[CONTRIBUTION FROM THE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides. VII. The Mechanism of the Base-catalyzed Reaction of Trichloroethylene with Thiols[1]

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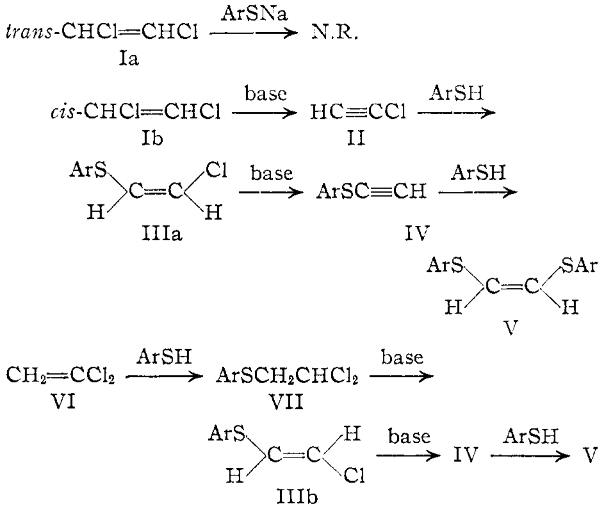
Evidence is presented in support of a mechanism for the conversion of trichloroethylene to 1,1,2-tris-(*p*-tolylmercapto)-ethene. The proposed sequence involves elimination–addition and "addition"–elimination reactions.

Previous work in this Laboratory[2,3] has indicated that reactions of nucleophilic agents with halogenated ethylenes may proceed by at least two different mechanisms, *i.e.*, either initial β-elimination to form an acetylenic intermediate followed by nucleophilic addition, or initial nucleophilic addition to form a saturated intermediate or an incipient carbanion followed by elimination of HX or X^-, respectively. Which path is followed will be determined in large measure by the basicity of the reagent and the tendency of the haloethylene system to undergo dehydrohalogenation on the one hand, and by the nucleophilicity of the reagent and the "electrophilicity" of the vinyl grouping on the other hand. For example, the base-catalyzed reaction of *p*-toluenethiol with the readily dehydrohalogenated *cis*-dichloroethylene[4a,b] proceeds by initial elimination,[2] whereas similar treatment of the more polar and much less readily dehydrohalogenated vinylidine chloride gives initial nucleophilic addition[3] although the same final product, *cis*-bis-(*p*-tolylmercapto)-ethene (V), is obtained.



where Ar = $p\text{-}CH_3C_6H_4^-$

The stereospecificities observed in these reactions were accounted for by applying the Rule of *trans*-Elimination,[5] the Rule of *trans*-Nucleophilic Addition[6] and the *cis*-Effect.[7]

The mechanism(s) of the reactions of nucleophilic agents with the tri- and tetrahalogenated ethylenes has not yet been elucidated. It is the purpose of this paper to describe the mechanism of the reaction of trichloroethylene with sodium *p*-toluenethiolate. Previous reports indicate that several nucleophilic agents (Y) react with trichloroethylene, *i.e.*, sodium ethoxide,[8a] sodium ethanethiolate[8b] sodium phenoxides,[8c] sodium benzenethiolate[8c] and sodium *p*-toluenethiolate.[8d] The major product reported in all these instances, even in the presence of an excess of the nucleophilic agent, was of the type YCCl=CHCl, but of unknown geometry. However, it has been observed in this Laboratory that on treatment of trichloroethylene with excess sodium *p*-toluenethiolate for an extended reaction time, a solid product is obtained which contains sulfur but no chlorine. This product has been assigned the structure 1,1,2-tris-(*p*-tolylmercapto)-ethene (XIV). It has been verified by analysis of the trisulfide as well as the trisulfone, and by a determination of the molecular weight of XIV by the freezing point depression method. In addition, it has been observed that treatment of XIV with *n*-butyllithium produces bis-(*p*-tolylmercapto)-ethyne (XIII) in 30% yield. The utility of this reaction for making arylmercaptoacetylenes has been described recently by Parham and co-workers.[9] The reaction which is proposed for the formation of 1,1,2-tris-(*p*-tolylmercapto)-ethene (XIV) from trichloroethylene and sodium *p*-toluenethiolate is scheme I.

$$\underset{\text{XIV}}{(ArS)_2C{=}CHSAr} + n\text{-}BuLi \longrightarrow \underset{\text{XIII}}{ArSC{\equiv}CSAr} + ArSLi$$

On the basis of the structural similarity of trichloroethylene to both *cis*-dichloroethylene and vinylidine chloride it would be difficult to predict the first step in the mechanism of this reaction. However, it has been observed that a mixture of *p*-toluenethiol and its sodium salt does not react with

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[1] For preceding paper see ref. 6. Taken from Mr. Kassinger's Ph.D. thesis. Presented at the San Francisco Meeting of the American Chemical Society, April, 1958.

[2] W. E. Truce, M. M. Boudakian, R. F. Heine and R. J. McManimie, THIS JOURNAL, **78**, 2743 (1956).

[3] W. E. Truce and M. M. Boudakian, *ibid.*, **78**, 2748 (1956).

[4] (a) G. Chavanne, *Bull. soc. chim. Belges*, **26**, 287 (1912); **28**, 234 (1914); F. Martin and Z. Bruylants, *ibid.*, **60**, 259 (1951); S. I. Miller and R. M. Noyes, THIS JOURNAL, **74**, 629 (1952). (b) *trans*-Dichloroethylene, when treated in a similar manner, is recovered unchanged.

[5] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 7.

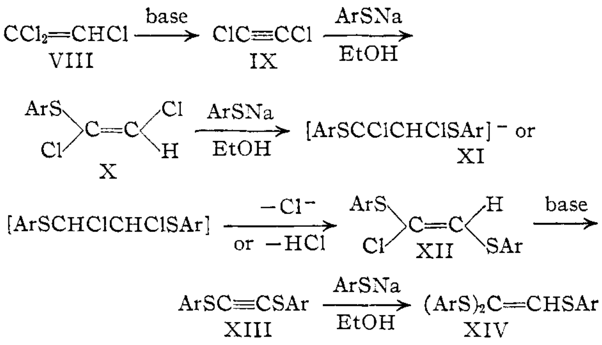
[6] W. E. Truce and R. F. Heine, THIS JOURNAL, **79**, 5311 (1957), and references cited therein; Handbook, Organic Division, XVI International Congress of Pure and Applied Chemistry, Paris, July, 1957, p. 175.

[7] D. Y. Curtin, *Rec. Chem. Progr.*, **15**, 111 (1954); Abstracts 13th National Organic Chemistry Symposium, American Chemical Society, Ann Arbor, Mich., June, 1953.

[8] (a) H. Crompton and P. L. Vanderstichele, *J. Chem. Soc.*, 691 (1920); O. C. Stephens, *J. Soc. Chem. Ind.*, **43**, 313T (1924); (b) U. S. Pat. 2,501,896, *C. A.*, **44**, 6436 (1950); (c) N. W. Cusa and H. McCombie, *J. Chem. Soc.*, 767 (1937); (d) R. J. McManimie, Ph.D. Thesis, Purdue University (1953).

[9] W. E. Parham and P. L. Stright, THIS JOURNAL, **78**, 4783 (1956).

SCHEME I



trichloroethylene; whereas sodium *p*-toluenethiolate in the presence of sodium ethoxide gives an 81% yield of 1,2-dichloro-1-(*p*-tolylmercapto)-ethene (X). Since the necessity of excess base in the *cis*-dichloroethylene reaction has been attributed to initial dehydrohalogenation, this suggests itself as the first step of the reaction sequence in the trichloroethylene system. In order to verify the intermediacy of dichloroacetylene in the reaction of trichloroethylene with sodium *p*-toluenethiolate to give X, dichloroacetylene (IX) was independently generated by the vapor phase dehydrohalogenation of trichloroethylene over a potassium hydroxide–calcium oxide mixture, and a mixture of *p*-toluenethiol and its sodium salt was added to an ether–ethanol–dichloroacetylene solution.[10] The product of the reaction had an infrared spectrum identical with that of the product of the reaction of thiolate with trichloroethylene. Furthermore, both products could be oxidized to the same crystalline sulfone Xa, as shown by mixed melting point determinations.

One basis on which X has been assigned the *trans*-dichloro structure[11] is the Rule of *trans*-Nucleophilic Addition.[6] Furthermore, treatment of X with a solution of refluxing sodium ethoxide in ethanol for 24 hours produced only 56% dehydrohalogenation, as determined by chloride ion formation. In the case of the analogous *cis*- and *trans*-1-chloro-2-(*p*-tolylmercapto)-ethenes (IIIa and b), the *trans* isomer dehydrohalogenates much more slowly than the *cis* isomer. Whereas the *cis* compound gave a 98.3% yield of *cis*-bis-(*p*-tolylmercapto)-ethene on treatment with sodium *p*-toluenethiolate, the *trans* compound reacted only to the extent of 10.2%.[2,3] The Rule of *trans*-Elimination[5] may be applied to these cases, to account for the difference in reactivities of the isomer pair. The sluggish behavior of X in the dehydrohalogenation is in keeping with its assigned structure, and is consistent with these observations.

trans - 1,2 - Dichloro - 1 - (*p* - tolylmercapto)-ethene (X) may be converted to XIV in 78% yield by treating it with an excess of sodium *p*-toluenethiolate. If, on the other hand, it is treated with *p*-toluenethiol and a catalytic amount of sodium *p*-toluenethiolate, 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene (XII)[12] can be isolated. Presumably this arises by way of an initial nucleophilic attack to form an incipient carbanion or symmetrical intermediate (XI).

If *trans*-1-chloro-1,2-di-(*p*-tolylmercapto)-ethene[13] (XII) is treated with *p*-toluenethiol and a deficiency of base, no reaction occurs and 85% of XII is recovered. However, when this intermediate is treated with sodium *p*-toluenethiolate and an excess of base, the final product is isolated in 97% yield. Since an excess of base is again observed to be necessary, an elimination–addition reaction is suggested. Furthermore, XII is readily dehydrohalogenated to bis-(*p*-tolylmercapto)-ethyne (94% yield), which reacts with *p*-toluenethiol in 90% yield, to produce 1,1,2-tris-(*p*-tolylmercapto)-ethene (XIV).

Experimental

Reaction of Trichloroethylene and Sodium *p*-Toluenethiolate. A. Preparation of 1,1,2-Tris-(*p*-tolylmercapto)-ethene (XIV).—A solution of 6.6 g. (0.05 mole) of freshly distilled trichloroethylene in 50 ml. of absolute ethanol was added dropwise over a one-hour period to a solution prepared from 200 ml. of absolute ethanol containing 24. 8 g. (0.20 mole) of *p*-toluenethiol and 5.75 g. (0.25 mole) of sodium. The mixture was refluxed for an additional 24 hours under a nitrogen atmosphere. Sodium chloride was isolated by filtering the hot ethanolic solution, which was then concentrated, diluted with water and extracted with ether. The residue obtained after evaporating the ether was recrystallized from 95% ethanol to give a solid, m.p. 56–57°, wt. 13.0 g. (97% yield, 66% conversion). Elemental analysis of this product showed that it contained sulfur but no chlorine.

Anal. Calcd. for $C_{23}H_{22}S_3$: C, 70.05; H, 5.30. Found: C, 69.88; H, 5.58.

The sulfone was prepared by treating 1 g. (0.0025 mole) of the solid with 4.0 ml. (0.030 mole) of 30% hydrogen peroxide in 50 ml. of glacial acetic acid. The reactants were heated on a steam-bath for 2 hours, and the contents poured onto ice to give a crude product (wt. 0.75 g., 60% yield), which was recrystallized twice from 95% ethanol and melted at 131–131.5° (wt. 0.50 g., 40% yield).

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[10] In order to make dichloroacetylene, an ether–trichloroethylene solution is vaporized and dehydrohalogenated over base in the vapor phase. The product IX forms a weak molecular complex with ether according to E. Ott [*Ber.*, **75**, 1517 (1942)], which is much less hazardous to handle than the uncomplexed product. The dichloroacetylene–ether mixture is added to the solvent, absolute ethanol, for reaction with the thiolate.

[11] Montanari and Negrini [*Boll. sci. fac. chim. ind. Bologna*, **15**, 27 (1957); *C. A.*, **51**, 12849 (1957)] have synthesized a number of 1,2-dichloro-1-arylmercaptoethenes by the reaction of arylmercaptides with trichloroethylene, and have assigned the *trans* structure to their products. Due to the inaccessibility of the publication we are unable to comment on their assignment of configuration. However, it should be pointed out that they have been able to obtain the *cis* isomer by treating chloroacetylene with the arylsulfenyl chloride. Kharasch and Assony [THIS JOURNAL, **77**, 3390 (1955); **75**, 1081 (1953)] have reported that the addition of arylsulfenyl chlorides to acetylenes proceeds in a *trans* fashion. This also has been found by Truce and coworkers. In reference 3, *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene (IIIb) was synthesized from acetylene and *p*-toluenesulfenyl chloride. The observations of Montanari and Negrini are in accord with these results.

[12] Fromm and Seibert [*Ber.*, **55**, 1014 (1922)] have reported making both XI and the bromine-containing analog. These were made by either chlorination or bromination of bis-*p*-tolylmercaptoethene in chloroform solution. Although it has been possible to make the dibromo compound, all attempts at making XI were unsuccessful. These authors, however, did mention that neither of these compounds is very stable, both of them dehydrohalogenating quite easily. This would account for the inability to isolate intermediate XI.

[13] Montanari and Negrini (see ref. 11) have reported both the *cis*- and *trans*-disulfone of 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene, made by treating 1,2-dichloro-1-(*p*-tolylsulfonyl)-ethene with *p*-toluenethiol and sodium bicarbonate, and subsequent oxidation. The sulfone obtained on oxidizing XII is the one to which they have assigned the *trans* configuration. In addition we have observed that XII dehydrohalogenates very readily (see Experimental). In view of the facts already presented, this is in agreement with the structure assigned.

Anal. Calcd. for $C_{23}H_{22}S_3O_6$: C, 56.12; H, 4.39. Found: C, 56.33; H, 4.49.

The mother liquor from the recrystallization of XIV was concentrated, diluted with water and extracted with petroleum ether (60–70°). After drying this solution over magnesium sulfate, it was chromatographed through a column (20 cm. × 2.5 cm.) containing silica gel (Davison, 200-mesh), using petroleum ether (60–70°) as the eluent. Two distinct compounds were isolated. The first material, identified by its infrared spectrum and sulfone (see below), m.p. 76.5–77.5°, was 1,2-dichloro-1-(*p*-tolylmercapto)-ethene (1.30 g., 0.060 mole), while the second was *p*-tolyl disulfide, m.p. 46°, (1.90 g., 0.077 mole).

The aqueous layer, remaining from the original ether extractions, was acidified with concd. hydrochloric acid, extracted with ether, dried over magnesium sulfate and evaporated to give unreacted *p*-toluenethiol, m.p. 39.0–40.5°, wt. 9.25 g. (0.075 mole).

Preparation of 1,2-Dichloro-1-(*p*-tolylmercapto)-ethene (X).—A solution of 13.2 g. (0.10 mole) of trichloroethylene in 50 ml. of absolute ethanol was added dropwise over a 15-minute period to a solution prepared from 150 ml. of absolute ethanol, 14.9 g. (0.12 mole) of *p*-toluenethiol and 4.6 g. (0.20 mole) of sodium. The mixture was refluxed for a total of 1.5 hours, under a nitrogen atmosphere. Sodium chloride was isolated by filtering the hot ethanolic solution, which was then concentrated, diluted with water, and the organic layer extracted with ether. The ether extract was dried over magnesium sulfate and evaporated to an oil, wt. 21.2 g., which distilled at 70–72° (0.12 mm.) to give 17.58 g. (0.081 mole) of X (81% yield), n^{20}_{D} 1.5965. The sulfone of X, m.p. (76.5–77.5°), was made by oxidizing the sulfide with 30% hydrogen peroxide in glacial acetic acid.[8d]

Anal. Calcd. for $C_9H_8SO_2Cl_2$: C, 43.27; H, 3.20; Cl, 28.52; S, 12.72. Found: C, 42.94; H, 3.45; Cl, 28.22; S, 12.90.

The undistilled residue, wt. 2.7 g., yielded 1 g. of solid, m.p. 56–57°, when recrystallized from 95% ethanol. This did not depress the melting point of an authentic sample of XIV.

The aqueous solution was acidified with concd. hydrochloric acid, extracted with ether, dried over magnesium sulfate and evaporated to give unreacted *p*-toluenethiol, m.p. 39–41°, wt. 1.45 g. (0.011 mole).

Reaction of Trichloroethylene with a *p*-Toluenethiol-Sodium *p*-Toluenethiolate Mixture.—Sodium (0.10 g., 0.004 mole) and *p*-toluenethiol (12.4 g., 0.10 mole) were dissolved in 150 ml. of absolute ethanol and refluxed under a nitrogen atmosphere. To this was added a solution of 10.5 g. (0.08 mole) of trichloroethylene in 50 ml. of absolute ethanol and refluxing was continued for an additional 11 hours.

The ethanolic solution was diluted with 700 ml. of 1 *N* sodium hydroxide and extracted with petroleum ether (35–37°). The alkaline solution was acidified with concd. hydrochloric acid, extracted with petroleum ether (35–37°), dried over magnesium sulfate and evaporated to give unreacted *p*-toluenethiol, m.p. 40–42°, wt. 11.4 g. (0.075 mole, 92% recovery).

Reaction of Dichloroacetylene (IX) and *p*-Toluenethiol. A. Preparation of Dichloroacetylene (IX).—Trichloroethylene (100 g., 0.76 mole) was dehydrohalogenated in the vapor phase, by the method of Ott and co-workers.[10] The combined material of two runs, on distillation through a Vigreux column, yielded 130 ml. of ether solution containing 0.23 g. of dichloroacetylene per cc. (32 g. of IX, 21% conversion, 42% yield) based on the refractive index curve as determined by Ott and co-workers. The undistilled material contained 100 g. of trichloroethylene (0.76 mole).

B. Preparation of 1,2-Dichloro-1-(*p*-tolylmercapto)-ethene (X).—A solution prepared from 0.23 g. (0.10 mole) of sodium, 18.6 g. (0.15 mole) of *p*-toluenethiol and 150 ml. of absolute ethanol was added dropwise to 68 ml. of an ether-dichloroacetylene solution (0.23 g. of C_2Cl_2/cc.; 14.25 g., 0.15 mole) in 100 ml. of absolute ethanol at room temperature, over a one-hour period, during which time a Dry Ice condenser was used in addition to the water condenser to prevent any loss of the low boiling dichloroacetylene. The mixture was refluxed for an additional 12 hours under a nitrogen atmosphere.

A small amount of sodium chloride was filtered from the hot ethanolic solution, which was then concentrated, diluted with aqueous sodium hydroxide and extracted with ether. The ether extracts were dried over magnesium sulfate and on evaporation yielded 31 g. of oil which distilled at 70–74° (0.11 mm. to 0.16 mm.) to give 30.0 g. (0.137 mole) of X (92%). The infrared spectrum of this material was identical with that of the product obtained from trichloroethylene and sodium *p*-toluenethiolate.

C. Preparation of 1,2-Dichloro-1-(*p*-tolylsulfonyl)-ethene.—A fraction (2.2 g., 0.01 mole) of the oil obtained from the dichloroacetylene–thiolate reaction (2.2 g., 0.01 mole) was dissolved in 20 ml. of glacial acetic acid and 8 ml. (0.060 mole) of 30% H_2O_2 and refluxed for two hours. The hot oxidation mixture was poured on crushed ice and the sulfone obtained was recrystallized once from petroleum ether to give 2.1 g. (0.0088 mole) of sulfone, m.p. 76.5–77.5° (88% yield). This product did not depress the melting point of the sulfone obtained from the reaction of trichloroethylene and a deficiency of thiolate.

Reaction of 1,2-Dichloro-1-(*p*-tolylmercapto)-ethene and Excess Sodium *p*-Toluenethiolate.—A solution of 11.7 g. (0.054 mole) of X in 25 ml. of absolute ethanol was rapidly added to a solution prepared from 150 ml. of absolute ethanol, 16.6 g. (0.13 mole) of *p*-toluenethiol and 3.45 g. (0.15 mole) of sodium. The mixture was refluxed for a total of 24 hours under a nitrogen atmosphere. Sodium chloride was isolated by filtering the hot ethanolic solution; upon cooling it gave a white solid, m.p. 54–57°. One recrystallization from methanol gave 16.5 g. (0.042 mole) of solid, m.p. 56–57°, which did not depress the melting point of an authentic sample of 1,1,2-tris-(*p*-tolylmercapto)-ethene (78% yield).

Reaction of 1,2-Dichloro-1-(*p*-tolylmercapto)-ethene (X) and a Deficiency of Sodium *p*-Toluenethiolate.—Sodium (1.72 g., 0.09 mole) was dissolved in 150 ml. of absolute ethanol followed by 8.80 g. (0.07 mole) of *p*-toluenethiol. A solution of X (14.65 g., 0.067 mole) in 50 ml. of ethanol was added slowly to the refluxing thiolate solution and was refluxed for 24 hours under a nitrogen atmosphere. Sodium chloride was isolated by filtering the hot ethanolic solution, which was then concentrated and cooled. As a result of this operation, a solid (7.14 g., 0.018 mole) was obtained, m.p. 55–56°, which did not depress the melting point of an authentic sample of XIV. The mother liquor was diluted with water, and extracted with petroleum ether (35–37°). The aqueous fraction was acidified with concd. hydrochloric acid and extracted with petroleum ether (35–37°). Both ether extracts were dried over magnesium sulfate, and on evaporation of solvent, the organic extract gave an oil (10.9 g.) which on distillation gave 5.2 g. (0.024 mole) of unreacted X (the pot residue, 4.9 g., solidified and gave an additional 3.0 g. of XIV) while the other extract gave 1.05 g. of unreacted *p*-toluenethiol. The yield of XIV based on the amount of X consumed was 61%.

Reaction of 1,2-Dichloro-1-(*p*-tolylmercapto)-ethene with *p*-Toluenethiol and a Deficiency of Sodium Ethoxide.—A solution of 15.35 g. (0.07 mole) of X in 50 ml. of absolute ethanol was added slowly to a solution prepared from 150 ml. of absolute ethanol, 9.90 g. (0.08 mole) of *p*-toluenethiol and 0.10 g. (0.004 mole) of sodium. The solution was refluxed for 22 hours and kept at room temperature for an additional two hours under a nitrogen atmosphere.

The solution was diluted with 700 ml. of 0.3 *N* sodium hydroxide and extracted with petroleum ether (35–37°) and dried over magnesium sulfate. The aqueous layer was acidified with concd. hydrochloric acid, extracted with petroleum ether (35–37°), dried over magnesium sulfate and evaporated to give unreacted *p*-toluenethiol, m.p. 40–42°, wt. 3.63 g. (0.033 mole). The organic extract, on evaporation of the solvent, gave 21.3 g. of oil. A fraction of the oil (1.0 g.) was dissolved in a solution of 20 ml. of glacial acetic acid and 5 ml. of 30% hydrogen peroxide and heated on the steam-bath for one hour. The hot oxidation mixture was poured onto ice, and the resulting sulfone filtered and recrystallized from ethanol. The product (0.80 g.) melted at 157–158°, contained both sulfur and chlorine and rapidly decolorized 5% permanganate solution. The sulfone was assumed to be 1-chloro-1,2-di-(*p*-tolylsulfonyl)-ethene (XIIa).[13]

Anal. Calcd. for $C_{16}H_{15}S_2ClO_4$ (XIIa): C, 51.75; H, 4.04. Found: C, 51.50; H, 4.13.

The remainder of the oil (20.3 g.), dissolved in 200 ml. of ethanol, was treated with 100 ml. of alcoholic potassium hydroxide (11 g., 0.20 mole) and refluxed for 15 minutes. As the ethanolic solution was concentrated 15.6 g. of a white, needle-like solid was obtained, m.p. 101–102°. This gave no melting point depression when mixed with an authentic sample of bis-(*p*-tolylmercapto)-ethyne.[12] Based on the amount of XIII formed and *p*-toluenethiol recovered, the conversion in the addition reaction was 75% and the yield 90%.

A sample of the oil obtained in a repetition of the addition reaction could be caused to crystallize from methanol to give a crystalline solid, m.p. 46–47°. This compound also contained both chlorine and sulfur. A fraction of the solid (0.68 g.) was dissolved in a solution of 20 ml. of glacial acetic acid and 5 ml. of 30% hydrogen peroxide and heated on the steam-bath for 1 hour. The hot oxidation mixture was poured on ice, and the resulting sulfone filtered and recrystallized to give 0.74 g. of a crystalline solid, m.p. 157–158° (90% yield). This sulfone did not depress the melting point of an authentic sample of 1-chloro-1,2-di-(*p*-tolylsulfonyl)-ethene (XIIa). On this basis, the product was assigned the structure 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene (XII).

Reaction of 1-Chloro-1,2-di-(*p*-tolylmercapto)-ethene with *p*-Toluenethiol in the Presence of a Catalytic Amount of Sodium *p*-Toluenethiolate.—A solution prepared from 0.85 g. (0.0069 mole) of *p*-toluenethiol, 2.0 g. (0.0059 mole) of 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene, 10 ml. of a sodium ethoxide solution (0.2 g./100 ml., 0.02 g., 0.0008 mole) and 75 ml. of absolute ethanol was refluxed for 18 hours under a nitrogen atmosphere. No sodium chloride was isolated. On concentrating the ethanol solution, 1.70 g. of a solid was obtained, m.p. 157–158°. This did not depress the melting point of an authentic sample of XII. This represents 85% recovery of starting material.

Reaction of 1-Chloro-1,2-di-(*p*-tolylmercapto)-ethene with Sodium *p*-Toluenethiolate in the Presence of Sodium Ethoxide.—The following mixture was heated to reflux under a nitrogen atmosphere for 2 hours: 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene (2.43 g., 0.0071 mole), *p*-toluenethiol (1.06 g., 0.009 mole) and sodium (0.23 g., 0.10 mole) in 75 ml. of absolute ethanol. Sodium chloride was filtered from the hot solution, which on concentration and cooling gave 2.70 g. of solid (XIV), m.p. 56–57° (97% yield). No depression was observed in the melting point of an authentic sample of 1,1,2-tris-(*p*-tolylmercapto)-ethene.

Dehydrohalogenation of 1-Chloro-1,2-di-(*p*-tolylmercapto)-ethene (XII) with Alcoholic Potassium Hydroxide.—A solution prepared from 2.0 g. (0.0065 mole) of 1-chloro-1,2-di-(*p*-tolylmercapto)-ethene, 2.0 g. (0.035 mole) of potassium hydroxide and 50 ml. of ethanol was refluxed for 15 minutes. On cooling the ethanolic solution, 1.65 g. (94% yield) of solid was crystallized, m.p. 101–102°. This did not depress the melting point of an authentic sample of bis-(*p*-tolylmercapto)-ethyne (XIII).[12]

Reaction of Bis-(*p*-tolylmercapto)-ethyne (XIII) with *p*-Toluenethiol.—Sodium (0.10 g., 0.004 mole) was dissolved in absolute ethanol followed by *p*-toluenethiol (2.4 g., 0.0195 mole) so that the total volume was 100 ml. This was added rapidly to a refluxing solution of XIII (5.0 g., 0.020 mole) in 50 ml. of absolute ethanol and allowed to reflux for an additional hour under a nitrogen atmosphere. After concentration to approx. 100 ml., the solution on cooling gave 6.5 g. (90% yield) of solid, m.p. 56–57°. No depression was observed in the mixed melting point of the above product and an authentic sample of 1,1,2-tris-(*p*-tolylmercapto)-ethene.

Reaction of 1,1,2-Tris-(*p*-tolylmercapto)-ethene (XIV) with *n*-Butyllithium.—A solution of *n*-butyllithium in ether (100 ml.) was prepared from lithium wire (1 g., 0.14 mole) and *n*-butyl bromide (7.6 g., 0.055 mole) by the method of Gilman.[14] A solution of XIV (10.0 g., 0.025 mole) in 50 ml. of anhydrous ether was added to the *n*-butyllithium solution with stirring, and maintained at 0° for 2 hours under a nitrogen atmosphere. The solution was allowed to warm up to room temperature and stirred for an additional 2 hours and then quenched with 50 ml. of water. The ether layer was separated and dried over magnesium sulfate while the aqueous layer was acidified with concd. hydrochloric acid, and extracted with petroleum ether (35–37°) which was dried over magnesium sulfate. On evaporation of petroleum ether, 3.55 g. (0.028 mole) of *p*-toluenethiol, m.p. 40–42°, was obtained. Evaporation of the ether solution gave a material, which was recrystallized from ethanol to give 1.84 g. of solid, m.p. 101–102°. This did not depress the melting point of an authentic sample of bis-(*p*-tolylmercapto)-ethyne. The yield of XIV was 37%.

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(14) H. Gilman and J. W. Morton, Jr., "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 285.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Epoxyethers. XII.[1] Reduction with Lithium Aluminum Hydride

BY CALVIN L. STEVENS AND THOMAS H. COFFIELD[2,3]

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Five epoxyethers were subjected to reduction with lithium aluminum hydride reagent. Each of the epoxyethers I–IV was reduced in *ca.* 80% yield by attack of hydride ion upon the carbon containing the ether group. No evidence was found for partial attack upon the other carbon of the oxide. The triphenyl substituted epoxyether V was not reduced. The structures of the methoxy alcohols VI, VII and IX were proven by independent synthesis. A new and convenient method for the preparation of solid ester derivatives of tertiary alcohols was found which involved reaction with sodium dispersion to form the alcohol salt and then reaction with *p*-nitrobenzoyl chloride.

From the various acid-catalyzed openings of epoxyethers that have been investigated, previously the epoxyethers have been shown to open significantly faster than ordinary oxides and the opening reaction has been shown to proceed by attack of the nucleophilic agent on the epoxide carbon that contained the ether group.[4] The ease and direction of opening are predictable from the known ability of the ether group to facilitate the development of a positive charge on an adjacent carbon (in this example, the ketal carbon of the epoxyether). This property of the ether group has also been used to explain the ease and direction of the acid-catalyzed rearrangement of epoxyethers.[5]

The chemical reduction of epoxyethers with lithium aluminum hydride is here shown to follow the course of the previous acid-catalyzed ring opening reactions. In the reactions, hydride ion attacked the ketal carbon to give methoxy alcohols. The

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(1) Paper XI is the THIS JOURNAL, **79**, 3448 (1957).

(2) Abstracted from the dissertation submitted by T. H. Coffield in partial fulfillment of the requirement for the degree of Doctor of Philosophy, Wayne University, 1955.

(3) Ethyl Corporation Fellow.

(4) C. L. Stevens, M. L. Weiner and C. T. Lenk, THIS JOURNAL, **76**, 2698 (1954), and preceding papers in the epoxyether series.

(5) C. L. Stevens and S. J. Dykstra, *ibid.*, **76**, 4402 (1954).