

3d-ORBITAL RESONANCE IN DIVALENT SULPHIDES—XIII*

THE E2 REACTION OF *p*-SUBSTITUTED- β -PHENYLMERCAPTO CHLORIDES AND THE CORRESPONDING OXYGEN ANALOGUES

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Abstract—The rates of the base-catalysed elimination of a series of *p*-substituted- β -phenylmercaptoethyl chlorides and the corresponding oxygen analogues have been determined both in *t*-butanol containing potassium *t*-butoxide and in ethanol containing sodium ethoxide. The rates of the E2 reaction of the sulphur compounds are found to be 10^2 – 10^3 times as great as those of the corresponding oxygen analogues in both media. These rates can be correlated with Hammett σ values. The ρ values obtained for sulphur compounds are 1.98 and 2.14 in *t*-butanol and ethanol, while those for oxygen analogues are 1.33 and 1.50 respectively. The faster kinetic rates and the higher Hammett ρ values of the sulphur compounds, as compared with the oxygen counterparts suggest that 3d-orbital resonance is important in the E2 elimination reactions of these sulphur compounds. Other implications of the rates and the effect of the substituent are discussed.

SINCE the pioneering work of Hughes and Ingold, base-catalysed elimination reactions¹ have been extensively studied and a substantial amount of information is available concerning the effects of polar substituents, but very few of the investigations concern the base-catalysed elimination reactions of organic halides bearing a hetero atom at the β -position. Hine *et al.*² have found the relative rates to be 1 : 130 : 190 for fluoro, chloro and bromo compounds in the E2 reactivities of β -haloethyl bromides in aqueous dioxan with sodium hydroxide. As the rate is markedly increased by a substituent from the 2nd and 3rd row elements, these reactions probably proceed through a carbanion-like transition state and the d-orbital resonance effect of a Cl or a Br atom is important. When methyl- β -hydroxyethyl sulphide was treated with a strong alkali, methylvinyl sulphide was obtained, whereas under similar conditions methyl cellosolve does not react.³

In order to test the importance of 3d-orbital resonance in E2 elimination reactions, the title compounds were investigated. The previous data on the base-catalysed α -hydrogen-isotopic exchange of a number of divalent sulphur compounds and the decarboxylation of various α -mercapto carboxylic acids provided a rough quantitative estimation of the 3d-orbital resonance of sulphur groups in the E2 reactions. In addition, both ether and sulphide groups having large electron-releasing conjugative effects, are able to stabilize the developing double bond much more readily than the corresponding halogen atoms and may shift the transition state toward an ideal or a central transition state, and this can be estimated by the Hammett ρ values.

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RESULTS AND DISCUSSION

As base-catalysed elimination reactions proceed together with substitution reactions, the determination of olefins has to be carried out very carefully. In this work, the olefin yields were determined by gas chromatography for the sulphur compounds, while iodometry was used for the estimation of the oxygen-containing olefins. The rate of the E2 reaction of an individual organic chloride was estimated by determining the amount of the organic chloride consumed by a conventional method and multiplying this value by the ratio of olefin:ether of the particular reaction, previously determined by the product analysis. The results are shown in Tables 1–3. The reaction follows the second-order kinetics in which the rate depends on the concentrations of the organic chloride and the base used.

TABLE 1. THE RATE CONSTANTS OF E2 REACTION IN *t*-BuOH WITH *t*-BuOK^a











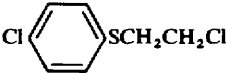
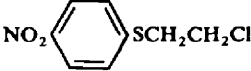
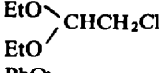
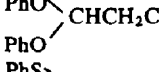
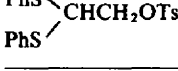
Compounds	Temp °	<i>k</i> (l/mole sec)	Olefin Yield (%)	Rel. rate
 -CH ₂ CH ₂ CH ₂ Cl	60.60 ± 0.26	3.67 ± 0.26 × 10 ⁻⁵	100	1
 -CH ₂ CH ₂ Cl	58.80 ± 0.01	2.75 ± 0.03 × 10 ⁻³	100	75
EtOCH ₂ CH ₂ Cl ^b	49.95 ± 0.01	1.65 ± 0.03 × 10 ⁻⁵	82.4	0.45
CH ₃ O-  -OCH ₂ CH ₂ Cl	59.95 ± 0.01	5.34 ± 0.05 × 10 ⁻⁵	76.2	1.5
CH ₃ -  -OCH ₂ CH ₂ Cl	59.95 ± 0.01	5.55 ± 0.23 × 10 ⁻⁵	83.0	1.5
H-  -OCH ₂ CH ₂ Cl	59.95 ± 0.01	7.41 ± 0.32 × 10 ⁻⁵	81.3	2.0
Cl-  -OCH ₂ CH ₂ Cl	59.95 ± 0.01	15.6 ± 0.1 × 10 ⁻⁵	87.4	4.3
NO ₂ -  -OCH ₂ CH ₂ Cl	59.95 ± 0.01	116.4 × 10 ⁻⁵	85.4	32
EtSCH ₂ CH ₂ Cl	59.80 ± 0.01	1.35 ± 0.02 × 10 ⁻²	100	370
iso-PrSCH ₂ CH ₂ Cl	59.80 ± 0.01	1.24 ± 0.01 × 10 ⁻²	100	340
sec-BuSCH ₂ CH ₂ Cl	59.80 ± 0.01	1.03 ± 0.01 × 10 ⁻²	100	280
CH ₃ O-  SCH ₂ CH ₂ Cl	40.05 ± 0.01	0.228 ± 0.004 × 10 ⁻²	100	—
	49.94 ± 0.01	0.575 ± 0.013 × 10 ⁻²	100	—
	59.80 ± 0.01	1.05 ± 0.01 × 10 ⁻²	100	290
CH ₃ -  SCH ₂ CH ₂ Cl	40.05 ± 0.01	0.375 ± 0.01 × 10 ⁻²	100	—
	49.94 ± 0.01	0.850 ± 0.01 × 10 ⁻²	100	—
	59.80 ± 0.01	1.60 ± 0.02 × 10 ⁻²	100	440
H-  SCH ₂ CH ₂ Cl	40.05 ± 0.01	0.743 ± 0.04 × 10 ⁻²	100	—
	49.95 ± 0.01	1.55 ± 0.02 × 10 ⁻²	100	—
	59.80 ± 0.01	3.28 ± 0.05 × 10 ⁻²	100	900

TABLE 1—continued

Compounds	Temp °	<i>k</i> (1/mole sec)	Olefin Yield (%)	Rel. rate
	40.05 ± 0.01	$2.15 \pm 0.01 \times 10^{-2}$	100	—
	49.95 ± 0.01	$4.89 \pm 0.02 \times 10^{-2}$	100	—
	59.80 ± 0.01	$7.82 \pm 0.10 \times 10^{-2}$	100	2,100
	40.05 ± 0.01	$46.8 \pm 2.0^c \times 10^{-2}$	100	—
	49.95 ± 0.01	$78.5 \pm 3.0^d \times 10^{-2}$	100	—
	59.80 ± 0.01	$126^e \times 10^{-2}$	100	34,000
	60.60 ± 0.02	3.83×10^{-6}	<i>f</i>	0.1
	60.60 ± 0.02	5.40×10^{-6}	<i>f</i>	0.15
	—	too fast to be measured		

^a The concentration of chlorides and *t*-BuOK is 2×10^{-2} M and 3×10^{-2} M for sulphur compounds and 1×10^{-1} M and 1.5×10^{-1} M for oxygen compounds.

^b Kinetics was carried out in a sealed tube. The concentration of the chloride and the base is 0.499M and 0.708M, respectively.

^c The concentration of the chloride and the base is 0.393×10^{-2} M and 0.616×10^{-2} M;

^d 0.351×10^{-2} M and 1.010×10^{-2} M.

^e Value extrapolated from other data at low temperatures.

^f Not corrected for the yield of the olefin.

TABLE 2. THE RATE CONSTANTS OF E2 REACTION IN EtOH WITH EtON₃

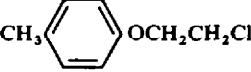

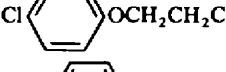
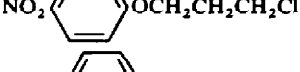
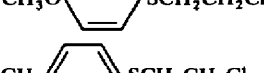
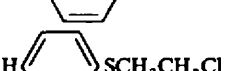

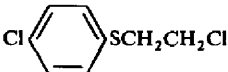
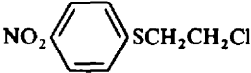
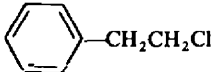

Compounds	Temp°	<i>k</i> (1/mole sec)	Olefin Yield (%)	Rel. rate
	60.60 ± 0.01	$1.68 \pm 0.03 \times 10^{-6}$	13.7	0.62
	60.60 ± 0.01	$2.71 \pm 0.07 \times 10^{-6}$	17.6	1
	60.60 ± 0.01	$5.14 \pm 0.08 \times 10^{-6}$	21.6	1.9
	60.60 ± 0.01	$43.4 \pm 0.6 \times 10^{-6}$	28.2	16
	60.60 ± 0.01	$0.569 \pm 0.006 \times 10^{-3}$	42.5	210
	60.60 ± 0.01	$0.597 \pm 0.009 \times 10^{-3}$	47.0	220
	60.60 ± 0.01	$1.03 \pm 0.03 \times 10^{-3}$	76.0	380

TABLE 2 (contd.)

Compounds	Temp°	<i>k</i> (l/mole sec)	Olefin Yield (%)	Rel. rate
	60.60 ± 0.01	4.22 ± 0.02 × 10 ⁻³	100	1,600
	60.60 ± 0.01	77.4 ± 2.0 × 10 ⁻³	100	29,000
	60	2.41 × 10 ⁻⁴ ^b	100	89

^a The concentration of chlorides and EtONa is 2 × 10⁻²M and 3 × 10⁻²M for sulphur compounds and 2 × 10⁻¹M and 3 × 10⁻¹M for oxygen compounds.

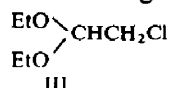
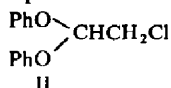
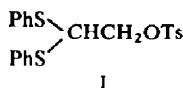
^b C. H. Depuy and C. A. Bishop, *J. Am. Chem. Soc.* **82**, 2535 (1960).

TABLE 3. THE RELATIVE RATES OF THE E2 REACTION OF X——ZCH₂CH₂Cl (Z = O or S) IN t-BuOK-t-BuOH AND EtONa-EtOH AT 60°

Base-solvent	X = CH ₃ O	CH ₃	H	Cl	NO ₂
<i>k_S</i> / <i>k_O</i> t-BuOK-t-BuOH	200	290	440	500	1,100
<i>k_S</i> / <i>k_O</i> EtONa-EtOH	—	360	380	820	1,800

^a *k_S* and *k_O* are the rate constants of sulphur and oxygen compounds respectively.

Effects of heteroatoms at β-carbon. Table 3 reveals that in sulphur compounds, the rates are 10²–10³ times as high as those of the corresponding oxygen analogues. This remarkable rate enhancement by the substitution of a mercapto group at the β-carbon is undoubtedly associated with the large acid-enhancing 3d-orbital resonance effect of the S atom. It also suggests that the E2 reaction proceeds via a carbanion-like transition state where the proton-removal proceeds a little earlier than the C–Cl heterolysis when the double bond between C_α and C_β is not fully developed. If the reaction proceeds via a carbanion at the transition state, the relative rates of the sulphur compounds would be at least 10⁵–10⁶ times as high as those of the corresponding oxygen compounds in view of our previous studies.⁴ If on the other hand, the E2 reaction proceeds via an ideal transition state, the oxygen compounds should react much faster than the sulphur analogues since the 2p-orbital of the developing double bond overlaps the 2p-orbital of the O atom more effectively than it does the 3p-orbital of the S atom.⁵ As the sulphur compounds are roughly 10²–10³ times more reactive than the corresponding oxygen analogues, either a negative charge must be developing at the β-carbon, which is stabilized by the 3d-orbital resonance of the S atom, during the transition state; or in the case of the oxygen compounds, the repulsion between the 2p-orbital of the developing negative pole of the β-carbon and the 2p-orbital of the O atom may retard proton removal. In the following dimercapto






and dioxy compounds (I, II, III), if the 3d-orbital resonance effect is in operation at the transition state of the reaction of I, the rate of the elimination must be at least

10^2 – 10^3 times as fast as that of the mono mercapto compound in view of our previous work.⁴ In the present investigation the rate of the E2 reaction of compound I was too fast to be measured. It decomposes instantly when exposed to air to give a dark polymeric substance formed perhaps by the polymerization of the elimination product. A similar observation was reported by Rothstein⁶ on the facile elimination of 1,1'-diethylmercapto-2-bromopropane. Meanwhile the substitution of a phenoxy or an ethoxy group at the β -carbon should increase the repulsion, thereby increasing the negative field effect to suppress the removal of a proton from the β -carbon, though this field effect may be partially eliminated by the highly electronegative nature of O atoms. As shown in Table 1, the substitution of an additional phenoxy or ethoxy group does not accelerate the rate but retards it, despite the strong electron-withdrawing inductive effect of these oxy groups, suggesting that the repulsion operates in these E2 reactions. However, the magnitude of this repulsive field effect must be small as compared to the large rate-enhancement of the 3d-orbital resonance effect of the sulfide group in these E2 reactions.

In order to shed further light on the nature of the substituent effects, the rates were plotted against the Hammett σ values and found to have good correlations. The results are summarized in Table 4 which shows that ρ values of the sulphur compounds are higher than those of the oxygen analogues both in *t*-BuOK–*t*-BuOH and in EtONa–EtOH systems.

TABLE 4. THE SUBSTITUENT EFFECT OF THE E2 REACTION OF THE TITLE COMPOUNDS IN *t*-BuOK–*t*-BuOH AND EtONa–EtOH

Compounds	Temp	Base-solvent	ρ^a	γ^b
X–  –SCH ₂ CH ₂ Cl	40	<i>t</i> -BuOK– <i>t</i> -BuOH	2.20	0.999
	50	<i>t</i> -BuOK– <i>t</i> -BuOH	2.06	0.998
	60	<i>t</i> -BuOK– <i>t</i> -BuOH	1.98	0.992
	60	EtONa–EtOH	2.14	0.992
X–  –OCH ₂ CH ₂ Cl	60	<i>t</i> -BuOK– <i>t</i> -BuOH	1.33	0.987
	60	EtONa–EtOH	1.50	0.997
	60	EtONa–EtOH	2.58	—
 –CH ₂ CH ₂ Cl				

X: CH₃O–, CH₃–, H–, Cl–, NO₂–.

^a These values were calculated by the method of least squares.




^b Coefficient of correlation.

^c C. H. Depuy and C. A. Bishop, *J. Am. Chem. Soc.* **82**, 2535 (1960).

Studies on the substituent effect in the ionization constants of phenylpropionic, phenoxy and phenylmercapto acetic acids⁷ reveal that an inductive effect is apparently weakened to a greater extent by a divalent S atom than an O atom. In the case of these E2 reactions, the rates are not controlled by the inductive effect alone. Since the E2 reactions of the sulphur compounds are presumed to be carbanionic in the transition state, an electron-accepting group must decrease the density on the S atom which in turn is expected to display the 3d-orbital resonance effect more effectively to stabilize the developing negative charge at the β -carbon thus enhancing the reactivity. The effect of substituents, therefore, would be transmitted more effectively to the reaction

site than merely through the chain. In the case of oxygen compounds, no resonance effect can be transmitted through the O atom and hence the effects of the substituents are diminished considerably, thus giving a relatively smaller ρ value compared to that for the sulphur compound. The comparison of the substituents on the β -carbon is listed in Table 5.

TABLE 5. THE RELATIVE RATES OF A SERIES OF $Y-CH_2CH_2Cl$ IN t -BuOK- t -BuOH AT 60°

Y	Rel. rate ^a
 -CH ₂ -	0.013
 -	1
EtS-	4.9
iso-PrS-	4.5
sec-BuS-	3.8
 S-	12

^a From Table 1.

The rate-retarding effect of an alkyl group attached to the S atom must be due to the electron-releasing inductive effect of an alkyl group. It is interesting that a phenylmercapto or even an alkylmercapto group at the β -carbon enhances the rate of the E2 reaction 5 or 10 times more than a β -phenyl group, although the ρ value of a series of p -substituted- β -phenylethyl derivatives is larger than that of sulphur compounds (Table 4). This may mean that these mercapto groups are more effective in stabilizing the developing negative charge than a phenyl group in these reactions. In fact, it is reported that the α -hydrogen atom of thioanisole is more acidic than that of toluene.⁸

The effects of solvents and bases. As shown in Tables 1 and 2, the rates are about 20 times faster in t -BuOK- t -BuOH than in EtONa-EtOH. As E2 reactivity is accelerated by strong bases, the larger ρ value in EtONa-EtOH may be similarly explained as in the case of p -substituted- β -phenylethyl halides.⁷

EXPERIMENTAL

Purification of solvents and preparation of basic solutions. t -BuOH was purified by distillation over Na under a stream of N_2 . Distillation was carried out repeatedly as in the Cram's experiment⁹ and the fraction of b.p. $82-83^\circ$ was collected and used. EtOH was purified by the same procedure and a fraction of b.p. 78.5° was collected. All the kinetic runs were carried out with the same batch of solvents. The basic solns were prepared as follows. Dry oxygen-free N_2 was bubbled through the solvent for more than 2 hr, and the desired amount of carefully cleaned metal in a dry N_2 box was added quickly. N_2 was bubbled through the soln until the metal dissolved completely.

Product analysis. In general, rate measurements of E2 reaction are complicated by competing SN_2 reactions. Hence, all the compounds were subjected to careful product analyses. The reaction mixture of an organic chloride and a base was poured into ice-water and extracted with diethyl ether as usual. The condensed ether soln was directly checked by gas chromatography. The analysis of the product from the reaction confirmed that only the peaks corresponding to an olefin (elimination product) and an ether (substitution product) were present and no other product was detected by gas chromatography.

Olefin determination. Generally, the quantitative determination of olefin was carried out by either the

iodometric or spectrometric method. However, in the case of olefins containing S atoms such as alkyl or arylvinyl sulfides, the above methods were not adequate, since sulphide groups also react with I_2 or Br_2 , while the UV spectra of the starting and final compounds differ very little. Therefore, the amount of olefin was determined by gas chromatography in the following manner. The final sample of a kinetic run was poured into ice-water and extracted with diethyl ether. The ether extract was subjected to gas chromatography, using a column packed with fire bricks covered with high vacuum silicon grease, and from the peak heights of the olefin (elimination product) and the ether (substitution product), E2 ratios were determined by comparing them with a calibration chart made by examination with authentic samples. In the case of oxygen compounds such as arylvinyl ethers, the amount of olefin was determined in the following manner: after titration of the remaining base in one of the kinetic runs, the soln was poured into 20 ml of water, and extracted twice with 5 ml CCl_4 and again with 10 ml CCl_4 . The combined CCl_4 solns were thoroughly washed twice with 20 ml of water to remove the remaining alcohol and then dried over $CaCl_2$. After removal of the $CaCl_2$, a known amount of Br_2-CCl_4 soln of a known concentration was added to the filtrate, which was then allowed to stand overnight in the dark. The excess Br_2 was titrated with a standard $Na_2S_2O_3$. The apparent value was corrected by a factor obtained in advance from an authentic sample under similar reaction conditions. The value obtained experimentally was within 3% of the calculated value. Ethyl vinyl ether was determined by the iodometric method.¹⁰

Kinetic measurement. A desired amount of an organic chloride was weighed accurately in a 100 ml volumetric flask. After equilibration at the reaction temp, it was made up to 100 ml with the desired amount of base soln and with the solvent at a fixed temp. The flask was shaken vigorously and kept in a thermostat. The initial concentration of the base was taken after one min. From time to time 5 ml of the soln was pipetted out and quenched into 10 ml anhyd EtOH which was kept at 0°, and the excess base was titrated with a standard HCl soln using phenolphthalein as an indicator. Anhyd EtOH containing dry HCl was used instead of an HCl aq, since alkylmercapto ethyl chlorides readily undergo hydrolysis when water is present. After 10 or more half-lives, the final sample was taken to measure the infinity value which accords well with a value calculated for the sulphur compounds. For other compounds, calculated values were taken as initial concentrations. The rate constant was calculated by the usual second-order equation and the rate constant for the elimination reaction was calculated by multiplying it with the olefin ratio.

Preparation of the starting materials

Ethylchloro acetal was prepared from vinyl acetate, abs EtOH and dry Cl_2 gas, yield: 80%, b.p. 62–63°/25 mm (lit.¹¹ 53–54°/16 mm). (Found: C, 46.87; H, 8.58. Calc. for $C_6H_{13}O_2Cl$: C, 47.21; H, 8.58%).

β,β' -Diphenoxyethyl chloride. Ethyl diphenoxycetate obtained from the reaction of dichloroethyl acetate with sodium phenoxide was reduced with LAH. The alcohol obtained was chlorinated with thionyl chloride and checked by NMR and also identified with one from another synthetic route in which β,β' -diphenoxyethyl tosylate was reacted with LiCl in DMF, yield: 69%, b.p. 153–155°/3 mm.

β,β' -Diphenylmercaptoethyltosylate. The corresponding alcohol was prepared by the method described above. Tosylation was performed in the presence of dry pyridine at 0°. The reaction mixture was poured into ice-water, and the colourless crystals formed collected quickly. They were purified by recrystallization four times from n-hexane-diethyl ether, yield: 25%, m.p. 64°. (Found: C, 60.44; H, 4.89. Calc. for $C_{21}H_{20}O_3S$: C, 60.54; H, 4.84%).

β -Phenethyl chloride and phenylpropyl chloride. The corresponding alcohols were prepared according to the method used by Kirner¹² and were chlorinated with thionyl chloride. The b.ps were 93–94°/23 mm (lit.¹² 68.5–69°/4 mm) and 84–85°/7 mm (lit.¹² 85–87°/9 mm), respectively. The purity was checked by gas chromatography. All other compounds were synthesized by the method described in the lit.^{13,14} and were purified by fractional distillation or recrystallization. The results are summarized in Table 6.

Preparation of elimination products and substitution products

Elimination products were isolated in the following manner. A mixture of the chloride (0.025 mole) and t-BuOK (0.05 mole) in t-BuOH (30 ml) was refluxed for 1 hr. The soln was then poured into 200 ml ice-water and extracted twice with 50 ml diethyl ether. The ether layer was washed twice with 100 ml water and dried over $CaCl_2$. The product was obtained by distillation as shown in Table 7.

Substitution products from the reaction with t-BuOK were prepared from t-BuOCH₂CH₂Cl and the corresponding mercaptans. Meanwhile substitution products when EtONa was used as a base were prepared from EtOCH₂CH₂Br and mercaptans. The yields and b.ps are listed in Table 8.

The detailed experimental method is described in the literature.²⁵

TABLE 6. THE PROPERTIES OF Y-CH₂CH₂Cl

Y	Yield (%)	B.p., m.p. (°/mm) (lit.)	Analysis; C%	Found (Calc.) H%
CH ₃ OPhS—	87	117/2	53.71 (53.33)	5.65 (5.57)
CH ₃ PhS—	85	127.5–128/7	57.51 (57.89)	5.65 (5.94)
PhS—	80	80/1 (115–117/9) ¹⁵	55.89 (55.69)	5.48 (5.22)
ClPhS—	83	33 ^a	46.46 (46.39)	4.09 (3.89)
NO ₂ PhS—	83	60–61 ^a (62) ¹³	—	—
CH ₃ OPhO—	83	48.5 ^b	57.89 (57.91)	6.05 (5.94)
CH ₃ PhO—	80	44–45 ^b (43.5) ¹⁶	63.53 (63.35)	6.73 (6.50)
PhO—	85	82–83/3 (122–123/26) ¹⁷	61.40 (61.38)	5.85 (5.75)
ClPhO—	88	40 ^b	50.74 (50.29)	4.47 (4.22)
NO ₂ PhO—	85	56 ^b	48.03 (47.66)	4.07 (4.00)
EtO—	55	105–106 (108–109) ¹⁸	43.07 (44.24)	8.39 (8.29)
EtS— ^c	80	72/35 (69–73/37) ¹⁹	38.68 (38.56)	7.52 (7.22)
iso-PrS—	85	64/18	—	—
sec-BuS—	85	84/23 (98–100/40) ²⁰	—	—

^a Recrystallized from n-hexane–acetone.^b Recrystallized from n-hexane or n-hexane–diethyl ether.^c These compounds were directly distilled after chlorination.

TABLE 7. ELIMINATION PRODUCTS

Compounds	Yield (%)	B.p., m.p.° (lit.) (°/mm)	Analysis; C%	Found (calc.) H%
EtSCH=CH ₂	50	92 (91.5–92) ²⁰	54.87 (54.52)	9.58 (9.15)
PhSCH=CH ₂	64	83/14 (84.5–85/15) ¹⁵	70.72 (70.62)	6.06 (5.88)
CH ₃ PhSCH=CH ₂	68	105/15 (102–104/16) ²¹	72.05 (71.95)	6.84 (6.71)
ClPhSCH=CH ₂	72	121/20	56.26 (56.30)	4.22 (4.13)
CH ₃ OPhSCH=CH ₂	81	130–132/18	65.00 (65.02)	6.16 (6.06)
PhOCH=CH ₂	39	158–160 (155–155.5) ²²	79.64 (80.01)	7.07 (6.66)
CH ₃ PhOCH=CH ₂	44	74/17 (75/18) ²³	80.56 (80.56)	7.56 (7.51)
ClPhOCH=CH ₂	48	48/20 (90/20) ²¹	62.13 (62.15)	4.63 (4.56)

TABLE 7 (contd.)

Compounds	Yield (%)	B.p., m.p. ° (lit.) (°/mm)	Analysis; C%	Found (calc.) H%
CH ₃ OPhOCH=CH ₂	62	103/20	71.88 (71.97)	6.64 (6.71)
NO ₂ PhOCH=CH ₂ ^a	49	61.5° (54–56) ²⁴	58.54 (58.18)	4.61 (4.27)

^a Recrystallized from n-hexane–diethyl ether.

TABLE 8. SUBSTITUTION PRODUCTS

Compounds	Yield (%)	B.p. (°/mm)	Analysis; Found (calc.) C%	H%
EtSCH ₂ CH ₂ O–t-Bu	78	92–93/33	58.93 (59.28)	11.16 (11.11)
PhSCH ₂ CH ₂ O–t-Bu	60	146/12	—	—
CH ₃ PhSCH ₂ CH ₂ O–t-Bu	58	126/2	69.58 (69.59)	8.97 (8.98)
CH ₃ OPhSCH ₂ CH ₂ O–t-Bu	52	160/3	—	—
ClPhSCH ₂ CH ₂ O–t-Bu	50	132–133/1	—	—
PhSCH ₂ CH ₂ OEt	95	115–117/8	—	—
CH ₃ PhSCH ₂ CH ₂ OEt	90	118/2	—	—
CH ₃ OPhSCH ₂ CH ₂ OEt	93	142/2	—	—

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