6 ft × $^1/_8$ in., 5% SE-30 on Chromosorb W, HMDS treated, at 70-V injector setting, 158° column temperature, and 20 ml/min carrier gas and hydrogen flow rates. Retention times were 8 min for unconjugated phenyl sulfide, 11.5 min for conjugated phenyl sulfide, and 45 min for fluoranthene.

---

(42) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1941, p 369.

(43) N. Holly, Ph.D. Thesis, Purdue University, 1968.