were calculated by the Hedestrand equation. A heterodyne beat method, using a 100 Kc. crystal-controlled oscillator, was used to measure the dielectric constants of the dilute dioxane solutions.

Acknowledgment.—The authors gratefully acknowledge support of this work by the Office of Ordnance Research, Department of the Army, under Contract No. DA 33-008-ORD-983 and by the Air Force Office of Scientific Research under Contract No. A. F49(638)531.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Stereochemistry of the Nucleophilic Addition of *p*-Toluenethiol to Ethoxyacetylene[1,2]

BY WILLIAM E. TRUCE AND DAVID L. GOLDHAMER

RECEIVED APRIL 20, 1959

The Rule of *trans*-Nucleophilic Addition has been tested further by the addition of *p*-toluenethiol to ethoxyacetylene and ethanol to *p*-tolylmercaptoacetylene (formed *in situ* from *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene) to yield *cis*-1-ethoxy-2-(*p*-tolylmercapto)-ethene, from both reactions. The configurational assignments were based on spectral studies, an independent stereoselective synthesis and the analogous addition of *p*-toluenethiol to *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene to give *cis*-bis-(*p*-tolylmercapto)-ethene.

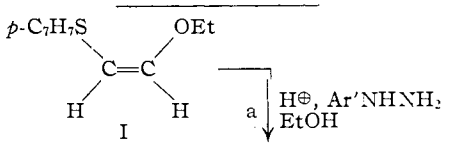
In the investigation of the reactivity of acetylenic ethers, Arens and co-workers have added ethyl mercaptan to ethoxyacetylene. This reaction, postulated as proceeding by a free radical mechanism, gives a mixture of *cis*- and *trans*-1-ethoxy-2-(ethylmercapto)-ethene.[3]

$$HC\equiv COC_2H_5 + C_2H_5SH \longrightarrow$$

cis- and *trans*-$C_2H_5SCH{=}CHOC_2H_5$

A more stereoselective addition occurred when sodium ethanethiolate was added to ethylmercaptoacetylene to give *cis*-1,2-bis-ethylmercaptoethene.[4] This report concerns our related work (begun in 1955) on the base-catalyzed addition of *p*-toluenethiol to ethoxyacetylene.

$$HC{\equiv}COEt + p\text{-}C_7H_7SNa(EtOH) \longrightarrow$$



Ar' = 2,4-dinitrophenyl

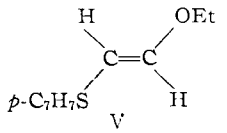
$$ClCH_2CH(OEt)_2 \xrightarrow[\text{abs. EtOH}]{p\text{-}C_7H_7SNa} p\text{-}C_7H_7SCH_2CH(OEt)_2 \xrightarrow[\text{EtOH}]{H^{\oplus},\ Ar'NHNH_2} p\text{-}C_7H_7SCH_2CH{=}NNHAr'$$

III IV b II, mixture of *syn* and *anti* isomers

Since *cis*-1-ethoxy-2-(*p*-tolylmercapto)-ethene (I) contains a vinyl ether group, it could be converted to *p*-tolylmercaptoacetaldehyde by acid hydrolysis and simultaneously derivatized to its corresponding hydrazone by initially placing 2,4-dinitrophenylhydrazine in the reaction mixture. Compound II was independently synthesized by the displacement reaction by sodium *p*-toluenethiolate on chloroacetaldehyde diethylacetal (III) to form *p*-tolylmercaptodiethylacetal (IV).[5] The same hydrolysis procedure used in reaction a was employed in reaction b to give II. The infrared absorption spectra of the hydrazone derivatives from reactions a and b were nearly identical except for the difference in relative proportions of *syn* and *anti* isomers; however, their analyses were identical.

An independent stereoselective synthesis of I together with a small amount of the *trans* isomer could be effected by heating IV with anhydrous potassium pyrosulfate.[6]

$$p\text{-}C_7H_7SCH_2CH(OEt)_2 \xrightarrow[\Delta]{K_2S_2O_7} I +$$

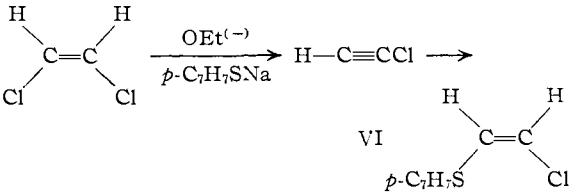


V

A facile separation of I and V was carried out with a spinning band column.

Samples of I and V were separately subjected to refluxing with alcoholic base for 48 hours to assure that isomerization did not occur during the formation of the adduct. In both cases original starting materials could be recovered.

An authentic sample of *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene (VI) was prepared by the stereospecific nucleophilic addition of *p*-toluenethiol to chloroacetylene.[7]



VI

(1) This constitutes Paper XIII in the series, "Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides"; for preceding paper see THIS JOURNAL, **81**, 5795 (1959).

(2) Abstracted from the Ph.D. Thesis of David L. Goldhamer, Purdue University, 1959.

(3) J. F. Arens, *et al.*, *Proc. Koninkl. Nederl. Akad. Wetenschap.*, **B58**, 78 (1955).

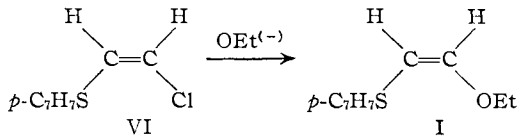
(4) H. C. Volger and J. F. Arens, *Rec. trav. chim.*, **76**, 847 (1957).

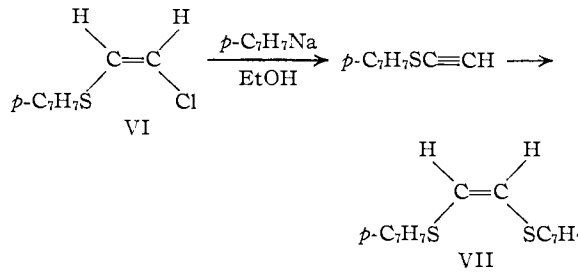
(5) F. Arndt and C. Martius, *Ann.*, **499**, 228 (1932).

(6) J. F. Arens, *et al.*, *Rec. trav. chim.*, **77**, 753 (1958).

(7) W. E. Truce, M. M. Boudakian, R. F. Heine and R. J. McManimie, THIS JOURNAL, **78**, 2746 (1956).

When VI was treated with sodium ethoxide in ethanol a 44% yield of I was formed. This reaction presumably proceeds with initial dehydrohalogenation to form the intermediate *p*-tolylmercaptoacetylene *in situ* followed by *trans* nucleophilic addition of ethanol to the acetylene. This elimination–addition sequence to over-all displacement of halogen is analogous to that observed when VI is treated with *p*-toluenethiol in the presence of excess sodium ethoxide to form *cis*-bis-(*p*-tolylmercapto)-ethene (VII).





The addition of *p*-toluenethiol to independently synthesized *p*-tolylmercaptoacetylene also furnished VII in a stereospecific manner.

Infrared spectra suggest that compound I is the *cis*-1-ethoxy-2-(*p*-tolylmercapto)-ethene and V is the corresponding *trans* isomer. Characteristic in-plane and out-of-plane bending vibrations of *cis*-ethylenic hydrogens were observed as strong bands, at 7.80 and 15.18 μ, respectively, for compound I. These bonds compare favorably with those of *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene (7.78 and 15.20 μ). Compound V exhibited the *trans*-ethylenic in-plane and out-of-plane bending vibration bands at 8.47(m) and 11.05(s)μ as compared to an authentic sample of *trans*-1-chloro-2-(*p*-tolylmercapto)-ethene at 8.44(m) and 11.05(s)μ.[8] A mixture of isomers I and V displayed two (C=C) stretching vibrations at 6.14 and 6.25 μ, exclusive of the aromatic stretching vibrations at 6.42 and 6.72μ.

In summary, the Rule of *trans*-Nucleophilic Addition has been demonstrated to apply to ethoxyacetylene. Configurational assignments to isomers I and V were based on (a) spectral studies, (b) an independent stereoselective synthesis to form I and (c) the analogous reaction of *p*-toluenethiolate reagent with *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene to give *cis*-bis-(*p*-tolylmercapto)-ethene.

Experimental[9]

Reaction of Ethoxyacetylene and *p*-Toluenethiol. Preparation of I.—Ethoxyacetylene was prepared by treating the diethyl acetal of chloroacetaldehyde with sodium amide in liquid ammonia and hydrolyzing the sodioethoxyacetylide, b.p. 51.0°, n^{20}D 1.3781 (lit.[10] b.p. 50–52°, n^{20}D 1.3796).

To a solution of 4.6 g. (0.20 mole) of freshly cut sodium dissolved in 200 ml. of absolute ethanol was added 24.8 g. (0.20 mole) of *p*-toluenethiol (Eastman Kodak Co., white label). Ethoxylacetylene (14 g., 0.20 mole) in an equal volume of absolute ethanol was introduced slowly by means of a dropping funnel into the solution which was refluxed under a nitrogen atmosphere for 18 hours. After the solvent was evaporated (no ethoxyacetylene was recovered) distilled water was added to the residue. This solution was extracted with ether several times and excess base was added to remove all traces of *p*-toluenethiol from the ether layer which was then separated, dried over sodium sulfate and evaporated. The residue furnished a clear colorless liquid which distilled completely at 135° (7 mm.), n^{25}D 1.5500, yield 20.9 g. (54%) of *cis*-1-ethoxy-2-(*p*-tolylmercapto)-ethene.

Anal. Calcd. for $C_{11}H_{14}OS$: C, 68.0; H, 7.27; S, 16.5; mol. wt., 194. Found: C, 68.25; H, 7.50; S, 16.45[11]; mol. wt., 187.

Acid Hydrolysis of *cis*-1-Ethoxy-2-(*p*-tolylmercapto)-ethene (I).—A solution of 0.194 g. (1 mmole) of I was introduced into a solution of 0.200 g. (1 mmole) of 2,4-dinitrophenylhydrazine containing 1 ml. of concentrated sulfuric acid 15 ml. of ethanol. When this mixture was heated to approximately 70° an orange precipitate formed, which was digested for about half an hour. The solution was cooled and filtered to give 0.18 g. (0.52 mmole) of the 2,4-dinitrophenylhydrazone of *p*-tolylmercaptoacetaldehyde (II). The crude material was crystallized by dissolving it in boiling ethanol and adding ethyl acetate drop by drop until the solution was clear. The boiling solution was then filtered and cooled. This process was carried out twice, using only the first crop of fine crystals which were then washed with cold ethanol and dried, m.p. 106.5°, yield 52%. Its infrared absorption band and intensities in Nujol mull were 3.10(s), 3.50(m), 6.20(s), 6.65(m), 7.05(s), 7.30(m), 7.55(s-m), 7.90(m), 8.25(s), 8.75(s), 9.40(m), 10.70(m), 10.90(b), 12.05(m), 12.43(s), 13.45(s) and 13.85(m) μ.

Anal. Calcd. for $C_{15}H_{14}N_4O_4S$: C, 52.0; H, 4.07; N, 16.2. Found: C, 52.29; H, 4.20; N, 16.08.

Preparation of *p*-Tolylmercapto Diethlyacetal (IV).—A solution of 2.3 g. (0.10 mole) of sodium and 12.4 g. (0.10 mole) of *p*-toluenethiol in 40 ml. of absolute alcohol was added slowly over a period of two hours to 15.3 g. (0.10 mole) of chloroacetaldehyde diethylacetal. Salt formation was observed within 15 minutes as the reaction mixture became cloudy. After cooling, the salt was filtered and the solution concentrated. After a preliminary micro-distillation, fractionation was carried out on the spinning bond column, b.p. 122° (1 mm.), n^{20}D 1.5219 (lit.[5] b.p. 165° (14 mm.), yield 82%.

Anal. Calcd. for $C_{13}H_{20}O_2S$: C, 64.8; H, 8.4. Found: C, 64.6; H, 8.2.

Acid Hydrolysis of *p*-Tolylmercapto Diethylacetal (IV).—A solution of 0.240 g. (1 mmole) of *p*-tolylmercapto diethylacetal in 3 ml. of ethanol was introduced into a solution of 0.200 g. (1 mmole) of 2,4-dinitrophenyl-hydrazine containing 1 ml. of concentrated sulfuric acid in 15 ml. of ethanol. When this mixture was slightly heated an orange solid precipitated and the solution was digested for 0.5 hour more. The solution was cooled and filtered to give 0.25 g. (0.72 mmole) of the 2,4-dinitrophenylhydrazone derivative of *p*-tolylmercaptoacetaldehyde (II). The crude material was worked up as stated before, m.p. 112°, yield 72%. Its infrared absorption bands and intensities were 3.10(s), 3.30(m), 6.20(s), 6.30(s), 6.65(m), 7.05(s), 7.75(s-m), 7.90(m), 8.25(s), 8.75(s), 9.40(m), 10.70(m), 10.90(b), 12.05(m), 12.40(s), 13.45(s) and 13.85(m)μ.

Anal. Calcd. for $C_{15}H_{14}N_4O_4S$: C, 52.00; H, 4.07. Found: C, 52.18; H, 3.80.

Independent Synthesis of *cis*-1-Ethoxy-2-(*p*-tolylmercapto)-ethene. Reaction of *p*-Tolylmercapto Diethylacetal with Potassium Pyrosulfate.—A 100-ml. round-bottom flask equipped with a magnetic stirrer and a 20-cm. Widmer column, was provided with 0.192 g. (0.75 mmole) of pow-

(8) W. E. Truce and M. M. Boudakian, THIS JOURNAL, **78**, 2748 (1956).

(9) The microanalyses were done by Dr. C. S. Yeh and Mrs. B. Groten of the Purdue Chemistry Microanalytical Laboratory. The infrared spectra were run by Miss M. Healy and Mrs. W Dilling of the Purdue Chemistry Infrared Laboratory with a Perkin–Elmer, infrared spectrophotometer, model 21. All boiling and melting points are uncorrected.

(10) E. R. H. Jones, *et al.*, *J. Chem. Soc.*, 1860 (1954).

(11) Analysis for sulfur done by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

dered anhydrous potassium pyrosulfate and 14.9 g. (0.062 mole) of *p*-tolylmercapto diethylacetal and then heated in an oil-bath with efficient stirring. At about 140° (oil-bath temperature) the elimination began and alcohol slowly distilled. This temperature was maintained until ethanol ceased to distil. The reaction mixture was cooled, filtered and then distilled on the spinning band column under vacuum to yield four fractions: (1) *trans*-isomer V (1.5 g.), b.p. 130-131° (7 mm.), $n^{25}D$ 1.5405; (2) an intermediate fraction (1.3 g.), b.p. 131–34° (7 mm.), $n^{25}D$ 1.5455; (3) *cis*-isomer I (7.5 g.), b.p. 135° (7 mm.), $n^{25}D$ 1.5500; (4) residue (0.83 g.), mainly unreacted IV.

An infrared spectrum of fraction 1 showed *trans*-ethylenic in-plane and out-of-plane bending vibration bands at 8.47(m) and 11.05(s) μ.

Anal. Calcd. for $C_{11}H_{14}OS$: C, 68.0; H, 7.27. Found: C, 67.69; H, 7.25.

Fraction 2 exhibited two (C=C) stretching vibrations at 6.14 and 6.25 μ. Fraction 3 had the same infrared spectrum as that obtained from the reaction product of *p*-toluenethiol and ethoxyacetylene.

Attempted Isomerizations of *cis*- and *trans*-1-Ethoxy-2-*p*-tolylmercapto)-ethene.—*cis*-1-Ethoxy-2-(*p*-tolylmercapto)-ethene (1.94 g., 0.01 mole) was dissolved in 200 ml. of a solution of 0.01 mole of sodium ethoxide in absolute ethanol. After 48 hours of refluxing, ethanol was evaporated and distilled water was added. This mixture was neutralized with cold dilute hydrochloric acid, extracted with ether and dried over sodium sulfate. This material distilled at the same temperature as starting material, b.p. 135° (7 mm.), and had the same infrared spectrum. Similar results were obtained with the *trans* isomer, V.

Reaction of *cis*-1-Chloro-2-(*p*-tolylmercapto)-ethene with Sodium Ethoxide. Preparation of I.—*cis*-1-Chloro-2-(*p*-tolylmercapto)-ethene (VI) was prepared by treating chloroacetylene with *p*-toluenethiol; b.p. 89–91° (0.75 mm.) (lit.[7] b.p. 99–102° (2.2 mm.). A soluton of VI (4.33 g., 0.0235 mole) in 30 ml. of absolute ethanol was slowly added to 50 ml. of an ethanolic sodium ethoxide solution [1.08 g. (0.047 g. atom) of sodium] at reflux with good stirring and under a nitrogen atmosphere. After 10 hours 0.66 g. (0.011 mole) of sodium chloride was isolated upon filtering the reaction mixture and washing the salt with hot absolute ethanol. The extract was combined with the filtrate, concentrated, diluted with water, and extracted with ether. The ether layer was neutralized with cold dilute hydrochloric acid, washed with water, dried over sodium sulfate and evaporated. Distillation on the spinning band column gave the same material as that formed from the addition of *p*-toluenethiol to ethoxyacetylene, b.p. 135° (7 mm.), 43.9% yield.

Acknowledgment.—The authors wish to express their appreciation for the financial support of this work by the Office of Ordnance Research, Department of the Army, under Contract No. DA-33-008-ORD-983.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

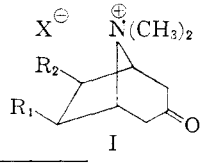
Elimination Reactions of Bicyclic Quaternary Salts. IV.[1] The Conversion of Scopinone into *m*-Hydroxybenzaldehyde

BY JERROLD MEINWALD AND ORVILLE L. CHAPMAN[2]

RECEIVED MARCH 23, 1959

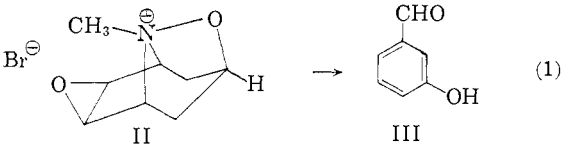
The report that scopinium bromide (II) gives rise to *m*-hydroxybenzaldehyde (III) upon treatment with base has led to a study of the corresponding ketone, scopinone (IV); IV, as well as its methobromide VI, was found to suffer a degradative rearrangement, yielding III, with extreme readiness. This observation presents a sharp contrast to the behavior of many closely related tropane derivatives, which are generally more stable to base, and whose quaternary salts undergo normal eliminations unaccompanied by skeletal rearrangement. Some tentative mechanisms for the transformation of IV and VI into III are discussed briefly.

Introduction.—Recent studies have shown that the base-catalyzed elimination reactions of tropinone methiodide (Ia)[3] and of a variety of closely related, substituted quaternary salts (Ib-f)[1,4,5] proceed to give the expected derivatives of cycloheptanone, without rearrangement of the parent carbon skeleton. In view of these results, the report by Polonovski and Polonovski that scopinium bromide (II) is degraded by base to *m*-hydroxybenzaldehyde (III)[6] as shown in equation 1 is of particular interest. The work described in this paper was undertaken with the aim of casting additional light on this anomalous transformation.



I

a, $R_1 = R_2 = H$
b, $R_1 = R_2 = OH$
c, $R_1 = R_2 = OCH_3$
d, $R_1, R_2 = -OC(CH_3)_2O-$
e, $R_1 = H, R_2 = OH$
f, $R_1 = OH, R_2 = OCH_3$



II III (1)

Discussion.—The preparation of scopinium bromide (II) was the first objective of the present study. Although the conversion of scopolamine to II by the action of hydrogen peroxide has been described in a fairly detailed manner,[6] several attempts to reproduce the procedure gave scopolamine-N-oxide hydrobromide as the only characterizable product.[7] A variety of other attempts

(1) For the previous paper in this series see J. Meinwald and O. L. Chapman, THIS JOURNAL, **80**, 633 (1958). A preliminary Communication describing some of the present results has appeared in *Tetrahedron*, **3**, 311 (1958). For an excellent review of the elimination reactions of bicyclic compounds, see A. Heusner, *Angew. Chem.*, **70**, 639 (1958).

(2) Procter and Gamble Fellow, 1956–1957.

(3) J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, THIS JOURNAL, **77**, 4401 (1955).

(4) J. Meinwald and O. L. Chapman, *ibid.*, **78**, 4816 (1956).

(5) E. E. van Tamelen, P. Barth and F. Lornitzo, *ibid.*, **78**, 5442 (1956).

(6) M. Polonovski and M. Polonovski, *Compt. rend.*, **180**, 1775 (1925); **185**, 277 (1927); **186**, 147 (1928); *Bull. soc. chim. France*, **43**, 79 (1928); **42**, 1468 (1927); **39**, 1162 (1926). See also R. H. F. Manske and H. C. Holmes, "The Alkaloids," Vol. I, Academic Press, Inc., New York, N. Y., 1950, pp. 302—307.

(7) Professor G. Fodor has kindly informed us that the published procedure for obtaining scopinium bromide was unsuccessful in his Laboratory as well.