from 200 ml. of methanol to give 55 g. (43% yield) of methyl 4-methylbenzilate, m.p. 100–102°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.42; H, 6.27.

Methyl Phenyl-2-thienylglycolate.—The Grignard of 2-bromothiophene in the above procedure gave the ester in 33% yield, m.p. 57–58° (lit.,[7] m.p. 62–63°).

Methyl α-Cyclohexyl-α-phenylglycolate.—The Grignard reagent from cyclohexyl bromide treated according to the general procedure gave the ester in 31% yield, b.p. 170–175° (9 mm.).

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 73.24; H, 8.45. Found: C, 72.90; H, 8.73.

Methyl 4-Chlorobenzilate.—The Grignard reagent derived from 4-chlorobromobenzene treated according to the general procedure gave the ester in 49% yield, m.p. 94–95°.

Anal. Calcd. for $C_{15}H_{13}ClO_3$: C, 65.10; H, 4.73. Found: C, 64.91; H, 4.73.

Preparation of the Substituted 3-Pyrrolidinol Glycolates (Table I). General Procedure.—A mixture of 0.07 mole of the 3-pyrrolidinol, 0.07 mole of the methyl glycolate, a trace of sodium methoxide, and 200 ml. of *n*-heptane was heated under reflux for 3 hr. using a Dean-Stark water separator to remove methanol as it was formed. The mixture was cooled and then was extracted with a 120-ml. and a 60-ml. portion of 1 *N* hydrochloric acid. The acid solution was washed with two 100-ml. volumes of benzene, and then it was made basic with potassium carbonate. The basic solution was extracted with two 50-ml. portions of benzene, the benzene solution was washed twice with 25-ml. volumes of water. The benzene solution was then dried with anhydrous potassium carbonate and concentrated by heating on a steam bath under reduced pressure. The residue dissolved in 50 ml. of ethyl acetate was treated with 50 ml. of hydrogen chloride-saturated ethanol. The crystalline hydrochloride that formed was collected and was recrystallized from ethanol–ethyl acetate or ethanol–ethyl acetate–isopropyl ether mixture.

Quaternary Salts.—When the quaternary salts were desired, the crude ester after solvent removal was dissolved in 50 ml. of methyl ethyl ketone and was treated with excess methyl bromide. The crystalline solid that formed was collected and recrystallized from the same solvent mixtures as the hydrochlorides.

Acknowledgment.—The microanalyses were determined by W. L. Brown, H. L. Hunter, G. M. Maciak, A. C. Brown, D. L. Cline, and R. L. Simon. The preliminary pharmacological test results were supplied by T. M. Lin, E. C. Powell, and associates.

Potential Anticancer Agents. LXXV.[1] Analogs of Chlorambucil. X.[1] Sulfur-Containing Analogs

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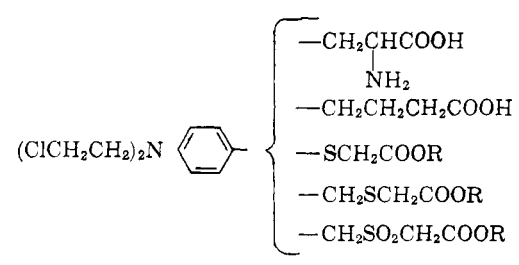
Conventional procedures for preparing aromatic nitrogen mustards have been successfully applied to the synthesis of *p*-mustards of (phenylthio)acetic acid and its methyl ester. Preparation of the benzyl homolog was prevented by the instability of derivatives of (benzylthio)acetic acid as intermediates. The *p*-mustard of methyl (benzylsulfonyl)acetate could be prepared under the same conditions, but resisted hydrolysis to the free acid.

Nitrogen mustards of cinnamic acid[3] and of phenoxyalkanoic acids[4] are active anticancer agents when tested on transplanted mouse tumors. Their animal tumor spectra resemble the spectrum of *p*-phenylalanine mustard (I), among clinically useful mustards, more than that of the structurally related chlorambucil (II). These facts suggested the synthesis of other alkylating agents related to chlorambucil, in which further significant changes in the character and oxidation level of the acidic side chain are made. Examples of such compounds which might show interesting biological activity and which might provide more insight into the relationship between structure and anticancer activity are the sulfur-containing acids III, V, and VII. This report describes a study of their preparation; success was encountered only in preparing III and the esters, IV and VIII.



I
II
III. R = H; IV. R = CH_3
V. R = H; VI. R = CH_3
VII. R = H; VIII. R = CH_3

The (phenylthio)acetic acid mustard III and the

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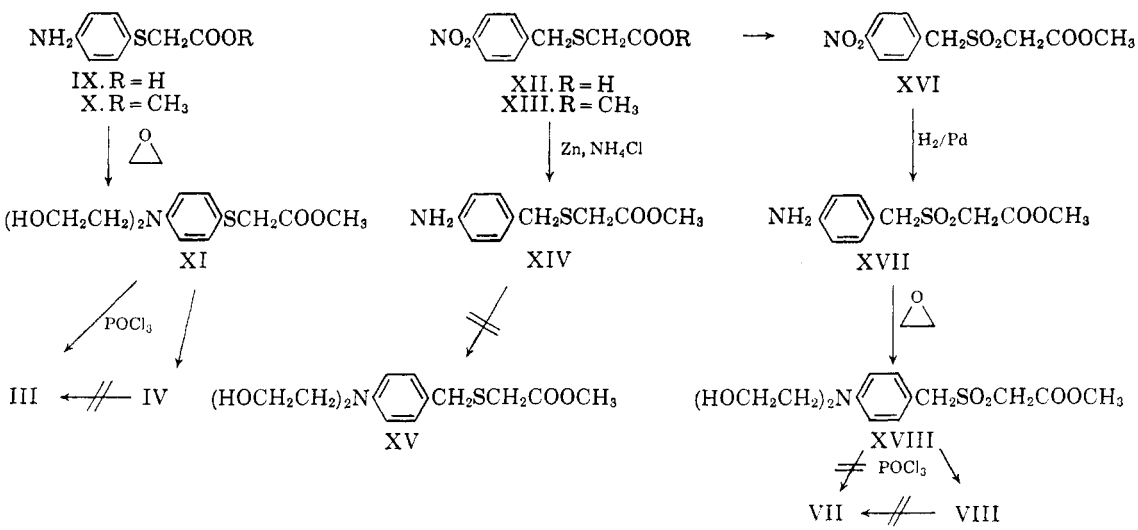
(2) (a) To whom inquiries should be sent; (b) School of Pharmacy, University of Buffalo, Buffalo 14, New York.

(3) W. A. Skinner, M. G. M. Schelstraete, and B. R. Baker, *J. Org. Chem.*, **26**, 1674 (1961).

(4) (a) W. A. Skinner, A. P. Martinez, and B. R. Baker, *ibid.*, **26**, 152 (1961); (b) W. Davis, J. J. Roberts, and W. C. J. Ross, *J. Chem. Soc.*, 890 (1955).

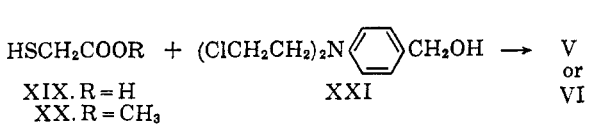
ester IV were obtained from (*p*-aminophenylthio)-acetic acid (IX)[5] by the hydroxyethylation and chlorination sequence (Scheme I) generally used for aromatic nitrogen mustards. The success of this sequence depended on use of the highly purified amine X to give the bis(2-hydroxyethyl)amine XI and of recrystallized XI in the subsequent conversion to the mustards III and IV. Chlorination of XI with phosphoryl chloride afforded the mustard ester IV after hydrolysis of the reaction mixture; the mustard acid III was obtained, free of ester, if the hydrolysis was prolonged for 60 to 70 hours. Although these products were stable when isolated and could be stored without decomposition, attempts to convert IV to III by deliberate acid hydrolysis resulted in C—S cleavage.

SCHEME I



The same sequence was used for the mustard of (benzylsulfonyl)acetic ester (VIII), starting with methyl (*p*-nitrobenzylthio)acetate (XIII) and its oxidation to the sulfone XVI; however, hydrolysis to the free acid VII could not be effected.

Lability of the benzyl-sulfur bond[6] prevented completion of the final steps in the synthesis of the benzylthio mustards, V and VI. An alternative preparation of the mustard, either the acid V or the ester VI, was investigated by alkylation of mercaptoacetic acid (XIX) or methyl mercaptoacetate (XX) with benzyl alcohol mustard (XXI)[7] in



acidic medium. Infrared spectra and elemental analyses suggested that the desired products, though impure, were formed in appreciable yields, but materials of adequate purity could not be isolated from these reactions.

Experimental[8]

Methyl (*p*-Aminophenylthio)acetate (X), and the Hydrochloride Salt.—Ten grams (0.547 mole) of (*p*-aminophenylthio)acetic acid[5] (IX) in 110 ml. of methanolic acetyl chloride was refluxed for 1 hr. The crude, solid hydrochloride salt (15.6 g.), obtained on concentration of the reaction mixture *in vacuo* at 35°, was recrystallized from 150 ml. of anhydrous methanol (first crop, 3.30 g., m.p. 162–172°), with the addition of 300 ml. of ether to the filtrate giving a second crop, 7.53 g., m.p. 165–175° (total yield 85%). The free base was regenerated by treating the salt with 300 ml. of saturated aqueous sodium bicarbonate and was extracted with 200 ml. of ether; the ether layer was washed with water, dried with magnesium sulfate, filtered, and concentrated to 8.97 g. (83%) of amino ester isolated as a brown sirup, with R_f[8] 0.88 in solvent system A and 0.24 in solvent system B.

Anal. Calcd. for $C_9H_{11}NO_2S$: C, 54.8; H, 5.62; N, 7.10; S, 16.3. Found: C, 55.8, 56.0; H, 5.73, 5.86; N, 7.23, 7.21; S, 16.1, 16.4.

Treatment of the amine in ether solution with dry hydrogen chloride and recrystallization of the precipitate from methanol afforded an analytical sample of the hydrochloride, m.p. 168–177° (63% yield).

Anal. Calcd. for $C_9H_{12}ClNO_2S$: C, 46.2; H, 5.18; Cl, 15.2; N, 6.00; S, 13.7. Found: C, 45.9; H, 5.16; Cl, 15.4; N, 6.15; S, 13.8.

Methyl {*p*-[Bis(2-hydroxyethyl)amino]phenylthio}acetate (XI).—Methyl *p*-(aminophenylthio)acetate (X) hydrochloride was treated with ethylene oxide in 50% aqueous acetic acid using a previously described procedure.[4a] The residual sirup (47%) was treated in methanol solution with Norit and the solution concentrated again. The resulting sirup crystal-

(5) Evans Chemetics, Inc., New York.

(6) D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 15, 25, 27, 31, 34 (1951).

(7) R. H. Iwamoto, E. M. Acton, B. R. Baker, and L. Goodman, *Chem. Ind.* (London), 1404 (1961).

(8) Melting points (obtained with the Fisher-Johns apparatus) and boiling points are uncorrected. The compounds described were homogeneous to paper chromatography by the descending technique. Spots were detected by visual examination under ultraviolet light. Solvent systems referred to are A, water-saturated 1-butanol on Whatman No. 1 paper; and B, benzene–methanol–water (2:6:1), on Schleicher and Schuell No. 2043B acetylated paper unless otherwise indicated.

lized on standing for 1 month at room temperature, m.p. 93–95.5°; recrystallization from absolute methanol afforded a 35% yield of the analytical sample, m.p. 94–95°, R_f[8] 0.82 in solvent system A and 0.51 in system B.

Anal. Calcd. for $C_{18}H_{19}NO_4S$: C, 54.7; H, 6.71; N, 4.91; S, 11.2. Found: C, 54.7; H, 6.70; N, 5.07; S, 11.2.

A bis-*p*-nitrobenzoate, m.p. 108–109°, was prepared from the sirup and recrystallized from aqueous acetone.

Anal. Calcd. for $C_{27}H_{25}N_3O_{10}S$: C, 55.6; H, 4.32; N, 7.21. Found: C, 55.6; H, 4.13; N, 7.22.

Methyl {*p*-[Bis(2-chloroethyl)amino]phenylthio}acetate (IV).—A solution of 7.5 g. (0.026 mole) of methyl {*p*-[bis-(2-hydroxyethyl)amino]phenylthio}acetate (XI) (m.p. 94–95°) in 30 ml. of phosphoryl chloride was heated on a steam bath for 1.5 hr., then added in portions, with vigorous stirring, to 300 g. of ice and water. It was important that each portion be completely hydrolyzed before the next was added, so that a layer of phosphoryl chloride did not accumulate on the bottom of the beaker. The aqueous solution was stirred at room temperature for 1 hr. and then extracted with 250 ml. of dichloromethane. The organic layer was washed with saturated aqueous sodium bicarbonate (200 ml.) and with water (100 ml.), dried with magnesium sulfate, filtered, and concentrated *in vacuo* to a yellow sirup (8.2 g., 97% yield). The sirup was partly purified by stirring first in a benzene solution (70 ml.) with 22 g. of neutral alumina (Brockmann activity I) and then in a warm ether solution with Norit; after each operation the sirup was recovered by filtration (the alumina was washed well with benzene) and concentration of the filtrate. The final yield was 5.82 g. (68.5%), R_f[8] 0.91 in solvent system A and 0.06 in solvent system B.

Anal. Calcd. for $C_{13}H_{17}Cl_2NO_2S$: C, 48.4; H, 5.32; Cl, 22.0; N, 4.35; S, 9.95. Found: C, 48.8; H, 6.16; Cl, 21.4; N, 4.44; S, 9.83.

An analytical sample was obtained by evaporative distillation (0.2 mm., bath temperature 140–170°) of the purified sirup; paper chromatographic and infrared spectral data were identical to those of the alumina-treated sample above.

Anal. Found: C, 48.5; H, 5.34; Cl, 21.9; N, 4.46; S, 10.0.

{*p*-[Bis(2-chloroethyl)amino]phenylthio}acetic Acid (III).—The solid bishydroxy compound (XI) (7.7 g., 0.027 mole) was chlorinated by the above procedure. The aqueous hydrolysate was stirred at room temperature for 68 hr., heated for 1 hr. on the steam bath, and extracted at room temperature with 700 ml. of dichloromethane. The organic layer was washed with water (500 ml.), dried with magnesium sulfate, filtered, and concentrated *in vacuo* to a pale yellow sirup (7.0 g., 85% yield) which crystallized rapidly on seeding or slowly on standing. The solid, under a layer of petroleum ether (b.p. 30–60°), was ground to a white, insoluble powder, then recovered by filtration and dried to afford 6.4 g. (77%) of product, m.p. 59.5–60.0°, R_f[8] 0.52 in solvent system A and 0.16 in solvent system B.

Anal. Calcd. for $C_{12}H_{15}Cl_2NO_2S$: C, 46.8; H, 4.91; Cl, 23.0; N, 4.55; S, 10.4. Found: C, 46.7; H, 4.90; Cl, 22.8; N, 4.36; S, 10.7.

Methyl (*p*-Nitrobenzylthio)acetate (XIII).—Six grams (0.0264 mole) of (*p*-nitrobenzylthio)acetic acid (XII),[9] m.p. 103–104° (lit., 114°), in 66 ml. of 10% methanolic acetyl chloride was refluxed for 1 hr., and the solution concentrated *in vacuo*. The residual sirup in benzene solution (70 ml.) was washed with 30 ml. each of saturated aqueous sodium bicarbonate and water. After removal of benzene at 30–40° *in vacuo*, the sirup (6.15 g., 96% yield) upon standing for several days slowly formed a solid. Recrystallization from methanol afforded 5.20 g. (81%) of product, m.p. 47–48°, R_f[8] 0.88 in solvent system A and 0.72 in solvent system B, both on Whatman No. 1 paper.

Anal. Calcd. for $C_{10}H_{11}NO_4S$: C, 49.8; H, 4.59; N, 5.80; S, 13.3. Found: C, 50.0; H, 4.58; N, 5.84; S, 13.2.

Methyl (*p*-Aminobenzylthio)acetate (XIV) and the *p*-Toluenesulfonic Acid Salt.—A solution of 10.0 g. (0.0415 mole) of XIII in 208 ml. of methanol at 50° was treated with ammonium chloride (3.84 g., 0.0720 mole) and water (20.8 ml.), swirled, and the clear solution treated slowly at room temperature with 13.3 g. (0.204 g.-atom) of zinc powder. The mixture was refluxed for 7 hr., then filtered while hot through a pad of Celite. The filter cake was washed with boiling methanol and the combined filtrates were concentrated *in vacuo*. The crude product (13.6 g.) was partitioned between 500 ml. of dichloromethane and saturated aqueous sodium bicarbonate. The organic layer was separated, washed with two 200-ml. portions of water, dried with magnesium sulfate, filtered, and concentrated *in vacuo* at 40° to an orange sirup (7.38 g., 84% yield). Partial purification to a pale yellow sirup (63% recovery, 53% yield) was effected by short-path distillation (of as much as 15 g.) at 0.01 mm. (bath temp. 135–140°). An analytically pure sample was obtained from this distillate by evaporative distillation (bath temp. 90°) at 0.01 mm. Both distilled samples were homogeneous to paper chromatography, R_f[8] 0.81 in solvent system A and 0.20 in system B (both on Whatman No. 1 paper), and were identical in infrared spectra, which differed only slightly (in relative intensities of C=O and aryl bands) from that of the initial orange sirup.

Anal. Calcd. for $C_{10}H_{13}NO_2S$: C, 56.8; H, 6.20; N, 6.63; S, 15.2. Found: C, 56.7; H, 6.05; N, 6.56; S, 15.3.

A crystalline *p*-toluenesulfonic acid salt, m.p. 130–139°, was obtained in nearly quantitative yield from the undistilled sirup in anhydrous ether solution by slow precipitation with an excess of the acid, but could not be recrystallized without decomposition. Analytically pure salt, m.p. 132–137°, was obtained by a second treatment of regenerated amine.

Anal. Calcd. for $C_{17}H_{21}NO_6S_2$: C, 53.2; H, 5.52; N, 3.66; S, 16.7. Found: C, 53.2; H, 5.87; N, 3.65; S, 16.6.

Methyl (*p*-Nitrobenzylsulfonyl)acetate (XVI).—A solution of 8.96 g. (0.0370 mole) of undistilled methyl (*p*-nitrobenzylthio)acetate (XIII) in glacial acetic acid (160 ml.) was treated with 40 ml. of 30% hydrogen peroxide solution and stirred at room temperature for 48 hr. The product (7.32 g., m.p. 133.5–134.5°) precipitated on chilling and stirring at 0° for 5 hr. A second crop (1.65 g., m.p. 133–134°) was obtained from the filtrate on dilution with water to 500 ml. (total yield, 88%). The analytical sample, m.p. 134.5–135.5°, was recrystallized from acetonitrile, R_f[8] 0.77 in solvent A.

Anal. Calcd. for $C_{10}H_{11}NO_6S$: C, 43.9; H, 4.06; N, 5.12; S, 11.7. Found: C, 44.2; H, 4.09; N, 5.16; S, 11.8.

Methyl (*p*-Aminobenzylsulfonyl)acetate (XVII).—A solution of 20.0 g. (0.0732 mole) of XVI in 350 ml. of 2-methoxyethane was hydrogenated under an initial pressure of 45 p.s.i.g. with 6.0 g. of 5% palladium-on-charcoal for 1 hr. The catalyst was removed by filtration through a Celite pad and the filtrate, combined with the 2-methoxyethane washings of the catalyst, was concentrated *in vacuo* at 50°. The residual sirup (nearly quantitative yield) formed a solid, m.p. 95–97°, on standing at room temperature for 3 days. The analytical sample, m.p. 98.5–99.5°, R_f[8] 0.54 in solvent system A and 0.25 in solvent system B, was obtained by recrystallization of a small quantity from benzene; larger (up to 100 g.) quantities were more easily recrystallized (25% recovery) from boiling methanol.

Anal. Calcd. for $C_{10}H_{13}NO_4S$: C, 49.4; H, 5.38; N, 5.75; S, 13.2. Found: C, 49.4; H, 5.48; N, 5.94; S, 13.3.

A hydrochloride salt was formed from the sirupy amine in methanol solution by treatment with hydrogen chloride, followed by addition of ether. The precipitate was purified for analysis by reprecipitation with ether from 1 *M* methan-

(9) A. Schönberg and Y. Iskander, *J. Chem. Soc.*, 90 (1942).

olic hydrogen chloride. The substance decomposed slowly when heated on the Fisher-Johns apparatus.

Anal. Calcd. for $C_{19}H_{14}ClNO_4S$: C, 42.9; H, 5.04; Cl, 12.7; S, 11.5. Found: C, 43.4; H, 4.93; Cl, 12.7; S, 11.6.

Methyl {*p*-[Bis(2-hydroxyethyl)amino]benzylsulfonyl}-acetate (XVIII).—A solution of 9.15 g. (0.0376 mole) of the recrystallized amine (XVII) in 70 ml. of methanol containing 0.65 g. (0.0030 mole) of *p*-toluenesulfonic acid was treated at 5° with 60 ml. of liquefied ethylene oxide. The mixture was stirred in a stoppered flask at room temperature for 7 days, treated again at 0° with 10 ml. of ethylene oxide in 15 ml. of methanol, and stirred as before for 2 more days, then was concentrated *in vacuo* to a residual sirup. A solution of the sirup in 200 ml. of dichloromethane was washed with saturated aqueous sodium bicarbonate (150 ml.) and water (150 ml.), dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residual solid (11.2 g., 91% yield) was recrystallized from a chloroform–benzene mixture to give a 37% yield of product, m.p. 106–109°. Further recrystallization afforded an analytically pure sample, m.p. 108–109°, R_f identical to that of XVII in solvent system A and 0.39 in solvent system B.[8]

Anal. Calcd. for $C_{14}H_{21}NO_6S$: C, 50.7; H, 6.39; S, 9.68. Found: C, 50.8; H, 6.37; S, 9.87.

Methyl {*p*-[Bis(2-chloroethyl)amino]benzylsulfonyl}acetate (VIII).—Recrystallized XVIII (10.0 g., 0.0300 mole) was heated with 50 ml. of phosphoryl chloride on a steam bath for 25 min. The dark solution was poured (with precautions described for IV) into 750 ml. of stirred ice and water. When hydrolysis was complete, the gummy product that separated was dissolved by addition of dichloromethane (200 ml.). Stirring was continued for 15 hr. while the mixture warmed to room temperature. The organic layer was separated and the aqueous layer was washed with dichloromethane (250 ml.); the combined dichloromethane solutions were washed with water (300 ml.) and saturated aqueous sodium bicarbonate, dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The solid residue was stirred and ground under a layer of ether and then collected on a filter, yielding 8.80 g. (79%) of product, m.p. 97–98°. Recrystallization from aqueous acetone afforded 6.80 g. (61%) of the analytical sample, m.p. 101.5–102°, R_f[8] 0.77 in solvent system A and 0.06 in solvent system B.

Anal. Calcd. for $C_{14}H_{19}Cl_2NO_4S$: C, 45.6; H, 5.20; Cl, 19.2; O, 17.4; S, 8.70. Found: C, 45.6; H, 5.52; Cl, 19.0; O, 17.5; S, 8.66.

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The *ortho*-Claisen Rearrangement. VI. The Rates of Rearrangement of Allyl *m*-*X*-Phenyl Ethers to 2-Allyl-5-*X*-phenols[1]

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Received April 3, 1961

The rates of rearrangement of seven allyl *m*-*X*-phenyl ethers to the corresponding 2-allyl-5-*X*-phenols are correlated most satisfactorily using σ_p^+ (*not* σ_m^+) constants and a ρ value of -0.66 in Hammett's equation. This unusual result can be explained best on the basis of simultaneous homolysis of the allyl-oxygen bond and homogenesis of the *ortho* carbon-allyl bond in a transition state involving a highly electronegative oxygen atom.

The electrical nature of the transition state of the Claisen rearrangement has been the subject of several recent investigations. To obtain information on this problem, the rates of rearrangement of a series of allyl *p*-*X*-phenyl ethers[4,5] and a series of *X*-cinnamyl *p*-tolyl ethers[6] have been determined.

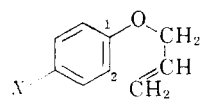
It was found[4,5] that a good correlation of substituent effects on the rate of reaction of allyl *p*-*X*-phenyl ethers was obtained when σ_p^+ constants[7] and a negative value of ρ were used in the ordinary form of Hammett's equation,[8,9]

$$\log \frac{k}{k_0} = \rho^+\sigma_p^+$$

However, a further satisfactory correlation of the data[4] was obtained by application of the two-parameter equation,[9]

$$\log \frac{k}{k_0} = \rho_1\sigma_p + \rho_2\sigma_m$$

in which ρ_1 and ρ_2 define the effect of the substituent on the reaction occurring at the 1- and 2-positions of the ring.



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(2) Monsanto Fellow, 1959–1960; Ethyl Corp. Fellow, 1958–59.

(3) From the thesis submitted by Carl D. Slater in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at the Ohio State University.

(4) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

(5) H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3278 (1958).

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(9) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).