10^{-6} molar concentrations that were used, it is not possible to see the precipitation visibly so that the best indication was failure to follow Beer's law.

In several cases the sulfuric acid solutions of the diarylalkyl cations were not completely stable. Readings were made during the first 100 sec. and the data extrapolated to obtain an estimate of the optical density at zero time.

With several diarylalkyl cations, only visual observations were made, generally because of extreme instability. These visual estimates of the equilibria appear in Table II.

Recovery Experts.—Samples of the diarylolefins were shaken for 3 min. with 10 times their weight of 97% sulfuric acid and then poured into water. The yields of products recovered were 1,1-diphenylethylene (35%) and its dimer (50%), 1,1-diphenyl-2-methylpropene (75%), 1,1-diphenylpropene (80%), 1,1-bis-(4′-methoxyphenyl)-ethylene (100%), 1,1-bis-(4′-methylphenyl)-ethylene (100%) and 1,1-bis-(4′-chlorophenyl)-ethylene (90%). All precautions were taken to prevent any dehydration of alcohol to olefin during the recovery procedure, and in the last four cases, the olefins were crystalline and were directly filtered off and recrystallized. With several of the olefins, recovery experiments were also conducted at the acid concentration at which the olefin is half-converted to cation.

UNIVERSITY PARK, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Stereochemistry of the Base-catalyzed Addition of *p*-Toluenethiol to Sodium and Ethyl Phenylpropiolate[1,2]

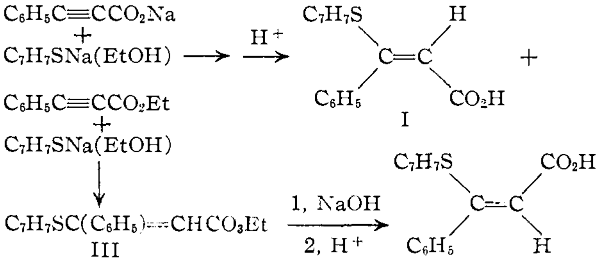
BY WILLIAM E. TRUCE AND DAVID L. GOLDHAMER

RECEIVED APRIL 20, 1959

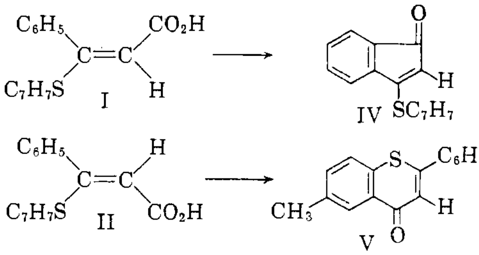
p-Toluenethiol was added to ethyl phenylpropiolate to give, after saponification, *trans*-β-*p*-tolylmercaptocinnamic acid, in accord with the Rule of *trans*-Nucleophilic Addition. However, a violation of this rule is observed when *p*-toluenethiol is added to sodium phenylpropiolate to give *cis*-β-*p*-tolylmercaptocinnamic acid.[3] Dipole moment measurements are used in support of these tentative configurational assignments.

Ruhemann added sodium *p*-toluenethiolate, in toluene, to ethyl phenylpropiolate to form ethyl β-*p*-tolylmercaptocinnamate, which was converted to "*trans*"-β-*p*-tolylmercaptocinnamic acid, m.p. 167° dec.,[4] upon saponification with alcoholic base and subsequent acidification. When the latter acid was treated with phosphorus pentachloride and aluminum chloride, 6-methylthioflavone was formed.

In order to establish the configuration of Ruhemann's addition product, it was decided to synthesize both *cis*- and *trans*-β-*p*-tolylmercaptocinnamic acids, compounds I and II, respectively. Accordingly, *p*-toluenethiol in the presence of a small amount of sodium *p*-toluenethiolate was refluxed in an aqueous ethanolic solution with sodium phenylpropiolate to give a 65% yield of a mixture of two acids, m.p. 189° dec. (I) and 175° dec. (II), after a series of fractional crystallizations. Isomer I made up 92% of the total product, the remainder being II. Characterization of the isomeric acids was based on analyses, neutral equivalents, mixture melting points[5] infrared spectra and the ability to isomerize I and cyclize it, as well as II, by Friedel–Crafts conditions, to the same 6-methylthioflavone (V), m.p. 150°.



An attempt was made to establish the geometrical configurations of the isomeric acids I and II by relating them to two different possible cyclic compounds IV and V, or at least to the single cyclic compound V which would be preferentially formed from isomer II, as outlined.



However, treatment of both of the isomeric arylmercaptocinnamic acids I and II with phosphorus pentachloride followed by aluminum chloride as well as treatment with anhydrous liquid hydrogen fluoride resulted in the formation of one and the same product from each acid.

$$\text{I or II} \xrightarrow{PCl_5}\ ;\ \xrightarrow{AlCl_3} \text{V} \xleftarrow{HF} \text{I or II}$$

These apparent isomerizations, preceding cyclization, are also noted in Ruhemann's cyclization of a mixture of I and II, leading to compound V exclusively.[4,5]

Perhaps this isomerization occurs in the following manner, at the stage shown below.

Presumably a greater contribution from resonance forms b and d (involving C–C single bonds

---

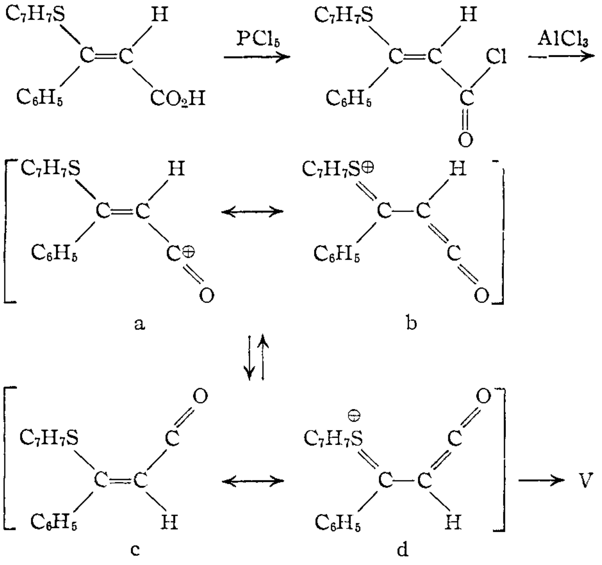
[1] This constitutes Paper XII in the series, "Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides"; for preceding paper see THIS JOURNAL, **81**, 4931 (1959).

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

[3] An exception to the Rule of *trans*-Nucleophilic Addition was noted in the base-catalyzed addition of *p*-toluenethiol to sodium propiolate to give *trans*-β-*p*-tolylmercaptoacrylic acid; W. E. Truce and R. F. Heine, THIS JOURNAL, **79**, 5311 (1957).

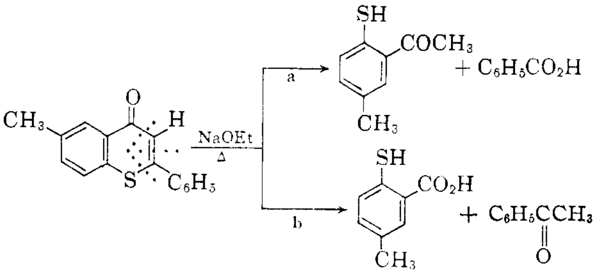
[4] Upon heating, β-arylmercaptocinnamic acids liberate carbon dioxide and are converted to arylmercaptostyrenes; S. Ruhemann, *Ber.*, **46**, 3388 (1913).

[5] Ruhemann reports a product with a melting point of 167° resulting from the addition of sodium *p*-toluenethiolate to ethyl phenylpropiolate. This melting point corresponds closely to that of the mixture melting point of acids I and II, m.p. 165–166°; see ref. 4.



at the olefinic linkage) would facilitate interconversion between the isomeric incipient acylium ions (drawn as full-fledged ions in the accompanying diagram). The driving force for over-all conversion to cyclic product V in preference to IV probably arises from a combination of factors including the formation of a more stable ring system,[6] and electrophilic attack on the more activated nucleus.

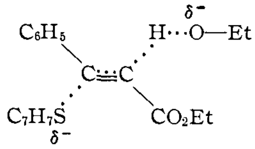
A structure determination of V has been carried out by degradation studies to eliminate the alternative possibility of formation of 3-*p*-tolylmercaptoindenone (IV) during the cyclization.[4,7] The degradation was accomplished with concentrated so-



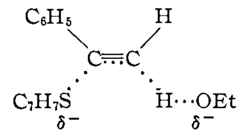
dium ethoxide forming two sets of compounds, paths a and b, in addition to some disulfide formation from the thiophenols. Characterization of these products establishes the fact that the sulfur atom is indeed incorporated in the new ring which is not the case with structure IV.

Thiolate reagent was then added to an absolute ethanolic solution of ethyl phenylpropiolate containing a catalytic amount of sodium ethoxide. A solid ester, ethyl β-*p*-tolylmercaptocinnamate (III, m.p. 72°), was formed. A mild saponification of III with ethanolic sodium hydroxide followed by acidification yielded II exclusively. In an attempt to preclude isomerization possibilities during the course of formation of these acids, I and II were refluxed with alcoholic base for a period of 48 hours. Isolation of the original acids demonstrated that isomerization had not occurred.

Hence, although the Rule of *trans*-Nucleophilic Addition is adhered to by the acetylenic ester, an anomalous *cis*-addition to the acetylenic acid salt is observed again.[3]

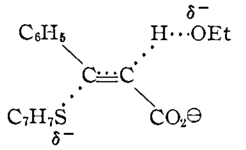


1

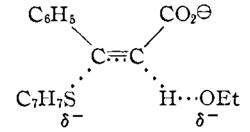


2

Diagrams 1 and 2 represent possible transition states for *trans* and *cis* addition of *p*-toluenethiol to ethyl phenylpropiolate. Based on the lower coulombic repulsion of partial negative charges in 1 as opposed to 2, *trans* addition would be favored due to a lower activation energy.



3



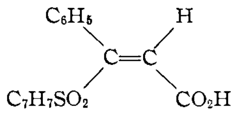
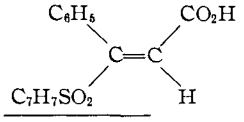
4

The pattern of addition to sodium phenylpropiolate reverses itself due to the presence of the negatively charged carboxylate ion. The incipient bond formation of the thiol would force a partial negative charge into the field of the carboxylate ion in 3, whereas the more favorable *cis* addition involves the lower energetic interaction of two partial negative charges as depicted in 4. Proponents of a theory of steric inhibition of solvation influencing the stereochemistry of addition, in the case of sodium propiolate, would have difficulty in explaining the more rigid steric requirements for the transition state of sodium phenylpropiolate in view of almost pure *trans* addition.

The tentative assignments of geometrical configurations to I and II were based on a series of dipole moment measurements. Dipole moment studies are useful in the determination of configuration, being especially applicable to rigid molecules, such as benzene derivatives and symmetrically substituted olefins.[8] These determinations can be extended to unsymmetrically substituted olefins where the relative magnitude of the dipole moments for the *cis* and *trans* compounds are predictable and both isomers are measured. Table I shows a greater differential

TABLE I

DIPOLE MOMENTS OF *cis*- AND *trans*-β-*p*-TOLYLMERCAPTO AND SULFONYLCINNAMIC ACIDS

Structures	M.p., °C.	$P_{2\infty}$	P_e	μ, D
II	175	247.37	38.10	3.20
I	189	242.94	24.66	3.27
	150	446.39	58.74	4.35
	148	349.83	45.83	3.85

---

[6] W. S. Johnson, "Organic Reactions," Vol. II, Chapter 4, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 116.

[7] W. Feuerstein and St. v. Kostanecki, *Ber.*, **31**, 1760 (1898).

[8] W. H. King and H. A. Smith, THIS JOURNAL, **72**, 3459 (1950).

and magnitude between dipole moments when I and II are oxidized to the corresponding *cis*- and *trans*-β-*p*-tolylsulfonylcinnamic acids, m.p. 150° and 148°, respectively. These sulfones were characterized by their analyses, neutralization equivalents, infrared spectra and mixture melting point, m.p. 123–133°. Our dipole moment measurements are all being repeated by a single operator (B. Groten) and with improved apparatus in order to make such comparisons more meaningful.

Experimental[9]

Addition of *p*-Toluenethiol to Sodium Phenylpropiolate.—Phenylpropiolic acid was prepared by the addition of bromine to cinnamic acid followed by dehydrohalogenation with methanolic potassium hydroxide and finally acid hydrolysis, m.p. 136° (lit.[10] 136–138°). A solution prepared from 0.46 g. (0.02 mole) of sodium, 12.4 g. (0.10 mole) of *p*-toluenethiol (Eastman Kodak Co., white label) and 100 ml. of absolute ethanol was added dropwise, with efficient stirring and under a nitrogen atmosphere, to a solution prepared from 2.3 g. (0.1 mole) of sodium and 14.6 g. (0.1 mole) of phenylpropiolic acid in 150 ml. of absolute ethanol. Just enough water was added to dissolve the sodium phenylpropiolate. The mixture was refluxed for 7 hours. Excess ethanol was evaporated and a saturated solution of sodium bicarbonate was added to the mixture. This new solution was extracted with ether and the aqueous layer was neutralized with dilute hydrochloric acid, in the cold. Crystals precipitated and were filtered to give 13.5 g. of crude product, m.p. 185–187° dec., m.p. 189° dec. after recrystallizaton from ethanol. The chilled mother liquor yielded 4.05 g. of crystals which could be fractionally crystallized from methanol to give 2.64 g., m.p. 189° dec., and 2.32 g., m.p. 175° dec.; total yield 65%.

Anal. Calcd. for $C_{16}H_{14}O_2S$: C, 71.1; H, 5.21; neut. equiv., 270.3. Found for m.p. 189°: C, 71.22; H, 5.50; neut. equiv., 273.1. Found for m.p. 175°: C, 71.00; H, 5.05; neut. equiv., 273.8.

Addition of *p*-Toluenethiol to Ethyl Phenylpropiolate.—Ethyl phenylpropiolate was prepared by saturating a solution of phenylpropiolic acid in absolute ethanol with anhydrous hydrogen chloride gas[11] or by treating a suspension of sodiophenylacetylene with ethyl chlorocarbonate; b.p. 128° (10 mm.), n^{25}D 1.5505 (lit.[12] b.p. 153° (22 mm.). A solution prepared from 0.392 g. (0.017 mole) of sodium and 10.6 g. (0.085 mole) of *p*-toluenethiol in 150 ml. of "superdry ethanol"[13] was added dropwise with stirring and under a nitrogen atmosphere to 14.8 g. (0.085 mole) of ethyl phenylpropiolate in an equal volume of "superdry ethanol." The mixture was refluxed overnight. Upon cooling, ethanol was evaporated to concentrate the solution, which was then extracted with ether. The ether extract was then treated with cold 5% sodium hydroxide, the aqueous layer separated, and the ether layer neutralized with dilute acid, washed with water and dried over sodium sulfate. The ether was evaporated and the remaining solid taken up in 30–60° petroleum ether, charcoal filtered and recrystallized several times from the petroleum ether to yield 8.5 g. of ester, m.p. 72°, yield 33.4%.[14]

Anal. Calcd. for $C_{18}H_{18}O_2S$: C, 72.4; H, 6.09. Found: C, 72.42; H, 6.06.

Ethyl-β-*p*-tolylmercaptocinnamate (1.19 g., 0.004 mole), was added to a solution containing 0.092 g. (0.004 mole) of sodium, 90 ml. of alcohol and 10 ml. of water. The mixture was refluxed for two hours. Then the ethanol was evaporated, the solid residue taken up in water, neutralized, filtered, washed with cold ethanol and finally recrystallized several times from ethanol, m.p. 175°. This sample had an identical spectrum to *trans*-β-*p*-tolylmercaptocinnamic acid (II), and a mixture melting point with II gave no depression, m.p. 175°.

Attempted Isomerization of β-*p*-Tolylmercaptocinnamic Acids.—*cis*-β-*p*-Tolylmercaptocinnamic acid (I) (2.70 g., 0.01 mole) was refluxed for 48 hours in 200 ml. of a solution of 0.01 mole of sodium ethoxide in absolute ethanol. Dilute hydrochloric acid was slowly added. in the cold, to neutralize the base. The resulting precipitate was filtered, washed and air-dried to yield 2.63 g. of residue, m.p. 189°, which showed no depression in a mixture melting point determination with starting material. The *trans* isomer II, m.p. 175°, was treated in a similar manner and yielded only unaltered starting material.

Cyclizations of β-*p*-Tolylmercaptocinnamic Acids.—To a solution of *trans*-β-*p*-tolylmercaptocinnamic acid (1.12 g., 0.0042 mole) in 60 ml. of anhydrous benzene was added, with stirring over a 30-minute period, phosphorus pentachloride (0.86 g., 0.0042 mole). Upon addition of 3.34 g. (0.0084 mole) of anhydrous aluminum chloride, a dark red coloring of the solution was observed. The solution was stirred for one hour at room temperature and then the reaction mixture was poured over cracked ice. The mixture was extracted with ether and the extracts dried over sodium sulfate. When the benzene and ether were evaporated an orange solid remained. After charcoal filtration and several recrystallizations from methanol, an almost quantitative yield of 6-methylthioflavone was obtained, m.p. 150° (lit.[15] m.p. 149–150°).

Anal. Calcd. for $C_{16}H_{12}OS$: C, 76.25; H, 4.79. Found: C, 76.00; H, 4.81.

Similar results were obtained when *cis*-β-*p*-tolylmercaptocinnamic acid was subjected to the Friedel–Crafts cyclization.

To 0.48 g. (0.0018 mole) of *trans*-acid II, in a platinum crucible immersed in a Dry Ice-bath, was added anhydrous liquid hydrofluoric acid in approximately ten times the amount of acid by weight. A dark colored solution was formed immediately. The solution was left overnight to evaporate excess hydrofluoric acid. A saturated solution of sodium carbonate was used to neutralize the solid residue, and the resulting solution was extracted with ether. After drying over sodium sulfate, evaporating the ether, and recrystallizing the solid residue several times from methanol a quantitative yield of flavone was formed which did not depress a mixture melting point with a sample of the cyclic product obtained from the aluminum chloride cyclization, m.p. 150°. When this was repeated with the *cis* isomer I, the same product as above was obtained.

Preparation of *cis*- and *trans*-β-*p*-Tolysulfonylcinnamic Acids.—*cis*-β-*p*-Tolylmercaptocinnamic acid (0.6 g., 0.0022 mole) was dissolved in 25 ml. of glacial acetic acid, and 3 ml. of 30% hydrogen peroxide was added slowly, with external cooling, to this solution. The mixture was warmed to room temperature and left at room temperature for one week to assure sulfone rather than sulfoxide formation under these mild conditions and more important to reduce the possibility of isomerization during oxidation. At the end of this period the mixture was evaporated in an air stream, the solid residue was taken up in a methanol–water solution, and recrystallized slowly to give a 92.4% yield of *cis*-β-*p*-tolylsulfonylcinnamic acid, m.p. 150°. The same procedure was used to synthesize *trans*-β-*p*-tolylsulfonylcinnamic acid, m.p. 148°. These isomeric acids had different infrared spectra and gave a depressed mixture melting point, m.p. 123–33°.

Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.57; H, 4.67; neut. equiv., 302.3. Found for *cis* isomer: C, 63.35; H, 4.35; neut. equiv., 301.9. Found for *trans* isomer: C, 63.80; H, 4.50; neut. equiv., 302.1.

Dipole Moment Materials and Technique.—1,4-Dioxane was purified by the method of Hess[16] and employed as a solvent for the isomeric acids as described in a previous paper.[17] A solution method was employed and the molar polarizations

---

[9] All microanalyses were carried out by Mrs. C. S. Yeh and Mrs. B. Groten of the Purdue Chemistry Microanalytical Laboratory. All infrared spectra were run by Mrs. W. Dilling of the Purdue Chemistry Infrared Laboratory using a Perkin-Elmer infrared spectrophotometer, model 21. All boiling and melting points are uncorrected.

[10] M. Reimer, THIS JOURNAL, **64**, 2510 (1942).

[11] W. H. Perkin, *J. Chem. Soc.*, **45**, 174 (1884).

[12] J. U. Nef, *Ann.*, **308**, 280 (1900).

[13] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[14] The analogous ethyl β-phenylmercaptocinnamate was prepared in a 9.4% yield by the addition of thiophenol to ethyl phenylpropiolate according to the procedure of Ruhemann and Stapleton; E. Campaigne and J. R. Seal, THIS JOURNAL, **76**, 1274 (1954).

[15] F. Arndt, *Ber.*, **46**, 1620 (1925).

[16] K. Hess and H. Frahm, *ibid.*, **71**, 2627 (1938).

[17] W. E. Truce, D. L. Goldhamer and R. B. Kruse, THIS JOURNAL, **81**, 4931 (1959).

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

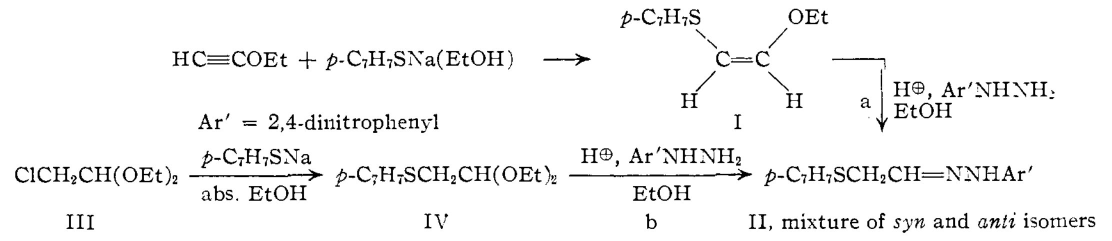
RECEIVED APRIL 20, 1959

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]

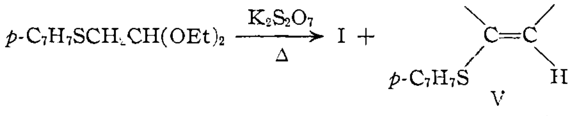
$$HC \equiv COC_2H_5 + C_2H_5SH \longrightarrow \textit{cis- and trans-}C_2H_5SCH{=}CHOC_2H_5$$

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.



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.

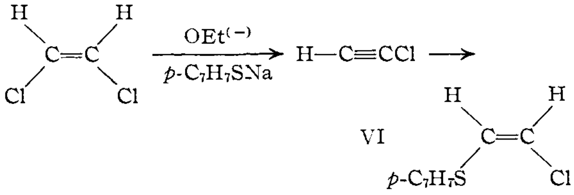
An independent stereoselective synthesis of I together with a small amount of the *trans* isomer could be effected by heating IV with anhydrous potassium pyrosulfate.[6]



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]



---

(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).