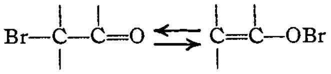
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

α-Bromosulfones[1]

BY WILLIAM M. ZIEGLER[2] AND RALPH CONNOR

The influence of labilizing groups (such as —COOR, —COR, —CN, etc.) upon an adjacent substituent may be attributed partly to the electron-attracting properties of these groups and partly to the ability of the groups to participate in reactions. Thus in α-bromo ketones the reactivity of the halogen does not depend entirely upon the polar influence of the keto group upon the carbon–bromine bond, but also upon reactions which involve the carbonyl function. For example, certain reactions[3] of α-bromo ketones occur by preliminary addition to the carbonyl. It has also been suggested[4] that the reaction of "positive halogen"[5] compounds are due to an anionotropic shift



$$Br—\overset{|}{\underset{|}{C}}—\overset{|}{C}=O \rightleftarrows \overset{|}{C}=\overset{|}{\underset{|}{C}}—OBr$$

although there is evidence that this is not always true.[6] From these considerations it may be concluded that our usual views of the influence of labilizing groups upon halogen in the alpha position are based upon a summation of many factors involved in the reactions studied.

It seemed that some of these factors would be eliminated, or at least minimized, in the reactions of α-bromosulfones. It has already been pointed out[6] that anionotropy would be unlikely in α-bromosulfones and that addition to the sulfone group would require expansion of the valence shell of sulfur. It might therefore be expected that in α-bromosulfones the labilizing group would have little or no tendency to participate in reactions and that the reactions would give an indication of the importance of the polar character of labilizing groups[7] in influencing the reactivity of alpha halogen.

While our chief interest was in the reactions of α-bromo derivatives of monosulfones, few of these compounds had been described previously[8,9] and it was first necessary to investigate methods for their synthesis. The three methods used were (a) reaction of a sulfone (I) with ethylmagnesium bromide and treatment of the bromomagnesium derivative (II)

$$\begin{tikzcd}
\underset{\text{(I)}}{p\text{-}CH_3C_6H_4SO_2CH_3} \arrow[r, "(a)", "C_2H_5MgBr"'] & \underset{\text{(II)}}{[p\text{-}CH_3C_6H_4SO_2CH_2]MgBr} \arrow[d, "Br_2"] \\
\underset{(R\,=\,p\text{-}CH_3C_6H_4\text{— or } n\text{-}C_4H_9\text{—})}{RSO_2Na + CH_2Br_2} \arrow[r, "(b)"] & RSO_2CH_2Br
\end{tikzcd}$$

$$\text{III, } R = n\text{-}C_4H_9\text{—}$$
$$\text{IV, } R = p\text{-}CH_3C_6H_4\text{—}$$

$$n\text{-}C_4H_9SO_2CH(C_2H_5)COONa \xrightarrow[NaOBr]{(c)} \underset{\text{V}}{n\text{-}C_4H_9SO_2CHBrC_2H_5}$$

$$p\text{-}CH_3C_6H_4SO_2CH_2COONa \xrightarrow[NaOBr]{(c)} \underset{\text{VI}}{p\text{-}CH_3C_6H_4SO_2CHBr_2}$$

with bromine, (b) reaction of the salt of a sulfinic acid with methylene bromide[10] and (c) treatment of an α-sulfonyl acid with bromine in alkaline solution.[11] Method (a), which had not been previously reported, was the most convenient but

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(1) This communication is constructed from a thesis submitted by William M. Ziegler in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pennsylvania in June, 1939.

(2) Harrison Fellow in Chemistry, 1938–1939.

(3) Kohler and Brown, THIS JOURNAL, **55**, 4299 (1933).

(4) Willstätter and Hattenroth, *Ber.*, **37**, 1778 (1904); Howk and McElvain, THIS JOURNAL, **54**, 282 (1932).

(5) Waters, "Physical Aspects of Organic Chemistry," 2d ed., George Routledge and Sons, London, 1937, p. 221.

(6) Kohler and Tishler, THIS JOURNAL, **57**, 218 (1935).

(7) The reactions of α-bromo-α-sulfonylamides [Ziegler and Connor, *ibid.*, **62**, 1049 (1940)] were like the reactions of the α-bromo derivatives of other active methylene compounds. This did not satisfy the purpose of the present investigation, for the C=O of the amide group could participate in the reactions. The results are, however, pertinent to this work because they show that the polar effect of the sulfone group upon halogen is similar to that of other labilizing groups. This seems to be justification for considering that the results obtained with α-bromosulfones are indicative of the polar influences of other labilizing groups.

(8) A few α-halosulfones were reported by Otto [*J. prakt. Chem.*, [2] **40**, 526 (1880)]. Shortly after the completion of this investigation, Shriner and Greenlee [*J. Org. Chem.*, **4**, 242 (1939)] described the bromo derivatives of three nitrobenzyl *p*-tolyl sulfones. Since these compounds contain, in addition to the sulfone group, a second labilizing group (phenyl) and the added influence of vinylogous [Fuson, *Chem. Rev.*, **16**, 1 (1935)] nitro groups, they are more comparable to the compounds described in our previous paper[7] than to the simple α-bromosulfones described here.

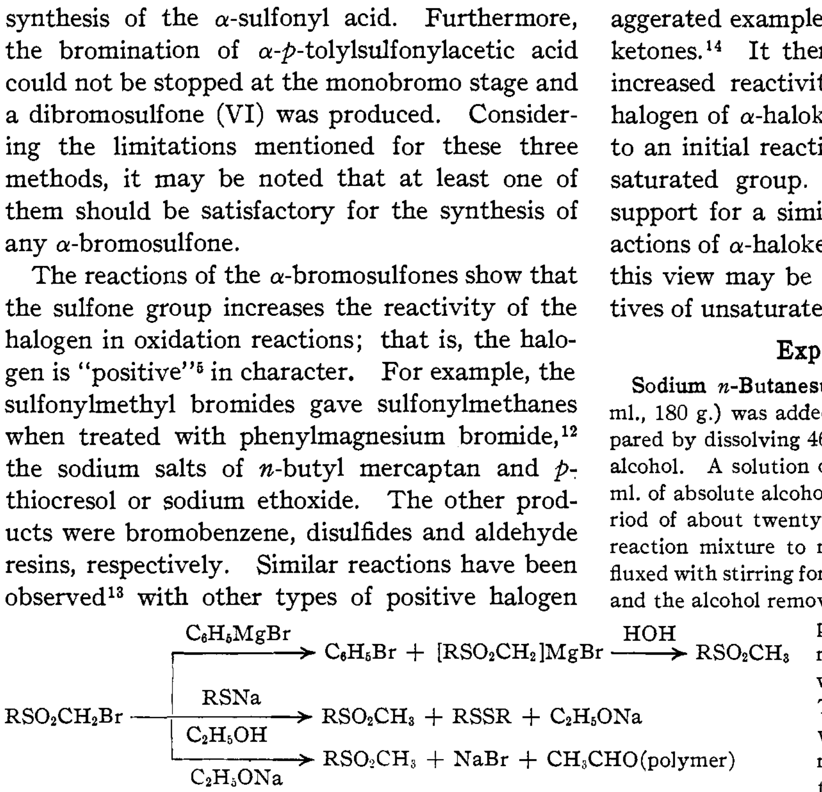
(9) The observation of Michael and Palmer [*Am. Chem. J.*, **6**, 253 (1884)] that phenylsulfonylmethyl iodide was dehalogenated by sodium ethoxide indicated that α-halosulfones possessed the reactions of positive halogen. Further indications of this were observed with the bromo derivatives of a disulfone and a trisulfone. Kohler and Tishler[6] reported the dehalogenation of diphenylsulfonyldibromomethane by the Grignard reagent and Samen [*Arkiv. Kemi, Mineral. Geol.*, **12B**, No. 51 (1938)] reported that triethylsulfonylmethyl bromide was reduced to triethylsulfonylmethane by hydrazine or hydriodic acid.

(10) Michael and Palmer[9] used a sealed tube for the reaction of sodium benzenesulfinate with methylene iodide. The reactions reported here occurred in boiling alcohol.

(11) This reaction was reported by Otto.[8]

would not be suitable for use with unsymmetrical dialkyl sulfones because of the probable formation of isomers. Method (b) gave satisfactory results with sodium *n*-butanesulfinate but aromatic sulfinates are less reactive[10] and this method was decidedly inferior to (a) for the preparation of IV. Method (c) was satisfactory for the synthesis of an α-bromosulfone (V) for which the other methods were not applicable. This was a rather laborious method, however, because it required the synthesis of the α-sulfonyl acid. Furthermore, the bromination of α-*p*-tolylsulfonylacetic acid could not be stopped at the monobromo stage and a dibromosulfone (VI) was produced. Considering the limitations mentioned for these three methods, it may be noted that at least one of them should be satisfactory for the synthesis of any α-bromosulfone.

The reactions of the α-bromosulfones show that the sulfone group increases the reactivity of the halogen in oxidation reactions; that is, the halogen is "positive"[5] in character. For example, the sulfonylmethyl bromides gave sulfonylmethanes when treated with phenylmagnesium bromide,[12] the sodium salts of *n*-butyl mercaptan and *p*-thiocresol or sodium ethoxide. The other products were bromobenzene, disulfides and aldehyde resins, respectively. Similar reactions have been observed[13] with other types of positive halogen compounds. The α-bromosulfones did not oxidize hydrazine or hydriodic acid under the conditions previously used.[7]



$$\mathrm{RSO_2CH_2Br}\begin{cases}\xrightarrow{\mathrm{C_6H_5MgBr}} \mathrm{C_6H_5Br} + [\mathrm{RSO_2CH_2}]\mathrm{MgBr} \xrightarrow{\mathrm{HOH}} \mathrm{RSO_2CH_3} \\ \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{RSNa}} \mathrm{RSO_2CH_3} + \mathrm{RSSR} + \mathrm{C_2H_5ONa} \\ \xrightarrow[\mathrm{C_2H_5ONa}]{} \mathrm{RSO_2CH_3} + \mathrm{NaBr} + \mathrm{CH_3CHO(polymer)}\end{cases}$$

With pyridine, the sulfonylmethyl bromides were largely unchanged but small amounts of disulfonylethanes were isolated. This novel dehalogenation is quite different from that previously noted[7] with α-bromo-α-sulfonylamides.

$$\mathrm{2RSO_2CH_2Br} \xrightarrow[\mathrm{C_5H_5N}]{-2\mathrm{Br}} \mathrm{RSO_2CH_2CH_2SO_2R}$$

The α-bromosulfones, except in reactions involving oxidation–reduction, were unusually inert. They were recovered unchanged from treatment with tetrahydroquinoline, dimethylamine, alcoholic silver nitrate, sodium acetate and sodium cyanide. Since the α-bromosulfones are less reactive than alkyl bromides with these reagents, it may be concluded that the sulfone group is a deactivating group so far as these reactions are concerned. While this may be a specific property of the sulfone group, it may be pointed out that the reactions of α-bromosulfones are actually exaggerated examples of a trend noted with α-haloketones.[14] It therefore seems probable that the increased reactivity generally attributed to the halogen of α-haloketones, esters, etc., may be due to an initial reaction of the reagent with the unsaturated group. This may be interpreted as support for a similar opinion[3] concerning the reactions of α-haloketones and as an indication that this view may be extended to the α-halo derivatives of unsaturated compounds in general.

Experimental Part[15]

Sodium *n*-Butanesulfinate.[16]—*n*-Butyl mercaptan (214 ml., 180 g.) was added to a sodium ethoxide solution prepared by dissolving 46 g. of sodium in 650 ml. of absolute alcohol. A solution of 220 g. of ethylene bromide in 100 ml. of absolute alcohol was added with stirring over a period of about twenty minutes at a rate which caused the reaction mixture to reflux gently. The mixture was refluxed with stirring for one hour, allowed to stand overnight and the alcohol removed by distillation. The residue was poured into cold water, the oil separated and the aqueous layer extracted with two 100-ml. portions of ether. The ether extracts were combined with the oil, dried over calcium chloride and the solvent removed by distillation. The residue of crude 1,2-di-*n*-butylthioethane was dissolved in 500 ml. of acetic acid–acetic anhydride solution (1:1) and the solution chilled in an ice–salt-bath. Five hundred fifty grams of 30% hydrogen peroxide was added with stirring over a period of about two hours at such a rate that the temperature remained between 20 and 40°. After the reaction mixture had stood for two days the crystals were removed by filtration through a Buchner funnel without paper and washed with water. The filtrate was poured into three times its volume of water and allowed to stand for several hours. The solid was washed with water and dried. The combined solids

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(12) Kohler and Tishler[6] reported a similar reaction with diphenylsulfonyldibromomethane.

(13) (a) Biltz and Behrens, *Ber.*, **43**, 1984 (1910); (b) Fisher, Oakwood and Fuson, THIS JOURNAL, **52**, 5036 (1930); Kohler and Tishler, *ibid.*, **54**, 1594 (1932); (c) Kohler and Potter, *ibid.*, **58**, 2166 (1936); (d) Ziegler and Connor.[7]

(14) For example, phenacyl halides do not react with alcoholic silver nitrate [Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 23]. α-Bromo derivatives of mesityl ketones, in which addition to the carbonyl is hindered, do not react with sodium acetate, react slowly with amines [Babcock, Nakamura and Fuson, THIS JOURNAL, **54**, 4407 (1932)] and give bromobenzene with phenylmagnesium bromide.[11b]

(15) Melting points are corrected.

(16) This preparation was suggested by the reaction reported by Otto, *J. prakt. Chem.*, [2] **30**, 361 (1884).

weighed 248 g. (92%), m. p. 177–179°. Recrystallization from alcohol–acetic acid (3:1) gave pure 1,2-di-*n*-butylsulfonylethane melting at 180–181°.[17]

To 172 g. of the crude disulfone in 360 ml. of 50% alcohol was added 175 g. of potassium cyanide and the mixture refluxed for twenty-four hours. About 185 ml. of solvent was removed by distillation, the residue diluted with 200 ml. of water and 480 ml. of 6 *N* hydrochloric acid added slowly, using an aspirator to remove the hydrogen cyanide liberated. The solution was extracted with five 200-ml. portions of ether and the combined extracts washed repeatedly with 50-ml. portions of 10% sodium hydroxide solution. When the extracts were alkaline, the ether layer was washed once more, the combined aqueous extracts neutralized with sodium bicarbonate, decolorized first with 20 g., then 10 g., of charcoal and evaporated to dryness. The residue was dissolved in about 150 ml. of alcohol, filtered and the filtrate evaporated until solid appeared. After chilling overnight in a refrigerator the solid was removed by filtration, washed with a little cold alcohol and dried. This product weighed 51 g. Evaporation of the filtrate gave an additional 73 g. The combined products corresponded to 72% of the theoretical amount of sodium *n*-butanesulfinate, based on the disulfone used. The product was characterized by reaction with chloroacetamide to give *n*-butylsulfonylacetamide.[18]

***n*-Butylsulfonylmethyl Bromide** (III).—To 28.8 g. of sodium *n*-butanesulfinate (obtained from the mother liquor of the reaction described above) dissolved in 150 ml. of alcohol was added 42.6 g. of methylene bromide. The mixture was heated for twenty hours on the water-bath, the alcohol removed by distillation and the residue extrated with benzene. The benzene was distilled and the residue recrystallized from ligroin (b. p. 70–90°). The yield of pure III was 19 g. (44%), m. p. 47–48°.

Anal. Calcd. for $C_5H_{11}SO_2Br$: Br, 37.2. Found: Br, 37.2, 37.4.

***p*-Tolylsulfonylmethyl Bromide** (IV).—To 0.20 mole of ethylmagnesium bromide in 40 ml. of ether was added a solution of 27.2 g. of methyl *p*-tolyl sulfone[19] in 150 ml. of benzene. After the evolution of ethane had ceased an additional 100 ml. of benzene was added and the mixture refluxed for three minutes. Twenty-four grams (0.15 mole) of bromine in 50 ml. of benzene was added while in an ice-bath. The mixture was vigorously stirred to prevent the formation of a lump. After stirring for two hours at room temperature the material was poured into 150 ml. of water. The excess bromine was removed by the addition of a solution of sodium bisulfite and the benzene layer separated and evaporated to 100 ml. After cooling overnight, the crystalline solid was removed by filtration and the filtrate again concentrated. The solid obtained by the latter concentration was brown and was decolorized by treatment with charcoal in alcoholic solution. The solid obtained in this manner was combined with the initial solid from the benzene layer and the combined materials recrystallized from alcohol. The yield of pure IV was 20 g. (50%), m. p. 89–90°.[8]

Reaction of sodium *p*-toluenesulfinate with methylene bromide was carried out as described above for the preparation of III. After removal of the alcohol the residue was poured on water and the solid recrystallized from alcohol. The yield was 17.5 g. (33%), m. p. 90–91°.[8]

Attempts to halogenate methyl *p*-tolyl sulfone with bromine, sodium hypobromide and *t*-butyl hypochlorite under conditions previously reported for α-bromo-α-sulfonylamides[7] were unsuccessful and 75–85% of the starting material was recovered unchanged.

α-*n*-Butylsulfonyl-*n*-propyl Bromide (V).—To a mixture of 25 g. of α-bromo-*n*-butyric acid and 75 ml. of water, sodium carbonate was added until a homogeneous solution, neutral to litmus, was obtained. Then 22 g. of sodium *n*-butanesulfinate was added and the solution refluxed for four hours. The reaction mixture was acidified with 6 *N* hydrochloric acid and extracted with one 75-ml. and two 50-ml. portions of ether. After removal of the solvent from the combined extracts by distillation, the residue was chilled but would not solidify. The oil was then dissolved in 25 ml. of water containing a slight excess of sodium carbonate and this solution added to a solution of 24 g. of bromine in 75 ml. of 20% sodium hydroxide at 0°. The solution was placed in a refrigerator for four hours and then allowed to stand at room temperature overnight. It was then acidified and refluxed until the bromine color was removed. During this procedure some gas was evolved. The mixture was extracted with one 75-ml. and two 50-ml. portions of ether. The ethereal solution was dried over magnesium sulfate, the ether removed and the oil chilled overnight. Since the product did not solidify, it was subjected to vacuum distillation and a fraction collected boiling at 127–142° (5 mm.). There was some decomposition when the bath reached 160°, before any distillate was obtained. This may have been due to decarboxylation of the α-sulfonyl-α-bromoacid. The product was redistilled and 8.9 g. (25% based on α-bromobutyric acid) of pure V obtained, b. p. 133–136° (5 mm.).

Anal. Calcd. for $C_7H_{15}O_2SBr$: Br, 32.9. Found: Br, 32.7, 32.6.

***p*-Tolylsulfonyldibromomethane** (VI).—To 5.7 g. of α-*p*-tolylsulfonylacetic acid[20] was added 300 ml. of 5% sodium hydroxide solution and the solution chilled to 5°. After the addition of 1.45 ml. of bromine the mixture stood for one and one-half hours in a refrigerator and was then warmed until the solid coagulated. The product was washed with cold water and recrystallized from alcohol. The yield was 3.2 g. (70%) of material melting at 116–117°.[21]

Reaction with Sodium Mercaptides.—To a sodium ethoxide solution prepared by dissolving 0.71 g. of sodium in 70 ml. of alcohol was added 3.2 ml. of *n*-butyl mercaptan. This solution was cooled in an ice-bath, 7.6 g. of *p*-tolylsulfonylmethyl bromide added, and the mixture allowed to come to room temperature as the ice melted. After standing at room temperature for five days most of the alcohol was removed under diminished pressure and the residue poured on ice. The solid was recrystallized from ether, then ligroin–ether (3:1) mixture and identified as methyl *p*-tolyl sulfone by a mixed melting point with an authentic specimen. The yield was 4.0 g. (76%) of I, m. p. 82–85°.

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[17] Whitner and Reid, This Journal, **43**, 640 (1921).

[18] d'Ouville and Connor, This Journal, **60**, 33 (1938).

[19] Shriner, Struck and Jorison, *ibid.*, **52**, 2060 (1930).

[20] Gabriel, *Ber.*, **14**, 833 (1881).

[21] This compound was previously prepared by Otto.[8]

Under similar conditions 2.5 g. of *p*-thiocresol and 4.3 g. of *n*-butylsulfonylmethyl bromide gave ditolyldisulfide and a product which did not crystallize. Recrystallization of the disulfide from alcohol gave 2.25 g. (90%), m. p. 45–46°.

Reaction with Phenylmagnesium Bromide.—To a solution of 0.15 mole of phenylmagnesium bromide in 70 ml. of ether was added with vigorous stirring a solution of 34.8 g. of IV in 400 ml. of ether. The addition required about one-half hour and the reaction mixture was refluxed an additional three hours, stirred for two hours without heating, and allowed to stand overnight. The residue remaining after filtration was washed with ether, suspended in iced hydrochloric acid and recrystallized from alcohol. The yield was 14.3 g. (56%) of methyl *p*-tolyl sulfone, m. p. 84–86°. The ether was removed from the filtrate of the reaction mixture by distillation from a water-bath through a fractionating column. The distillation residue was mixed with a little ether and ligroin (b. p. 70–90°) was added. The organometallic compound remaining was treated as before and gave 1 g. (3%) of IV. The ether-ligroin solution upon fractionation gave 18.2 g. (77%) of bromobenzene, b. p. 154–157°.

Reaction with Pyridine.—A solution of 12.5 g. of IV and 4.7 g. of pyridine in 100 ml. of absolute alcohol was refluxed for forty hours and the alcohol removed by distillation. The residue was diluted with 200 ml. of ether and the solid recrystallized from alcohol. This gave 1 g. (8%) of 1,2-di-*p*-tolylsulfonylethane, m. p. 201–202° which was identified by a mixed melting point with an authentic sample.[16] The ethereal solution was evaporated and the solid residue recrystallized from alcohol. This gave 9 g. (72%) of unreacted IV, m. p. 89–90°.

A similar experiment in which 2.15 g. of III was refluxed with pyridine in 25 ml. of alcohol for twenty-two hours gave 0.05 g. (2%) of 1,2-di-*n*-butylsulfonylethane, m. p. 177–179°, and 2.05 g. (95%) of unchanged III, m. p. 47–48°.

With Sodium Ethoxide.—To a sodium ethoxide solution prepared by dissolving 0.92 g. of sodium in 100 ml. of absolute alcohol was added 10 g. of IV and the mixture refluxed for fifteen hours. The solution was cooled, filtered and the solid washed with a little cold alcohol and then with water. There remained 0.2 g. of yellow, highly insoluble material which was not investigated further.[22] The alcoholic solution gave 5 g. (74%) of methyl *p*-tolyl sulfone, m. p. 85–86°, which was identified by a mixed melting point.

Other Results.—The recovery of unchanged bromosulfone was 80–95% in the following tests: (a) heating IV with two equivalents of tetrahydroquinoline at 100° for sixteen hours, (b) treatment of IV with two equivalents of dimethylamine for five days at room temperature and five hours at 40–50°, (c) refluxing IV for forty hours in 75% alcohol with two equivalents of potassium cyanide, (d) refluxing III for seven hours with two equivalents of sodium acetate in alcohol solution. No iodine was liberated when III and IV were treated with acidified potassium iodide under the conditions previously described.[7] No reaction occurred between III or IV and hydrazine hydrate under the conditions previously used[6] but VI reacted slowly, giving 3 ml. (8%) of nitrogen in five hours from 0.5 g. of the dibromosulfone.

Summary

Syntheses of three α-bromosulfones and one α,α-dibromosulfone have been described. The reactions of the α-bromosulfones showed that the sulfone group activates the halogen for oxidation reactions but deactivates it in metathesis reactions. The results suggest that the increased reactivity generally attributed to α-bromo-ketones, esters, etc., is due to preliminary reaction of the reagent with the unsaturated group, rather than to the polar influence of the group.

PHILADELPHIA, PENNA. RECEIVED MAY 24, 1940

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[22] This material was probably aldehyde resin. Willstätter and Hattenrote [*Ber.*, **43**, 1984 (1910)] reported the formation of aldehyde resins from the oxidation of alcohol by N-chloro compounds in which the hypochlorite character of the halogen is well known.

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. LXI. The Mechanism of Polymerization of Ethylene Oxide[1]

BY STANLEY PERRY AND HAROLD HIBBERT

In contrast with the now almost universally accepted long chain structure of polymer molecules, there is not as yet an undisputed mechanism for the formation of such molecules in simple polymerization reactions. Two main theories are generally recognized: the Free Radical Theory, the chief proponent of which is H. Staudinger[2] and the Stepwise Addition Theory, due to Whitby.[3]

Staudinger assumes that the monomeric molecule is capable of yielding an intermediate having two free valence bonds; such free radicals are enormously reactive and hence add to one another with extreme ease, giving very long chains. This free radical chain reaction is supposed[4] to

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[1] From a thesis presented by Stanley Perry to the Faculty of Graduate Studies and Research, McGill University, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy (October, 1938). Part LX of this series, Perry and Hibbert, THIS JOURNAL, **62**, 2561 (1940).

[2] Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932.

[3] Whitby and Katz, THIS JOURNAL, **50**, 1160 (1928).

[4] Schulz and Husemann, *Z. angew. Chem.*, **50**, 767 (1937).