800°, 17% CF_3Cl, 52% CF_2Cl_2, 31% $CFCl_3$, and unreacted CCl_4. The results of two quantitative runs at 600 and 800° are included in Table I.

Fluorination of $CCl_3CCl{=}CCl_2$.—The reactions were run in the same way as described above for the CCl_4. The $CCl_3CCl{=}CCl_2$-containing vessel was kept by an oil bath between 130 and 140° and the inlet to the reactor was heated by an infrared lamp in order to avoid condenstion of the starting material. Two reactions were run at 420 and 520°. The conversions and yields are given in Table I.

Fluorination of $CHCl_3$.—The reactions were run in the same way as described above for the CCl_4. The $CHCl_3$ container was kept at room temperature. Table I shows the results of four reactions between 450 and 670°.

Fluorination of $COCl_2$.—A 1:1 mixture of $COCl_2$ and SiF_4 was passed through an electrically heated quartz tube, filled with Hengar quartz granules. The reactions were run at different temperatures and the reaction products were condensed in two cold traps at −78 and −196°. The condensed products were transferred to the vacuum line and analyzed by gas chromatography, fractionation, and infrared spectroscopy. Three qualitative reactions at 500, 650, and 850° and five quantitative reactions between 360 and 700° were run. The results of the quantitative reactions are given in Table I.

Fluorination of CO_2.—Two reactions between CO_2 and SiF_4 were run in the same way as described above for $COCl_2$. Infrared analysis and gas chromatographic investigation of the reaction products showed that no reaction had occurred between the starting materials.

Fluorination of $CCl_2{=}CCl_2$.—The reactions were run in the same way as described for CCl_4. The $CCl_2{=}CCl_2$ container was kept at 80°. Four reactions were run with Hengar quartz granules as filling material. The results of these four reactions are given in Table I. In addition, three reactions between 500 and 800° were run using 15% of gaseous HCl as a catalyst. No improvement of the results could be obtained. In the same way, the addition of 10% BF_3 to the starting materials did not increase the amount of fluorinated products, as could be shown by three reactions between 500 and 800°. In another attempt the filling material of the reaction tube was replaced by an aluminum trifluoride catalyst on asbestos as carrier and three reactions were run between 550 and 850°, but also in this case no improvement of the results could be obtained.

Fluorination of $CHCl_2CCl_3$.—The reactions were run in the same way as described for CCl_4. The vapor pressure of $CHCl_2CCl_3$ was kept at 200 mm. Three reactions were carried out and showed the following results: at 400°, 7-sec. contact time—1.6% $CHCl{=}CCl_2$, 30.8% $CCl_2{=}CCl_2$, and 67.6% starting material; at 500°, 6-sec. contact time—3.6% $CHCl{=}CCl_2$, 91.2% $CCl_2{=}CCl_2$, 3.9% starting material, and 1.3% CCl_4; at 650°, 3-sec. contact time—0.3% $CHCl{=}CCl_2$, 84.7% $CCl_2{=}CCl_2$, 14.5% starting material, and 0.5% CCl_4. No fluorinated products were observed.

Fluorination of Aromatic Chlorine Compounds.—Three reactions between chlorobenzene and SiF_4 were run in the same way as described for CCl_4. At 480 and 600° no reaction occurred; at 700° the starting material started to decompose. Four reactions between hexachlorobenzene and SiF_4 were run. The hexachlorobenzene was placed in a quartz boat at the entrance of the tubular reactor and sublimed through the hot reaction tube. The reactions were run at 500, 650, 750, and 800°, but no fluorinated aromatic compounds could be obtained, as could be shown by n.m.r., infrared spectroscopy, and gas chromatography.

The Meerwein Arylation of Vinyl Sulfones[1]

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Received May 19, 1964

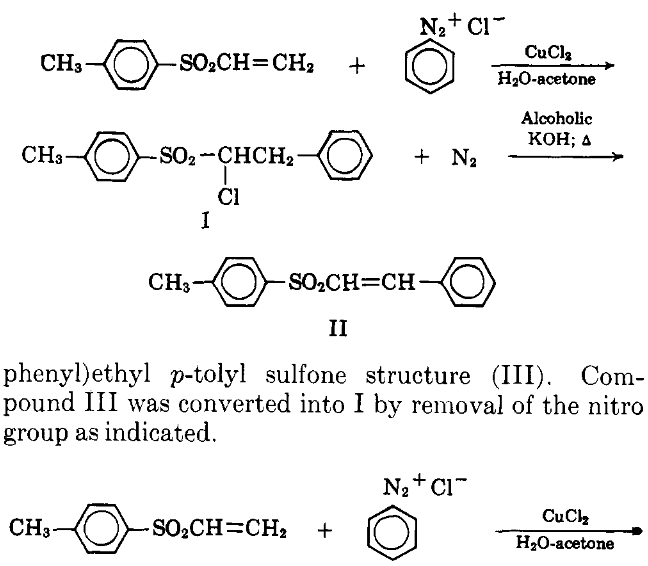
Meerwein arylation of vinyl sulfones with aromatic diazonium salts was shown to yield α-halo-β-aryl sulfones. Despite low yields, the reaction provides a convenient route to these comparatively inaccessible compounds.

The Meerwein arylation of vinyl sulfones was investigated as a synthetic approach to α-chloro-β-aryl sulfones [$RSO_2CH(Cl)CH_2Ar$], since methods for preparing such compounds are limited. The Meerwein reaction[2] normally gives a product in which the incoming halo substituent occupies a position α, and the incoming aryl group occupies a position β, to the activating, electron-withdrawing substituent.

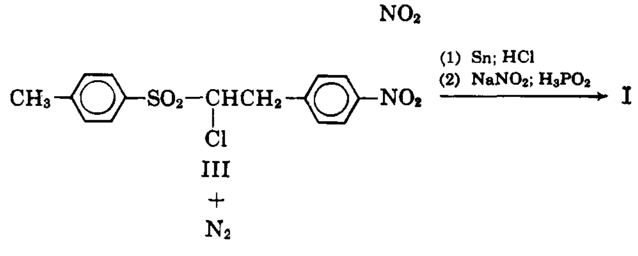
$$Z{-}CH{=}CH_2 + ArN_2^+X^- \longrightarrow Z{-}CH(X)CH_2Ar + N_2$$

Although a wide variety of olefins has been subjected to the Meerwein reaction, at the beginning of our investigation there were no reports in the literature of Meerwein arylations of vinyl sulfones.

Arylation of *p*-tolyl vinyl sulfone with benzenediazonium chloride produced an adduct in 15–20% yield. The 1-chloro-2-phenylethyl *p*-tolyl sulfone structure (I) was assigned to this product on the basis of its dehydrohalogenation product, ω-styryl *p*-tolyl sulfone. This dehydrohalogenation was smoothly effected by refluxing I in alcoholic potassium hydroxide.



Arylation of *p*-tolyl vinyl sulfone with *p*-nitrobenzenediazonium chloride produced an adduct in 20–30% yield, which was assigned the 1-chloro-2-(*p*-nitrophenyl)ethyl *p*-tolyl sulfone structure (III). Compound III was converted into I by removal of the nitro group as indicated.



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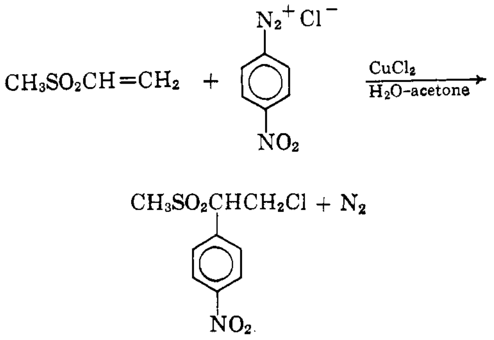
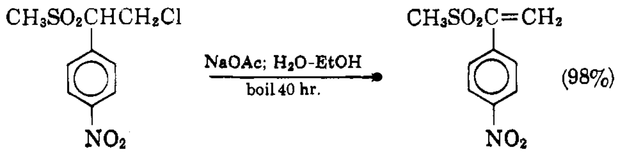
[1] Abstracted from the Ph. D. Thesis of J. E. Tracy Purdue University, 1965.

[2] C. S. Rondestvedt, Jr., *Org. Reactions*, **11**, 189 (1960).

At this point in our work, we were given occasion to question our structural assignments. In a short communication,[3] Siegel and Petersen reported that Meerwein arylation of methyl vinyl sulfone produced β-chloro-α-aryl products.

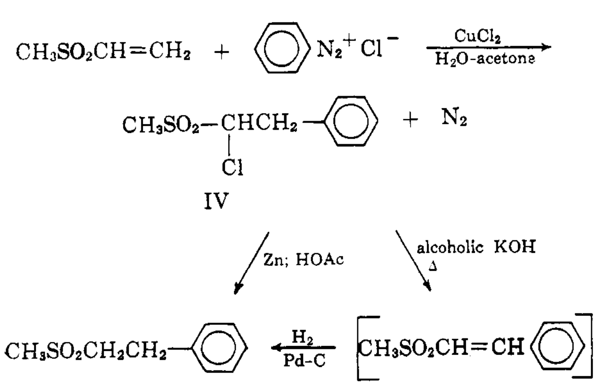


They noted that this adduct was dehydrohalogenated to an olefin by refluxing with sodium acetate. These

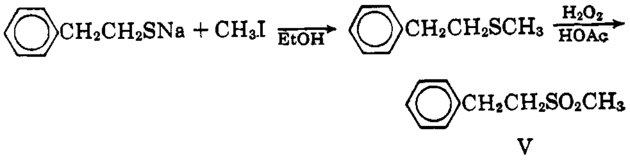


authors state that "the great mobility of the chlorine atom in these reaction products, and also their n.m.r. spectra, indicate a β-chloroethyl sulfone structure."

We found that arylation of methyl vinyl sulfone with benzenediazonium chloride produced 1-chloro-2-phenylethyl methyl sulfone (IV). This structural assignment,

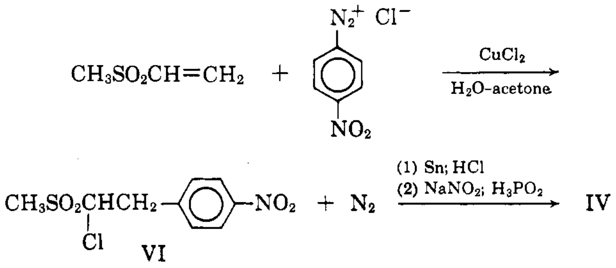


rather than the isomeric 2-chloro-1-phenylethyl methyl sulfone, is favored by the following evidence. Removal of the chlorine atom by treatment with zinc in acetic acid produced 2-phenylethyl methyl sulfone (V), identical with a sample prepared by an independent route.

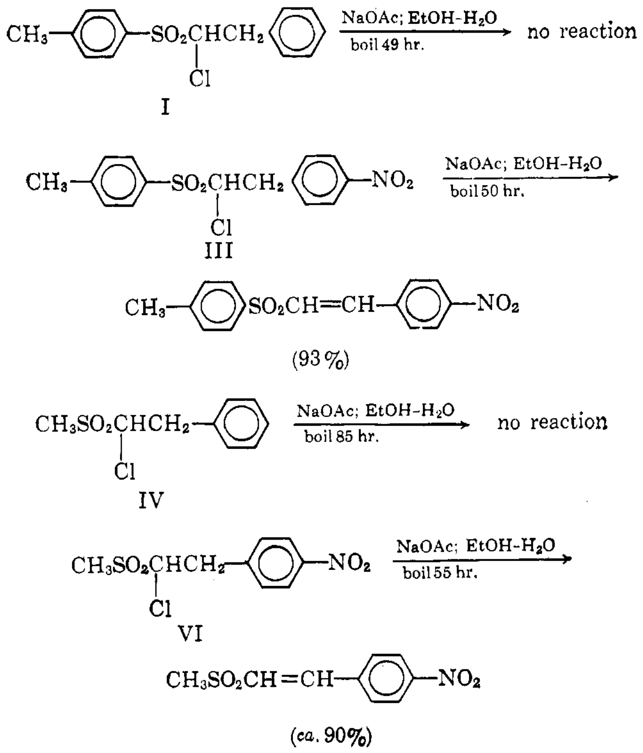


The isomeric 1-phenylethyl methyl sulfone, which would be expected to result from dehalogenation of 2-chloro-1-phenylethyl methyl sulfone, was also independently synthesized in the same manner starting with 1-phenylethyl mercaptan, and was shown to be distinctly different from the compound obtained by dehalogenation of the Meerwein product. Furthermore, dehydrohalogenation of IV by alcoholic potassium hydroxide produced an olefin, which was converted into 2-phenylethyl methyl sulfone (V) by catalytic hydrogenation.

Arylation of methyl vinyl sulfone with p-nitrobenzenediazonium chloride under the conditions used by Siegel and Petersen produced a product having the same melting point as the one to which they assigned a 2-chloro-1-(p-nitrophenyl)ethyl methyl sulfone structure. However, we assigned the 1-chloro-2-(p-nitrophenyl)ethyl methyl sulfone structure (VI) to this product, since it can be converted into IV by removal of the nitro group as indicated.



A study of the dehydrohalogenation of these adducts showed that "the high mobility of the chlorine atom" noted by Siegel and Petersen is due to the presence of the nitro group, and does not necessarily require a β-chloroethyl sulfone structure.



The n.m.r. spectrum of I (Fig. 1) fits the assigned 1-chloro-2-phenylethyl p-tolyl sulfone structure. The n.m.r. spectra of I and IV (Fig. 2) are very similar, the only differences being in the aromatic region and the position of the methyl group, which occurs at δ 2.5 in I and is shifted to 3.05 in IV owing to the effect of the sulfone group. This close similarity in n.m.r.

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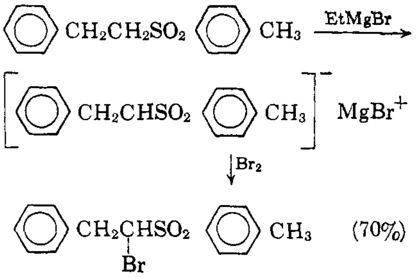
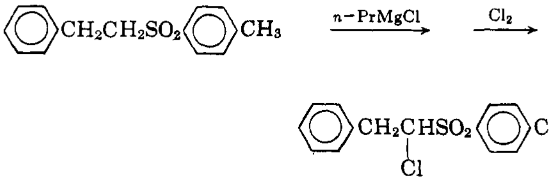
[3] E. Siegel and S. Petersen, *Angew. Chem.*, **74**, 873 (1962), *Angew. Chem. Intern. Ed. Engl.*, **1**, 593 (1962).

spectra shows that the same mode of addition occurs in both cases. The n.m.r. spectrum of III is very similar to that of I. Due to the insolubility of VI in deuteriochloroform, we were unable to obtain a satisfactory n.m.r. spectrum of this adduct. However, conversion of this product into IV by removal of the nitro group shows that it must surely have the same α-chloro-β-aryl structure as IV.

Finally, an independent synthesis of structure I was performed. α-Bromo sulfones have been prepared by bromination of the salts of Grignard reagents and sulfones.[4,5] When this procedure was carried out on 2-phenylethyl *p*-tolyl sulfone, 1-bromo-2-phenylethyl *p*-tolyl sulfone was produced in good yield. The n.m.r. spectrum of this compound was identical with the n.m.r. spectrum of I.



Chlorination of the 2-phenylethyl *p*-tolyl sulfone anion generated by the above procedure produced several products, one of which was 1-chloro-2-phenylethyl *p*-tolyl sulfone. This compound was obtained from the reaction mixture by column chromatography and was found to be identical in all respects with I.

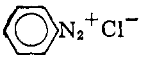
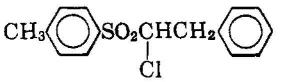
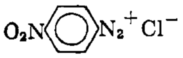
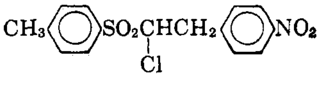
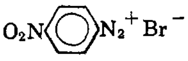
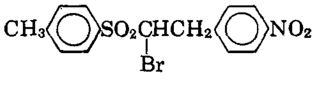


I

In summary, our investigations have shown that Meerwein arylations can be carried out on vinyl sulfones and give α-halo-β-aryl adducts. The results of several arylations of *p*-tolyl vinyl sulfone and methyl vinyl sulfone are summarized in Tables I and II. Although the yields are low and there is some difficulty in purification, such Meerwein additions can represent the most convenient route to certain α-halo-β-aryl sulfones.

Table I

Meerwein Arylations of *p*-Tolyl Vinyl Sulfone

Diazonium salt	Product	Yield, %
		20
		26
 (CuBr catalyst)		24

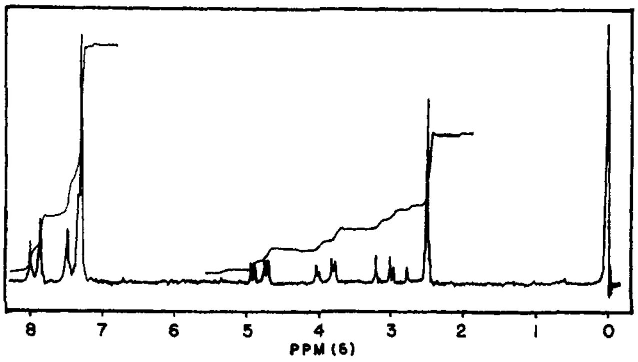


Fig. 1.—N.m.r. spectrum of 1-chloro-2-phenylethyl *p*-tolyl sulfone (I).

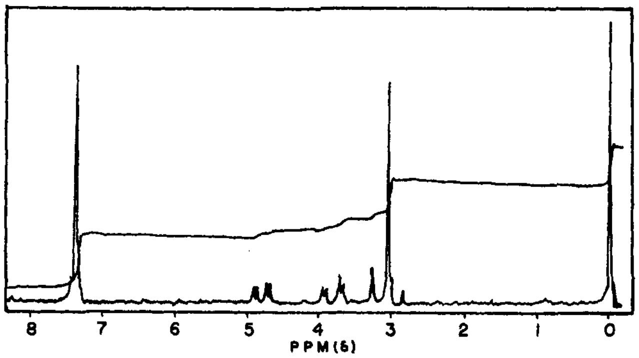
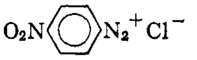
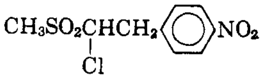
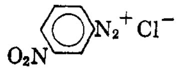
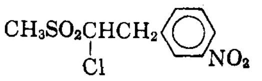
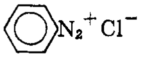
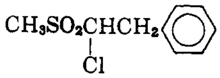


Fig. 2.—N.m.r. spectrum of 1-chloro-2-phenylethyl methyl sulfone (IV).

Table II

Meerwein Arylations of Methyl Vinyl Sulfone

Diazonium salt	Product	Yield, %
		21
		19
		6

Experimental[6]

***p*-Tolyl Vinyl Sulfide.**—*p*-Toluenethiol (124 g., 1.0 mole) was added to a solution of sodium (24 g., 1.04 g.-atoms) in absolute ethanol (1 l.) under nitrogen. 2-Chloroethanol (81.0 g., 1.0 mole) was added dropwise to the thiolate solution. The mixture was refluxed for 5 hr., cooled below room temperature, and concentrated hydrochloric acid (600 ml.) was added. The resulting solution was stirred at room temperature for 8 hr. After refluxing for another 6 hr., the reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with 10% sodium hydroxide and with water. After drying over anhydrous sodium sulfate, the ether solution was evaporated under reduced pressure, leaving an oil.

The above procedure was repeated, and the yields of crude 2-chloroethyl *p*-tolyl sulfide were combined and added dropwise under nitrogen to a stirred solution of 85% potassium hydroxide (132 g., 2 moles) in ethanol (1 l.). After refluxing and stirring

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[4] E. P. Kohler and H. Potter *J. Am. Chem. Soc.*, **57**, 1316 (1935).

[5] W. M. Ziegler and R. Connor *ibid.*, **62**, 2596 (1940).

[6] All melting points and boiling points are uncorrected. Microanalyses were performed by Dr. C. S. Yeh, M. Hudgens, T. Kalman, and T. Eikeri. N.m.r spectra were recorded on a Varian A-60 high resolution spectrometer by Mr. William Baitinger and staff.

for 16 hr., the reaction mixture was filtered to remove precipitated potassium chloride. The filtrate was evaporated under reduced pressure. The liquid residue, which contained more precipitated solid, was dissolved in ether and washed with 10% hydrochloric acid and water. After drying over anhydrous sodium sulfate, the ether was evaporated under reduced pressure. Distillation of the liquid residue under diminished pressure gave *p*-tolyl vinyl sulfide (139.2 g., 46%), b.p. 55–58° (0.3 mm.), lit.[7] b.p. 78° (4.0 mm.)

_p_-Tolyl Vinyl Sulfone.—*p*-Tolyl vinyl sulfide (100 g., 0.66 mole) was dissolved in glacial acetic acid (670 ml.), cooled in an ice bath, and 30% hydrogen peroxide (200 ml.) was added dropwise to the cold, stirred solution. After stirring at room temperature for 8 hr., the mixture was heated on a steam bath for another 5 hr., and poured into ice. The precipitated *p*-tolyl vinyl sulfone was recrystallized from aqueous ethanol, yield 84.4 g. (74%), m.p. 64–66°, lit.[8] m.p. 65–66°.

Methyl Vinyl Sulfone.—This compound was prepared from 2-chloroethyl methyl sulfide according to known procedures.[9] 2-Chloroethyl methyl sulfide (99.2 g., 0.9 mole) gave methyl vinyl sulfone (61.5 g.) in a 64% yield. The product had a boiling point of 85–87° (2.4 mm.)

1-Chloro-2-phenylethyl _p_-Tolyl Sulfone (I).—A solution of benzenediazonium chloride was prepared at −20 to 0° from freshly distilled aniline (2.8 g., 0.03 mole), 1:1 hydrochloric acid (25 ml.), and 30% sodium nitrite solution (2.2 g., 0.03 mole). The pH was adjusted to 3–5 by addition of solid sodium acetate. This diazonium solution was added to a solution of *p*-tolyl vinyl sulfone (5.46 g., 0.03 mole) in acetone (100 ml.) at 0°. Cupric chloride dihydrate (0.51 g.) was added. The reaction mixture was stirred at room temperature for 3 hr., during which time the evolution of nitrogen was observed. After the mixture was poured into water and extracted with ether, the ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the ether solution under reduced pressure left an oil, which was chromatographed on an alumina column, eluting with benzene–pentane (1:1) and collecting 200-ml. fractions. Fractions 1 through 4 contained crude 1-chloro-2-phenylethyl *p*-tolyl sulfone (2.7 g.). After recrystallizing from ethanol, the melting point was 79–82°.

Anal. Calcd. for $C_{15}H_{15}ClO_2S$: C, 61.12; H, 5.09; Cl, 12.05; S, 10.87. Found: C, 61.36; H, 5.07; Cl, 11.83; S, 11.00.

Fractions 5 through 7 contained *p*-tolyl vinyl sulfone (1.7 g.). Further elution with benzene–pentane and finally with ether produced only unidentified colored oils in small amounts.

The yields of purified 1-chloro-2-phenylethyl *p*-tolyl sulfone on this and several subsequent runs were 16–20%. The addition of sodium acetate was unnecessary; the yield of purified adduct was 16% when the reaction was carried out without sodium acetate. Several attempts were made to isolate the product from the crude reaction mixture without chromatographing; all were unsuccessful.

1-Chloro-2-(_p_-nitrophenyl)ethyl _p_-Tolyl Sulfone (III).—The diazo solution prepared from *p*-nitroaniline (4.15 g., 0.03 mole), 1:1 hydrochloric acid (25 ml.), and 30% sodium nitrite solution (2.2 g., 0.03 mole) was added to a solution of *p*-tolyl vinyl sulfone (5.5 g., 0.03 mole) in acetone (50 ml.) at 0°. Cupric chloride dihydrate (1.8 g.) was added and the mixture was stirred at room temperature for 6 hr. The reaction mixture was diluted with water and solid material was filtered. Recrystallization of this solid from ethanol produced 1-chloro-2-(*p*-nitrophenyl)ethyl *p*-tolyl sulfone (2.7 g., 26%), m.p. 154–155°.

Anal. Calcd. for $C_{15}H_{14}ClNO_4S$: C, 53.02; H, 4.15; Cl, 10.43; N, 4.12; S, 9.44; mol. wt., 339.8. Found: C, 53.06; H, 3.98; Cl, 10.34; N, 4.38; S, 9.73; mol. wt., 345.2.

Subsequent runs carried out in the same manner gave yields of 23–26%. Simply filtering the reaction mixture and washing the collected solid with ether produces a pure product (m.p. 154–155°) though in lower yield (18%). One run was carried out in dimethyl sulfoxide instead of acetone. The yield was 22%.

1-Bromo-2-(_p_-nitrophenyl)ethyl _p_-Tolyl Sulfone.—*p*-Nitroaniline (4.15 g., 0.03 mole) was stirred with 48% hydrobromic acid (10 ml.) as acetone (50 ml.) was added. After the amine hydrobromide had dissolved, the solution was cooled to 0° and diazotized beneath the surface with 30% sodium nitrite solution (2.2 g., 0.03 mole). The temperature was kept below 10° during diazotization. *p*-Tolyl vinyl sulfone (5.8 g., 0.03 mole) was added and after the solution was swept with nitrogen for 15 min., cuprous bromide (128 mg.) was added. The temperature rose to 28°, accompanied by vigorous evolution of nitrogen. The temperature was maintained at 25–30° by stirring and cooling for 2 hr., during which time a yellow precipitate formed. This precipitate was filtered and recrystallized from ethanol, yield 2.8 g. (24%), m.p. 147–148°.

1-Chloro-2-(_p_-nitrophenyl)ethyl Methyl Sulfone (VI).—The diazo solution from *p*-nitroaniline (13.8 g., 0.1 mole), water (60 ml.), concentrated hydrochloric acid (26.4 g.), and sodium nitrite (6.9 g.) was added to methyl vinyl sulfone (12.7 g., 0.12 mole) in acetone (90 ml.) at 0°. A solution of cupric chloride dihydrate (5.5 g.) in water (10 ml.) was added. Evolution of nitrogen began at 28°. The temperature was maintained at 28–30° and the mixture was stirred for 2 hr. Evaporation of the acetone under reduced pressure produced a brown liquid, which was extracted with ether. Evaporation of the ether under reduced pressure left a solid. Recrystallization from methanol gave a product with a melting point of 117–120°. Recrystallization from methylene chloride (cooled in a Dry Ice–trichloroethylene bath) gave 3.1 g. of 1-chloro-2-(*p*-nitrophenyl)ethyl methyl sulfone, m.p. 122–123.5°.

Anal. Calcd. for $C_9H_{10}ClNO_4S$: C, 40.98; H, 3.80; Cl, 13.47; N, 5.31; S, 12.14. Found: C, 40.86; H, 4.10; Cl, 13.20; N, 5.43; S, 12.40.

Evaporation of the filtrates and recrystallization of the residue from ethyl acetate–hexane gave an additional 2.6 g. of product, total yield 5.7 g. (21%).

1-Chloro-2-(_m_-nitrophenyl)ethyl Methyl Sulfone.—This compound was prepared as above, using *m*-nitroaniline. Recrystallization of the crude product from methylene chloride gave 1-chloro-2-(*m*-nitrophenyl)ethyl methyl sulfone (4.9 g., 19%), m.p. 121–125°.

Anal. Calcd. for $C_9H_{10}ClNO_4S$: C, 40.98; H, 3.80; Cl, 13.47; N, 5.31; S, 12.14. Found: C, 40.94; H, 3.85; Cl, 13.19; N, 5.47; S, 12.44.

1-Chloro-2-phenylethyl Methyl Sulfone (IV).—The diazo solution from aniline (21.0 g., 0.226 mole), concentrated hydrochloric acid (59.6 g.), water (150 ml.), and sodium nitrite (15.6 g.) was added to methyl vinyl sulfone (24.0 g., 0.226 mole) in acetone (200 ml.) at 0°. Cupric chloride dihydrate (15 g.) was added. After stirring at room temperature for 8 hr., the acetone was partially evaporated, and the reaction mixture was extracted with ether. The brown ether extracts were decolorized with charcoal, and the resulting yellow solution was dried over anhydrous magnesium sulfate. Evaporation of the ether left a yellow oil, which was distilled under reduced pressure. The fraction boiling at 138–139° (0.2 mm.) solidified upon standing. Recrystallization from methanol gave 1-chloro-2-phenylethyl methyl sulfone, m.p. 69–70.5°, yield, 3 g. (6%).

Anal. Calcd. for $C_9H_{11}ClO_2S$: C, 49.40; H, 5.03; Cl, 16.20; S, 14.65; mol. wt., 218.5. Found: C, 49.18; H, 5.11; Cl, 16.48; S, 14.60; mol. wt., 223.7.

Conversion of 1-Chloro-2-(_p_-nitrophenyl)ethyl _p_-Tolyl Sulfone (III) into 1-Chloro-2-phenylethyl _p_-Tolyl Sulfone (I).—To a solution of 1-chloro-2-(*p*-nitrophenyl)ethyl *p*-tolyl sulfone (1.7 g.) in ethanol (20 ml.) was added tin (*ca.* 5 g.) and concentrated hydrochloric acid (*ca.* 20 ml.). The mixture was heated at 60° for 3 hr. The resulting water-white solution was decanted from undissolved tin and evaporated to 30 ml. The solution was made alkaline by addition of concentrated sodium hydroxide solution, and was extracted with ether. The ether solution was filtered through a fine sintered-glass funnel to remove suspended tin salts. During this slow filtration, the ether evaporated from the filtrate, leaving 1.3 g. of crude amine. Recrystallization from ethanol gave 1-chloro-2-(*p*-aminophenyl)ethyl *p*-tolyl sulfone (1.05 g., 68%), m.p. 159–161°. This amine (0.95 g.) was dissolved in 50% hypophosphorous acid (15 ml.) and cooled to −10°. After diazotization with excess 30% sodium nitrite solution, the cooling bath was removed, and the temperature rose to 55°, accompanied by vigorous evolution of nitrogen. A yellow gum formed, and solidified when cooled. After vacuum drying, the melting point was 78–81°. The infrared (see Fig. 3) and n.m.r. spectra of this product were identical with those of 1-chloro-2-phenylethyl *p*-tolyl sulfone. A mixture melting point of this product and 1-chloro-2-phenylethyl *p*-tolyl sulfone showed no depression.

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(7) W. E. Truce, H. E. Hill, and M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2760 (1956).

(8) L. I. Smith and H. R. Davis, *J. Org. Chem.*, **15**, 824 (1950).

(9) G. D. Buckley, *et al.*, *J. Chem. Soc.*, 1514 (1947).

Conversion of 1-Chloro-2-(*p*-nitrophenyl)ethyl Methyl Sulfone (VI) into 1-Chloro-2-phenylethyl Methyl Sulfone (IV).—This conversion was carried out in the same manner as the previous one. The amine was obtained as a white gum. Treatment with sodium nitrite and hypophosphorus acid produced a yellow solid. Recrystallization from methanol–water gave a white solid with a melting point of 72–74°. The infrared (see Fig. 4) and n.m.r. spectra of this compound were identical with those of 1-chloro-2-phenylethyl methyl sulfone, and its melting point was not depressed upon admixture with 1-chloro-2-phenylethyl methyl sulfone.

Anal. Calcd. for $C_9H_{11}ClO_2S$: C, 49.40; H, 5.03; Cl, 16.20; S, 14.65; mol. wt., 218.5. Found: C, 49.40; H, 4.99; Cl, 16.62; S, 14.46; mol. wt., 218.00.

Conversion of 1-Chloro-2-phenylethyl Methyl Sulfone (IV) into 2-Phenylethyl Methyl Sulfone (V).—1-Chloro-2-phenylethyl methyl sulfone (0.98 g., 0.0045 moles) was mixed with zinc dust (1.62 g.) and glacial acetic acid (25 ml.) was added. The mixture was stirred and refluxed for 24 hr., then poured onto ice. The organic material was extracted with ether. Evaporation of the ether extracts left a small amount of acetic acid, from which a solid was obtained by diluting with water. Recrystallization from methanol–water, from hexane, and again from methanol gave 2-phenylethyl methyl sulfone, yield 0.3 g. (37%), m.p 87–89°, lit.[10] m.p. 88.5–89.5°. The infrared and n.m.r. spectra of this compound were identical with those of an independently synthesized sample of 2-phenylethyl methyl sulfone. The n.m.r. spectrum of this compound was distinctly different from that of 1-phenylethyl methyl sulfone.

Preparation of 2-Phenylethyl Methyl Sulfone.—2-Phenylethyl mercaptan (30.4 g., 0.22 mole) was added dropwise under nitrogen to a solution of sodium (5.7 g., 0.238 g.-atom) in absolute ethanol (300 ml.). Methyl iodide (31.3 g., 0.22 mole) was added dropwise and the mixture was refluxed for 3 hr. Most of the ethanol (*ca.* 250 ml.) was removed by distillation. The remaining reaction mixture was diluted with water and extracted with ether. After drying over anhydrous magnesium sulfate, the ether was evaporated under reduced pressure. The oil remaining was distilled under reduced pressure, giving 25.25 g. of 2-phenylethyl methyl sulfide (75%), b.p. 70–72° (0.8 mm.), lit.[10] b.p. 98–100° (6.0 mm.)

The sulfone was prepared by dissolving 2-phenylethyl methyl sulfide (10.6 g., 0.07 mole) in glacial acetic acid (100 ml.), cooling to 0°, and adding 30% hydrogen peroxide (25 ml.). After allowing the stirred mixture to come to room temperature, it was heated on a steam bath for 6 hr., then poured onto ice. The crude sulfone was filtered and recrystallized from ethanol, giving 8.6 g. of 2-phenylethyl methyl sulfone (67%), m.p. 88.5–90°, lit.[10] m.p. 88.5–89.5°.

Preparation of 1-Phenylethyl Methyl Sulfone.—This compound was prepared from 1-phenylethyl mercaptan according to the procedure described for 2-phenylethyl methyl sulfone. 1-Phenylethyl mercaptan (30.4 g., 0.22 mole) gave 1-phenylethyl methyl sulfide (33.44 g., 68%), b.p. 48–50° (0.1 mm.)

1-Phenylethyl methyl sulfide (10.0 g., 0.066 mole) gave 1-phenylethyl methyl sulfone (6.15 g., 50%), m.p. 89–91°. The n.m.r. spectrum of 1-phenylethyl methyl sulfone was different from that of 2-phenylethyl methyl sulfone.

Dehydrohalogenation of 1-Chloro-2-phenylethyl Methyl Sulfone (IV) and Hydrogenation of the Resulting Olefin.—1-Chloro-2-phenylethyl methyl sulfone (2.5 g., 0.0114 mole) was refluxed in a solution of alcoholic potassium hydroxide (1.2 g.) for 0.5 hr. Precipitated potassium chloride was filtered. Dilution of the filtrate with water caused the separation of a yellow oil. This oil was extracted with ether. After drying the ether layer over anhydrous magnesium sulfate, the ether was evaporated in a stream of air, leaving a solid. This solid, after recrystallization from hexane, had an infrared spectrum and melting point (66–71°) corresponding to a *cis–trans* mixture of ω-styryl methyl sulfone, lit.[10] m.p. (*cis*-) 64.5–66°, (*trans*-) 79–80°. A separation of the *cis–trans* mixture was attempted by chromatographing on an alumina column. Elution with hexane (800 ml.) produced nothing; elution with methylene chloride (200 ml.) produced 0.65 g. of *cis–trans* mixture containing a larger portion of *trans* isomer (m.p. 72–75°).

This material was dissolved in absolute ethanol (50 ml.), 5% palladium–carbon (1 g.) was added, and the mixture was hydrogenated in a Paar apparatus at 30 p.s.i. for 6 hr. The catalyst was removed by filtration, and the filtrate was evaporated under reduced pressure. Recrystallization of the residue from ethanol produced a small amount (*ca.* 0.1 g.) of 2-phenylethyl methyl sulfone, m.p. 85–87°. The infrared and n.m.r. spectra of this material were identical with those of 2-phenylethyl methyl sulfone. Evaporation of the ethanol filtrate produced starting olefin.

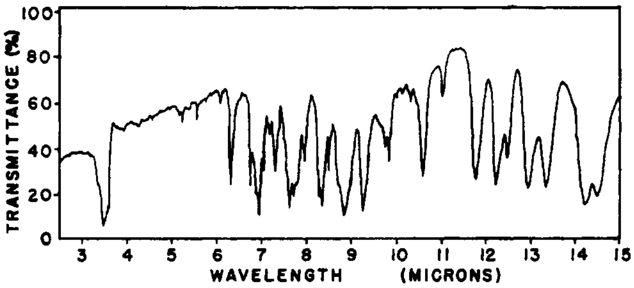

Fig. 3.—Infrared spectrum of 1-chloro-2-phenylethyl *p*-tolyl sulfone (I) (Nujol mull).

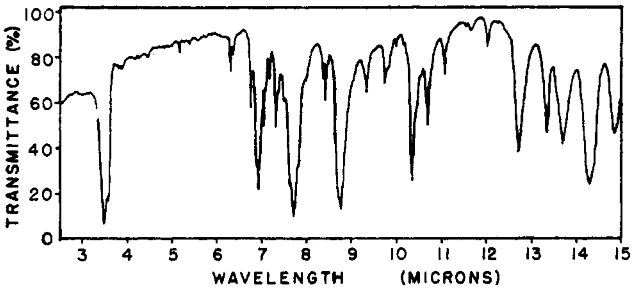

Fig. 4.—Infrared spectrum of 1-chloro-2-phenylethyl methyl sulfone (IV) (Nujol mull).

Dehydrohalogenation of 1-Chloro-2-phenylethyl *p*-Tolyl Sulfone (I.)—1-Chloro-2-phenylethyl *p*-tolyl sulfone (1.6 g., 0.005 mole) was refluxed for 2 hr. with potassium hydroxide (0.6 g.) in ethanol (*ca.* 20 ml.). Precipitated potassium chloride was removed by filtration. The filtrate was evaporated in a stream of air until a solid formed. This solid was filtered and vacuum dried, giving 0.24 g. of *trans*-ω-styryl *p*-tolyl sulfone, m.p. 116–122°, lit.[10] m.p. 121–122°. The infrared and n.m.r. spectra of this compound were identical with those of an authentic sample[11] of *trans*-ω-styryl *p*-tolyl sulfone.

Evaporation of the filtrate·to dryness and recrystallization of the residue from ethanol produced an additional 0.2 g. of ω-styryl *p*-tolyl sulfone (mixture of *cis* and *trans*). Evaporation of the ethanol filtrate to dryness gave a mixture of olefin and starting material (0.9 g.).

Dehydrohalogenation of 1-Chloro-2-(*p*-nitrophenyl)ethyl *p*-Tolyl Sulfone (III).—To a solution of sodium acetate (3.0 g.) in water (10 ml.) was added a solution of 1-chloro-2-(*p*-nitrophenyl)-ethyl *p*-tolyl sulfone (1.25 g., 0.0037 mole) in absolute ethanol (100 ml.). The mixture was refluxed for 52.5 hr., then evaporated to dryness under reduced pressure. The solids were washed well with acetone–ether, and the undissolved salts were filtered. Evaporation of the filtrate left a yellow solid. Recrystallization from methanol produced *p*-nitro-ω-styryl *p*-tolyl sulfone (1.05 g., 93%), m.p. 181–183°, lit.[12] m.p. 182–183°.

Attempted Dehydrohalogenation of 1-Chloro-2-phenylethyl *p*-Tolyl Sulfone (I) and 1-Chloro-2-phenylethyl Methyl Sulfone (IV) with Sodium Acetate.—1-Chloro-2-phenylethyl *p*-tolyl sulfone was treated with sodium acetate as described above for 49 hr. No reaction occurred; all of the starting material was recovered.

1-Chloro-2-phenylethyl methyl sulfone was refluxed with sodium acetate as described for 84.5 hr. The starting compound (95%) was the only organic material recovered on work-up of the reaction mixture.

Dehydrohalogenation of 1-Chloro-2-(*p*-nitrophenyl)ethyl Methyl Sulfone (VI).—1-Chloro-2-(*p*-nitrophenyl)ethyl methyl sulfone was refluxed with sodium acetate as described previously for 48 hr. The olefin crystallized from the reaction mixture as it

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[10] W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956).

[11] This compound was prepared by J. A. Simms at this laboratory.

[12] V. Baliah and Sp. Shanmuganathan, *J. Indian Chem. Soc.*, **35**, 31 (1958).

was formed. After cooling to room temperature, the solid was removed by filtration and recrystallized from ethyl acetate, giving *p*-nitro-ω-styryl methyl sulfone (*ca.* 90%), m.p. 192.5–193.5°.

Anal. Calcd. for $C_9H_9NO_4S$: C, 47.58; H, 3.96; N, 6.17; S, 14.10. Found: C, 47.42; H, 4.00; N, 6.35; S, 14.00.

Preparation of 1-Bromo-2-phenylethyl *p*-Tolyl Sulfone.—Ethylmagnesium bromide was prepared under nitrogen from magnesium (5.0 g., 0.208 g.-atom), ethyl bromide (21.8 g., 0.2 mole), and anhydrous ether (40 ml.). To this solution was added 2-phenylethyl *p*-tolyl sulfone (45.0 g., 0.173 mole) in dry benzene (150 ml.). After the evolution of ethane had ceased, an additional 100 ml. of dry benzene was added. The stirred mixture was refluxed for 3 min., then cooled in an ice bath. Bromine (24 g., 0.15 mole) in 50 ml. of dry benzene was added. The ice bath was removed, and the mixture was stirred at room temperature for 2 hr., then poured into water (*ca.* 300 ml.) Excess bromine was removed by addition of a solution of sodium bisulfite. Magnesium particles were removed by filtration. The benzene layer was separated and evaporated to dryness. Recrystallization of the solid residue from ethanol produced 36 g. of 1-bromo-2-phenylethyl *p*-tolyl sulfone (70%), m.p. 121–122°. The n.m.r. spectrum of this compound was identical with that of 1-chloro-2-phenylethyl *p*-tolyl sulfone (I) obtained by the Meerwein procedure.

Anal. Calcd. for $C_{15}H_{15}BrO_2S$: C, 53.10; H, 4.42; Br, 23.60; S, 9.44; mol. wt., 339. Found: C, 53.36; H, 4.41; Br, 23.72; S, 9.24; mol. wt., 339.

Independent Preparation of 1-Chloro-2-phenylethyl *p*-Tolyl Sulfone (I).—A solution of *n*-propylmagnesium chloride was prepared under nitrogen from magnesium (4.8 g., 0.2 g.-atom), *n*-propyl chloride (17.7 g., 0.228 mole), and anhydrous ether (40 ml.). To this was added 2-phenylethyl *p*-tolyl sulfone (45 g., 0.173 mole) in dry benzene (150 ml.). After the evolution of propane had ceased, an additional 100 ml. of dry benzene was added and the stirred mixture was refluxed for 5 min., then cooled in an ice bath. Excess chlorine was bubbled into the cold, stirred solution (for about 20 min. at a high rate). The solution was stirred for 2 hr., then poured into water (*ca.* 200 ml.). The benzene layer was washed with water to remove excess chlorine and evaporated to 100 ml. After cooling, the first crop of solid (4.1 g.) was collected (m.p. 177–179°, after recrystallization from absolute ethanol). The n.m.r. spectrum and molecular weight of this product indicate that it is 1,1-dichloro-2-phenylethyl *p*-tolyl sulfone.

Anal. Calcd. for $C_{15}H_{14}Cl_2O_2S$: mol. wt., 329. Found: mol. wt., 329.

Evaporation of the benzene filtrates to 50 ml. and filtration of the precipitate produced a second crop of solid (18.05 g.), m.p. 65–100°. A third crop of solid (10.3 g.) was obtained by evaporating the benzene filtrates to dryness and recrystallizing the residue from absolute ethanol. Chromatography of 3.8 g. of the third crop on an alumina column, eluting with benzene–pentane (1:1, 800 ml.), produced 1.08 g. of 1-chloro-2-phenylethyl *p*-tolyl sulfone, m.p. 79–82° after recrystallization from ethanol. This compound did not depress the melting point of 1-chloro-2-phenylethyl *p*-tolyl sulfone obtained by the Meerwein procedure, and the infrared and n.m.r. spectra of the two samples were identical.

Anal. Calcd. for $C_{15}H_{15}ClO_2S$: C, 61.12; H, 5.09; Cl, 12.05; S, 10.87; mol. wt., 294.5. Found: C, 61.31; H, 5.14; Cl, 11.88; S, 10.67; mol. wt., 290.

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Out-of-Ring Claisen Rearrangements[1]

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The objective was to investigate Claisen rearrangements of allyl groups to carbons that are located outside the parent phenol ring. Pyrolysis of the allyl ether (**7**) of 2,6-dimethyl-4-propenylphenol (**6**) in ethanol at 200° followed by catalytic hydrogenation gave 2,6-dimethyl-4-propylphenol (**9**, 8.5%) and 2,6-dimethyl-4-(2-methylpentyl)phenol (**12**, 32%). The formation of **12** from **7** is explicable by a sequence of *three* consecutive cyclic transition states, the last of which shifts the allyl group out-of-ring to the β-carbon of the *para* side chain. To examine if the olefinic unit acting as the allyl acceptor in out-of-ring rearrangements could itself be part of a second phenyl ring, the allyl ethers of 3,5-dimethyl-4-hydroxybiphenyl (**13**) and 2-hydroxy-3,5-dimethylbiphenyl (**15**) and the bisallyl ether of 3,5,3′,5′-tetramethyl-4,4′-dihydroxybiphenyl (**17**) were prepared. On pyrolysis these allyl ethers disproportionated to the corresponding parent phenols; consequently, the phenyl ring acted as a blocking group and not as an allyl acceptor. A crystalline 1:1 adduct was obtained when the allyl ether of **13** was heated with maleic anhydride.

The intramolecular, thermal rearrangement of allyl phenyl ethers to *o*-allylphenols (Claisen rearrangement) involves cyclic, six-membered transition states.[3] When the *ortho* positions of the aromatic ring are suitably blocked the allyl group can migrate to the *para* carbon in two successive cyclic stages, each accompanied by a "reversal"[4] of the allyl group.[5,6]

In 1926 Claisen and Tietze reported a variant in which the migrating allyl group eventually became attached to the central carbon of an *o*-propenyl side chain (*e.g.*, **1a** → **2a**).[7] Recent studies on this "out-of-ring" Claisen rearrangement by Lauer and Wujciak showed that pyrolysis of the γ-substituted allyl ether **1b** gave **2b** in 23% yield (along with some of the cleavage product, 2,4-dimethyl-6-propenylphenol). By analogy with the *para* Claisen rearrangement, they formulated this out-of-ring migration as a two-cycle

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[1] Taken from the Ph.D. Dissertation of B. R. Aaronoff, The Johns Hopkins University, 1962. A preliminary account of the work has been published [A. Nickon and B. R. Aaronoff, *J. Org. Chem.*, **27**, 3379 (1962)] and was presented at the 142nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962.

[2] Fellow of the Alfred P. Sloan Foundation.

[3] D. S. Tarbell, *Org. Reactions*, **2**, 1 (1944).

[4] An allyl unit attached initially by its α-carbon is said to be "reversed" (or "inverted") when the final attachment is through its (original) γ-carbon. The double bond undergoes an allylic shift in the process.

[5] (a) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1938); (b) S. J. Rhoads, R. Raulins, and R. D. Reynolds, *J. Am. Chem. Soc.*, **76**, 3456 (1954); (c) J. P. Ryan and P. R. O'Connor, *ibid.*, **74**, 5866 (1952); (d) H. Schmid and K. Schmid, *Helv. Chim. Acta*, **36**, 489 (1953); (e) H. Conroy and R. A. Firestone, *J. Am. Chem. Soc.*, **78**, 2290 (1956); (f) D. Y. Curtin and R. J. Crawford, *ibid.*, **79**, 3156 (1957); (g) E. N. Marvell and R. Teranishi, *ibid.*, **76**, 6165 (1954); (h) D. Y. Curtin and H. W. Johnson, *ibid.*, **76**, 2276 (1954); **78**, 2611 (1956); (i) K. Schmid, W. Haegele, and H. Schmid, *Experientia*, **9**, 414 (1953); (j) W. Haegele and H. Schmid, *Helv. Chim. Acta*, **41**, 657 (1958); (k) K. Schmid, W. Haegele, and H. Schmid, *ibid.*, **37**, 1080 (1954).

[6] For a recent review and leading references, see S. '. Rhoads, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, part 1, p. 655.

[7] L. Claisen and E. Tietze, *Ann.*, **449**, 89 (1926).