

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

The Stereochemistry of the Addition of Mesitylenethiol to Mesitylacetylene<sup>1-3</sup>

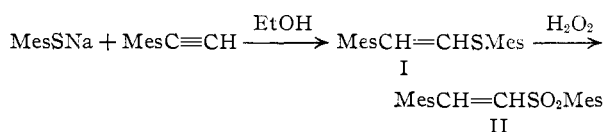
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The addition of mesitylenethiol to mesitylacetylene under basic and non-basic conditions proceeds *trans*. The configurational assignments to the adduct and its sulfone derivative are based on n.m.r., infrared and chemical evidence.

An investigation was undertaken to determine whether the addition of a bulky thiol to an acetylene bearing a bulky substituent might proceed in a *cis* manner due to steric interference of these large groups and thus be in violation of the Rule of *trans*-Nucleophilic Addition.<sup>4,5</sup> The present paper represents an initial study of the problem.

The addition of mesitylenethiol (present as its sodium salt in alcohol solution) to mesitylacetylene proceeded more slowly than for the analogous phenylacetylene-*p*-toluenethiol system, the adduct I being obtained in fair yield.

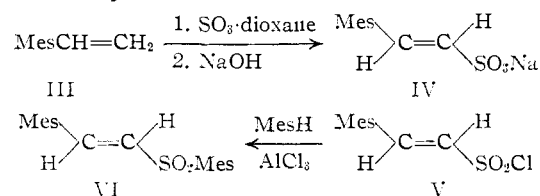


The addition of mesitylenethiol to mesitylacetylene in the absence of base also gave I. That this reaction probably proceeded *via* a free radical mechanism was supported by the fact that both ultraviolet light and azo-bis-isobutyronitrile caused a rate increase, whereas sulfur caused a decrease. Inhibitors such as diphenylamine and hydroquinone had a negligible effect. On the other hand, the addition under basic conditions was not enhanced by ultraviolet light or azo-bis-isobutyronitrile. There was a striking difference in the rates of the free thiol (radical?) and the sodium salt (nucleophilic?) reactions, the former being over after about 1 minute in refluxing ethanol and the latter proceeding only to an extent of 32% after 9 hours.

The infrared spectrum of compound I, m.p. 44.5–45°, suggested that this product was of the *cis* configuration, therefore arising from the usual mode of *trans* addition. The absence of a band in the 10.2–10.5  $\mu$  region characteristic of out-of-plane deformation of *trans*-ethylenic hydrogens<sup>6</sup> was consistent with this configurational assignment. The presence of a strong band at 10.47  $\mu$  in *trans*-1-phenyl-2-(phenylmercapto)-ethene and at 10.49  $\mu$  in *trans*-1-phenyl-2-(*p*-tolylmercapto)-ethene, whereas none was present in their corresponding *cis* isomers, further supported the *cis* configuration of I.

Compound I was readily oxidized to its sulfone derivative II, m.p. 183–183.3°. More convincing

evidence for the assignment of the *cis* configuration to I was afforded by comparison of its sulfone derivative with its configurational isomer VI, m.p. 116°, which was independently synthesized by the reaction sequence



The treatment of olefins such as III with sulfur trioxide and dioxane has been reported by various workers to yield unsaturated sulfonic acids (of type IV) of *trans* configuration.<sup>7</sup> Furthermore, the *trans* assignment to IV was supported by the presence of a strong infrared absorption band at 10.20  $\mu$ . Compound VI showed a band at 10.15  $\mu$ , whereas none was present in this region in the spectrum of II (likewise the *trans* isomer of both 1-phenyl-2-(phenylsulfonyl)-ethene and 1-phenyl-2-(*p*-tolylsulfonyl)-ethene displayed a band at approximately 10.2  $\mu$ ; however, this band was absent in the corresponding *cis* isomers).

Nuclear magnetic resonance data also support the assigned configurations. The proton-proton coupling constants for the vinylic hydrogens in I ( $J_{\text{HH}} = 12.2$  c.p.s.), and VI ( $J_{\text{HH}} = 15.8$  c.p.s.) when compared with the corresponding values for *cis*- and *trans*-1-phenyl-2-(phenylsulfonyl)-ethenes ( $J_{\text{HH}} = 12.4$  and 15.7 c.p.s., respectively) and *cis*- and *trans*-1-phenyl-2-(*p*-tolylsulfonyl)-ethenes ( $J_{\text{HH}} = 11.5$  and 16.0 c.p.s., respectively), were in agreement with the generalization that *trans* isomers have higher coupling constants than their corresponding *cis* isomers.<sup>8</sup> This study further illustrates the usefulness of n.m.r. analysis for assigning configurations to a pair of *cis-trans* isomers.

Chemical evidence for the *cis* and *trans* relationship of II and VI was shown by the formation of VII, m.p. 186–187°, when these compounds were catalytically hydrogenated in the presence of a palladium-on-charcoal catalyst. The reduction of II could only be achieved when freshly prepared catalyst was used.

Compound VII was shown to be different from II by a depressed mixture melting point. It was interesting to note that sodium borohydride in diglyme solution reduced VI to VII; however, II

(1) This constitutes Paper XIV in this series; for preceding paper see *J. Am. Chem. Soc.*, **82**, 6427 (1960).

(2) A preliminary report of this work appeared as a Communication to the Editor, *ibid.*, **82**, 3799 (1960).

(3) Abstracted from the Ph.D. Theses of Harvey G. Klein and Robert B. Kruse.

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

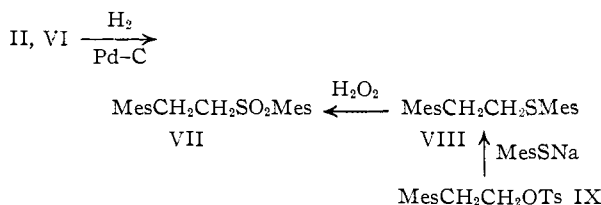
(5) S. I. Miller, *ibid.*, **78**, 6091 (1956).

(6) F. A. Miller in H. Gilman, "Organic Chemistry," Vol. III, Chapter 2, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 149.

(7) (a) A. P. Terent'ev, R. A. Gracheva and Z. F. Shcherbatova, *Doklady Akad. Nauk., S.S.S.R.*, **84**, 975 (1952); *C. A.*, **47**, 3202 (1953).

(b) C. S. Rondestvedt and J. C. Wygant, *J. Am. Chem. Soc.*, **73**, 5785 (1951).

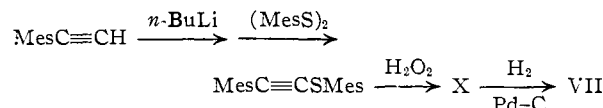
(8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter II.



proved resistant under these conditions. The preparation of VII was achieved by the oxidation of VIII, m.p. 92–94°, which was synthesized by displacing the tosylate ester of 2-mesitylethanol with sodium mesitylenethiolate. Compound VII, prepared by all these methods, gave identical infrared spectra and undepressed mixture melting points.

Moizingo, *et al.*,<sup>9</sup> found that unsaturated S-containing compounds were readily hydrogenated in the presence of a large excess of a palladium-on-barium sulfate catalyst. When Compound I was treated under the conditions reported by these workers, no reduction occurred, and only starting materials were isolated.

An attempt to synthesize II independently *via* the catalytic reduction of 1-mesityl-2-mesitylsulfonylacetylene (X), m.p. 116°, failed. This acetylenic sulfone had an infrared absorption band at 4.62  $\mu$  and was prepared by the reaction sequence



Catalytic reduction of X with a palladium-on-charcoal catalyst did not stop at the olefin stage, but gave a product identical with the saturated compound VII. In the presence of Lindlar catalyst,<sup>10</sup> only starting material was recovered.

Sodium borohydride reduction of X gave a product which was identical to VI obtained by the Friedel-Crafts approach.<sup>11</sup>

Partial isomerization of II to VI was effected by heating II in a sealed tube at 140° for 5 days in the presence of sodium *p*-toluenethiolate; under like conditions, VI gave addition product as well as recovered starting material.

Kohler and Potter<sup>12</sup> have reported the addition of *p*-toluenethiol to phenylacetylene in the absence of a solvent or added peroxides, and obtained a mixture of *cis*- and *trans*-sulfides, the ratio depending on the reaction temperature. At temperatures above the melting points of these adducts (m.p. 65° and 44°, respectively), a 1:1 ratio of isomers was obtained. In contrast, under nucleophilic conditions only the *cis* isomer was isolated.<sup>4</sup> When the conditions of Kohler and Potter were modified by carrying out the reaction in refluxing cyclohexane and added benzoyl peroxide to ensure that a free radical reaction was occurring, approximately the same isomer ratio was found. Since the free radical addition of *p*-toluenethiol to phenylacetylene resulted

(9) R. Moizingo, *et al.*, *J. Am. Chem. Soc.*, **67**, 2092 (1945).

(10) H. Lindlar, *Helv. Chim. Acta*, **35**, 450 (1952).

(11) We have found that 1-phenyl-2-phenylsulfonylacetylene can be reduced in high yield to *trans*-1-phenyl-2-(phenylsulfonyl)-ethene by treatment with sodium borohydride (unpublished results). This is in agreement with the above observation.

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

in a mixture of *cis* and *trans* isomers, a plausible approach to the preparation of the structural isomer of I, *trans*-1-mesityl-2-(mesitylmercapto)-ethene, was the benzoyl peroxide-catalyzed addition of mesitylenethiol to mesitylacetylene. However this reaction gave only one product, identified as I. Its infrared spectrum was identical with that of an authentic sample of *cis*-1-mesityl-2-(mesitylmercapto)-ethene.

In summary, under basic and non-basic conditions the addition of mesitylenethiol to mesitylacetylene proceeds *trans*, *i.e.*, the steric requirements of the mesityl groups in the transition state were not sufficiently large to change the mode of addition, *trans* to *cis*.

### Experimental<sup>13</sup>

**Mesitylacetylene.**—The procedure of Noller and Adams<sup>14</sup> was used to prepare acetylmesitylene from mesitylene, acetic anhydride and aluminum chloride; b.p. 90–91° at 2 mm. (reported b.p. 90° at 3 mm.). Acetylmesitylene was converted to 2,4,6-trimethyl- $\alpha$ -chlorostyrene by treatment with phosphorus pentachloride by the method of Vaughn and Nieuwland<sup>15</sup>; b.p. 122–124° at 24 mm. (reported b.p. 122–124° at 25 mm.). The procedure of these authors for the preparation of mesitylacetylene from this compound was modified as follows:

A suspension of 20 g. (0.50 mole) of sodium amide in 100 ml. of Ansol Ether 181 (tetraethylene glycol dimethyl ether) was prepared by grinding in a mortar. The suspension was heated to 160° in a Morton flask and stirred with a high-speed stirrer while nitrogen (H.P., dry) was passed through the system. To the hot suspension, 36 g. (0.20 mole) of 2,4,6-trimethyl- $\alpha$ -chlorostyrene was added dropwise over a period of about 0.5 hour. After an additional 2.5 hours of heating, the reaction mixture was cooled, poured on crushed ice, acidified with dilute hydrochloric acid, and extracted with small portions of ether. The extracts were dried over anhydrous magnesium sulfate, the solvent was evaporated, and the residue was distilled under reduced pressure to give 14 g. (53%) of mesitylacetylene, b.p. 94–97° at 20 mm.,  $n_D^{20}$  1.5422 (reported 103–107° at 23 mm.,  $n_D^{20}$  1.5429).

**Mesitylenethiol.**—Following the procedure of Huntress and Autenreith,<sup>16</sup> mesitylenesulfonyl chloride was prepared in a 63% yield, m.p. 55–57° (reported<sup>17</sup> m.p. 56–57°). The reduction of this compound was effected by means of lithium aluminum hydride, utilizing the procedure of Field and Grunwald.<sup>18</sup>

To a refluxing solution of 60.7 g. (0.280 mole) of mesitylenesulfonyl chloride in 600 ml. of anhydrous ether was added a suspension of 26.8 g. (0.671 mole) of lithium aluminum hydride (95% purity) in 600 ml. of ether over a 35-minute period. After the addition was completed, the mixture was refluxed for an additional 4 hours, then cooled in an ice-bath, and water added cautiously to decompose the unreacted hydride. An excess of 10% sulfuric acid was added to dissolve the precipitate, and the organic layer was separated. The aqueous layer was extracted with ether, the organic layers were combined, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residual liquid was distilled to give 33.3 g. (78.2%) of mesitylenethiol, b.p. 79–82° at 2 mm. (reported<sup>19</sup> b.p. 109.5–111.5° at 18 mm.).

**Reaction of Sodium Mesitylenethiolate with Mesitylacetylene.**—To a solution of sodium mesitylenethiolate in

(13) All microanalyses were carried out by Dr. 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.

(14) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **46**, 1889 (1924).

(15) T. H. Vaughn and J. A. Nieuwland, *ibid.*, **56**, 1207 (1934).

(16) E. H. Huntress and J. S. Autenreith, *ibid.*, **63**, 3446 (1933).

(17) C. S. Gibson, *J. Chem. Soc.*, **117**, 949 (1920).

(18) L. Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 946 (1951).

(19) W. E. Truce and O. L. Norman, *J. Am. Chem. Soc.*, **75**, 6023 (1953).

absolute ethanol, prepared from 1.0 g. (0.042 g. atom) of sodium, 6.1 g. (0.040 mole) of mesitylenethiol and 50 ml. of absolute ethanol, was added rapidly 5.8 g. (0.040 mole) of mesitylacetylene dissolved in 10 ml. of absolute ethanol. The mixture was refluxed for 18 hours, cooled, and then concentrated; water was added and the mixture was extracted with ether. The ether extracts were dried and the residual oil was distilled under reduced pressure to give 4.4 g. (37%) of product, b.p. 167–177° at 0.5 mm.,  $n_D^{25}$  1.5861–1.5938, identified as *cis*-1-mesityl-2-(mesitylmercapto)-ethene by its identical infrared spectrum with that of an authentic sample. The adduct was solidified by dissolving the oil in a small amount of absolute ethanol followed by cooling of the mixture with Dry Ice. It had a melting point of 39.5–41.5°. Further recrystallizations raised the melting point to 43–44.5°. The aqueous layer was oxidized with 30% hydrogen peroxide to give 3.34 g. of mesityl disulfide, m.p. 123.5–125°. The yield of adduct based on recovered starting materials was 92%.

**"Free Radical" Addition of Mesitylenethiol to Mesitylacetylene.**—A mixture of 0.79 g. (0.0052 mole) of mesitylenethiol, 0.75 g. (0.0052 mole) of mesitylacetylene and 7.5 ml. of absolute ethanol was stirred overnight at room temperature in an atmosphere of nitrogen. The reaction mixture was cooled in Dry Ice for about 1 hour and then filtered to give 1.2 g. (80%) of crude *cis*-1-mesityl-2-(mesitylmercapto)-ethene, m.p. 38.5–41°. After several recrystallizations from absolute ethanol the melting point rose to 43.5–44.5°. Its infrared spectrum was identical with that of the *cis*-sulfide and gave an undepressed mixture melting point with an authentic sample (m.p. 43.5–44.5°).

**Effect of Free Radical Accelerators on the Rate of Addition of Mesitylenethiol to Mesitylacetylene.** A. Azo-bis-isobutyronitrile.—In a flask equipped with a reflux condenser, nitrogen inlet tube, magnetic stirrer and a plugged opening for removing samples were placed 0.85 g. (0.0059) of mesitylacetylene and 5 ml. of absolute ethanol. The mixture was refluxed and 0.70 g. (0.0046 mole) of mesitylenethiol dissolved in 2.5 ml. of absolute ethanol was added all at once, the time being noted. Small aliquots (6  $\mu$ l.) were taken after 0.5, 7 and 13 minutes and analyzed for unreacted mesitylacetylene by V.P.C. analysis.

The above procedure was modified by adding 0.10 g. (13 mole %) of azo-bis-isobutyronitrile to the ethanol solution 0.5 minute prior to the addition of mesitylenethiol. Aliquots were taken at the same time intervals as in the previous experiment.

Time, minutes		0.5	7
Unreacted MesC $\equiv$ CH, <sup>a</sup> %	Absence AIBM	24	0
	Presence AIBN	4	0

<sup>a</sup> Corrected for the presence of an excess amount of mesitylacetylene at 0 time.

B. Ultraviolet Light.—In a blackened quartz flask protected from light were placed 0.50 g. (0.0035 mole) of mesitylacetylene and 3 ml. of absolute ethanol. The mixture was cooled in a Dry Ice-acetone bath and the reaction temperature was maintained between –30 to –35°. Mesitylenethiol (0.50 g., 0.0033 mole) dissolved in 2 ml. of absolute ethanol was added all at once and the mixture was stirred. The time was noted when solidification of the reaction mixture had occurred. The product was quickly filtered, dried, weighed, and a melting point taken.

The above procedure was modified by illuminating the quartz flask with ultraviolet light generated by a Hanovia mercury vapor lamp (550 watts).

	Absence	Presence of u.v. light
Solidification time, min.	10.75	6.5
Product, g.	0.60	0.58
M.p., °C.	38.5–40.5	39–41

**Effect of Free Radical Accelerators on the Rate of Addition of Sodium Mesitylenethiolate to Mesitylacetylene. General Procedure.**—Sodium (0.20 g., 0.0087 mole) was dissolved in 10 ml. of absolute ethanol and 1.06 g. (0.0070 mole) of mesitylenethiol dissolved in 2 ml. of ethanol was added, the mixture refluxed, and then 1.00 (0.0070 mole) of mesitylacetylene dissolved in 3 ml. of ethanol (total volume 15.0 ml.) was added. An aliquot was removed and analyzed at the following time intervals: 1, 2, 3, 5, 7, 9 and 11 hours.

A. Absence of Light.—The reaction was run in a blackened quartz flask in a dark room.

B. Ultraviolet Light.—The reaction mixture was illuminated as described above.

C. Azo-bis-isobutyronitrile.—Addition of AIBN (0.16 g., 14 mole %) was made immediately after adding the mesitylacetylene.

The kinetic results are summarized below.

Time, hr.	—Unreacted MesC $\equiv$ CH, U.v.	%—AIBN
0	100	100
1	92	94
2	90	94
3	88	89
5	72	76
7	70	74
9	68	72
11	66	69

**Vapor Phase Chromatography.**—The instrument employed in the V.P.C. analysis was a Perkin-Elmer model 154-C vapor fractometer with helium as the carrier gas and a polyethylene glycol (Carbowax 1500) column of 2-meter length. The column temperature was 150°, gas pressure 15 p.s.i., and the flow rate 34 ml. per min.

Areas under the peaks were measured with a planimeter and the percentage unreacted mesitylacetylene was calculated from area ratios.

**Sulfone Derivative II.**—The sulfide (0.75 g., 0.0025 mole) was dissolved in 50 ml. of glacial acetic acid, cooled in an ice-bath, and then 6 ml. of 30% hydrogen peroxide was added. After allowing the mixture to stand at 0° for 15 minutes, it was refluxed for 1.25 hours. The hot mixture was poured on crushed ice, and the crude sulfone was filtered off and dried; weight 0.7 g., m.p. 164–172°. The yield of pure sulfone was 0.5 g. (60%), m.p. 183–183.3°, after 2 recrystallizations from 95% ethanol. Its infrared spectrum showed the following bands and intensities in Nujol mull: 3.36(s), 6.19(w), 6.34(w), 6.81(s), 7.21(w), 7.62(s), 8.50(w), 8.74(s), 8.91(m), 9.44(w), 9.61(w), 11.46(w), 11.61(w), 11.82(m), 13.39(s), 13.72(m), 14.00(w), and 14.27(m)  $\mu$ .

*Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>S: C, 73.17; H, 7.32; S, 9.76; mol. wt., 328. Found: C, 73.10; H, 7.20; S, 9.39; mol. wt. (Rast), 320.

**2,4,6-Trimethylstyrene (III).**—Acetylmesitylene, prepared as described previously, was converted quantitatively to mesitylmethylcarbinol by reduction with lithium aluminum hydride; m.p. 68–69°. A mixture of the alcohol (130 g., 0.820 mole) and 296 g. (2.18 moles) of potassium bisulfate was prepared by grinding in a mortar. The mixture was placed in a distillation flask and heated on a steam-cone under reduced pressure (0.55 mm.). The resulting 2,4,6-trimethylstyrene was distilled as soon as it formed. Redistillation of the styrene gave 55 g. (46%) of product which boiled at 87–90° at 10 mm.,  $n_D^{17.5}$  1.5264 (reported<sup>20</sup> 205–207°,  $n_D^{17.5}$  1.5296).

**Sodium *trans*-2-Mesitylene-1-sulfonate (IV).**—2,4,6-Trimethylstyrene was sulfonated by the method of Bordwell, *et al.*<sup>21</sup>

Sulfan B (7.9 g., 0.99 mole) was distilled into a mixture of 15 ml. of dry dioxane and 15 ml. of ethylene chloride which was cooled in an ice-bath. When the suspension of dioxane sulfotrioxide was prepared, 14.6 g. (0.100 mole) of 2,4,6-trimethylstyrene was added dropwise over a 30-minute period, while stirring the cooled mixture rapidly. The mixture was then allowed to stand overnight, then heated on a steam-bath for 30 minutes, and finally poured into 100 ml. of water. The ethylene chloride layer was removed and the aqueous layer was neutralized with dilute sodium hydroxide. This solution was then boiled down to a small volume and cooled. A crop of crystals of sodium *trans*-2-mesitylene-1-sulfonate (17.6 g.) was obtained in a 71% yield. The crude product was recrystallized from water and dried. Its infrared spectrum showed a strong absorption at 10.20  $\mu$ .

(20) A. Klages and R. Keil, *Ber.*, **36**, 1645 (1903).

(21) F. G. Bordwell, C. M. Suter, J. M. Holbert and C. S. Rondstedt, *J. Am. Chem. Soc.*, **68**, 130 (1946).

*Anal.* Calcd. for  $C_{11}H_{13}O_3SNa$ : C, 53.26; H, 5.24; Na, 9.28. Found: C, 53.13; H, 5.15; Na, 9.57.

**trans-2-Mesitylethene-1-sulfonyl Chloride (V).**—A mixture of 10 g. (0.040 mole) of sodium *trans*-2-mesitylethene-1-sulfonate and 8.4 g. (0.040 mole) of phosphorus pentachloride was prepared by grinding the components together in a mortar. The mixture was heated on a steam-bath for 6 hours, after which the phosphorus oxychloride formed in the reaction was removed on a rotary film evaporator. The solid residue was pulverized under a mixture of ice and water, and then filtered. The solid was dried and recrystallized from cyclohexane to yield 7.4 g. (76%) of *trans*-2-mesitylethene-1-sulfonyl chloride, m.p. 95.5–97°. Its infrared spectrum showed a strong absorption at 10.18  $\mu$ .

**trans-1-Mesityl-2-(mesitylsulfonyl)-ethene (VI).**—To a solution of 12 g. (0.050 mole) of *trans*-2-mesitylethene-1-sulfonyl chloride in 125 ml. of carbon disulfide was added 6.9 g. (0.052 mole) of aluminum chloride. Mesitylene (6.0 g., 0.050 mole) was then added dropwise with stirring. After the addition was completed, the mixture was refluxed until no more hydrogen chloride was evolved. The mixture was then poured into ice-water which was acidified with a few drops of hydrochloric acid, the organic layer was separated, and the aqueous layer was extracted with two 50-ml. portions of ether. The extracts and the organic layer were combined, dried over anhydrous magnesium sulfate, the solvent evaporated, and the solid residue was recrystallized from 95% ethanol. *trans*-1-Mesityl-2-(mesitylsulfonyl)-ethene (12 g.) was obtained in an 81% yield, m.p. 116°. Its infrared spectrum showed the following bands and intensities in Nujol mull: 3.48(s), 61.8(s), 6.36(m), 6.84(s), 7.12(w), 7.24(m), 7.65(s), 8.13(w), 8.33(w), 8.43(w), 8.75(s), 9.48(m), 9.67(m), 10.15(m), 11.58(w), 11.85(m), 12.35(m), 12.77(m), 13.87(w) and 14.00(w)  $\mu$ .

*Anal.* Calcd. for  $C_{20}H_{24}O_2S$ : C, 73.17; H, 7.32; S, 9.76; mol. wt., 328. Found: C, 73.00; H, 7.22; S, 10.01; mol. wt. (Rast), 325.

**1-Mesityl-2-(mesitylsulfonyl)-ethane (VII). A. By the Catalytic Hydrogenation of trans-1-Mesityl-2-(mesitylsulfonyl)-ethene.**—Compound VI (0.15 g., 0.00046 mole) was dissolved in 175 ml. of absolute ethanol and was shaken with hydrogen for 24 hours in the presence of 0.14 g. of 5% palladium-on-charcoal catalyst at a pressure of 55 p.s.i. The catalyst was filtered off and washed with hot ethanol. The washings and the filtrate were combined, evaporated, and the solid residue was carefully recrystallized from 95% ethanol to give 0.08 g. (53% yield) of reduced compound, m.p. 186–187°. Its infrared spectrum showed the following bands and intensities in Nujol mull: 3.41(s), 6.20(w), 6.83(s), 7.10(w), 7.24(m), 7.60(m), 7.70(w), 7.98(w), 8.10(w), 8.80(s), 9.50(w), 9.70(w), 11.77(m), 12.31(w), 13.23(m), 13.83(w) and 14.23(w)  $\mu$ .

**B. By the Sodium Borohydride Reduction of trans-1-Mesityl-2-(mesitylsulfonyl)-ethene.**—Compound VI (0.27 g., 0.00082 mole) was added to a solution of 0.14 g. (0.0037 mole) of sodium borohydride in 35 ml. of diglyme. The mixture was stirred and heated at 50° for 5 hours and then poured on crushed ice to which a few drops of concentrated sulfuric acid was added. The mixture was cooled in a refrigerator for 2 days, the crude product (0.26 g.) was filtered off, and carefully recrystallized three times from 95% ethanol to give 0.08 g. (30%) of 1-mesityl-2-(mesitylsulfonyl)-ethane, m.p. 185–185.5°. The infrared spectrum of VII, obtained by the two methods, was identical. A mixture melting point showed no depression.

**C. By the Catalytic Hydrogenation of cis-1-Mesityl-2-(mesitylsulfonyl)-ethene.**—Compound II could be reduced only in the presence of freshly prepared 5% palladium-on-charcoal catalyst, which was prepared by the procedure of Mozingo.<sup>22</sup> Compound II (0.30 g., 0.00091 mole), was dissolved in a mixture of 85 ml. of absolute ethanol and 65 ml. of acetone and was shaken with hydrogen for 17 hours in the presence of 1.0 g. of freshly prepared 5% palladium-on-charcoal catalyst at a pressure of 53 p.s.i. The catalyst was filtered off, washed with hot acetone, the filtrate and washings were combined and then evaporated. The solid residue was recrystallized twice from 95% ethanol to give 0.15 g. (50%) of VII, m.p. 186–187°. The mixture melting point was depressed to 159.5–165° with a sample of starting material (m.p. 183.0–183.3°). A mixture of VII,

prepared by methods A and C, gave an undepressed melting point of 186–187° and the infrared spectra of the separate samples were identical.

*Anal.* Calcd. for  $C_{20}H_{26}O_2S$ : C, 72.72; H, 7.88. Found: C, 73.00; H, 7.98.

**Attempted Sodium Borohydride Reduction of cis-1-Mesityl-2-(mesitylsulfonyl)-ethene.**—The same procedure was used as for the reduction of VI with sodium borohydride. Compound II (0.1 g., 0.0003 mole) was treated with 0.1 g. (0.003 mole) of sodium borohydride in 35 ml. of diglyme. Only recovered starting materials (0.07 g.) were isolated, m.p. 183–184°, infrared spectrum superimposable on that of starting sulfone.

**2-Mesitylethyl Tosylate (IX).**—The general procedure of Tipson<sup>23</sup> was used to prepare this tosylate.

2-Mesitylethanol (30 g., 0.18 mole) was dissolved in 300 ml. of dry pyridine and the solution was cooled to –5° in an ice-salt-bath. *p*-Toluenesulfonyl chloride (38 g., 0.20 mole) was added all at once and the flask closed by a rubber stopper through which a thermometer was inserted. The suspension was swirled by hand with cooling until all the sulfonyl chloride had dissolved. After keeping at 0° for 2 hours, water (20 ml.) was added in portions (2 + 2 + 2 + 4 + 10 ml.) at intervals of 5 minutes, with swirling and cooling so that the temperature did not rise above +5°. The solution was diluted with 250 ml. of water and the aqueous pyridine solution was then extracted with three 200-ml. portions of chloroform, and the extracts were washed successively with ice-cold dilute sulfuric acid, water, and sodium bicarbonate solution. The chloroform solution was dried over anhydrous magnesium sulfate, filtered, and evaporated. The oily residue was solidified by cooling and gave 66 g. of crude tosylate ester, m.p. 51–55°. The product was used without further purification.

**1-Mesityl-2-(mesitylmercapto)-ethanol (VIII).**—To a solution of sodium mesitylenethiolate in absolute ethanol, prepared from 4.8 g. (0.032 mole) of mesitylenethiol, 0.80 g. (0.035 g. atom) of sodium and 120 ml. of absolute ethanol, was added 2-mesitylethyl tosylate (10 g., 0.031 mole). The mixture was refluxed for 4 hours, the insoluble salts were filtered off, and the filtrate was concentrated, diluted with water and extracted with ether. The extracts were dried over anhydrous magnesium sulfate, and then evaporated. The oily residue was dissolved in hot methanol and cooled to give 3.6 g. of product, m.p. 86.5–92°. The sulfide was purified by several recrystallizations from methanol and melted at 91–93°. The analytical sample had a melting point of 92–94°. Its infrared spectrum showed the following bands and intensities in Nujol mull: 3.34(s), 6.19(w), 6.80(s), 7.21(m), 7.58(w), 7.67(w), 8.16(w), 8.28(w), 8.47(w), 9.35(w), 9.65(w), 9.82(w), 11.71(s), 13.78(w) and 14.10(w)  $\mu$ .

*Anal.* Calcd. for  $C_{20}H_{26}S$ : C, 80.54; H, 8.72. Found: C, 80.64; H, 8.44.

**1-Mesityl-2-(mesitylsulfonyl)-ethane (VII).**—A mixture of 0.4 g. (0.001 mole) of VIII, 25 ml. of glacial acetic acid and 3 ml. of 30% hydrogen peroxide was refluxed for 1 hour, and then poured on crushed ice. The solid was filtered off and recrystallized from 95% ethanol to give 0.3 g. of VII, m.p. 185–186°. A mixture melting point determination with a sample of VII, obtained by the catalytic hydrogenation of VI, was undepressed (m.p. 185–186°). Their infrared spectra were identical.

**Attempted Catalytic Hydrogenation of I.**—The procedure of Mozingo, *et al.*,<sup>9</sup> was used.

Compound I (0.5 g., 0.0002 mole) was dissolved in 150 ml. of methanol. To this was added 1.5 ml. of concentrated sulfuric acid and 7.0 g. of a 5% palladium-on-charcoal catalyst. The mixture was shaken with hydrogen at a pressure of 49 p.s.i. for 15 hours. The catalyst was filtered off, washed with hot methanol, and the filtrate was concentrated, diluted with water, and finally extracted with ether. The extracts were dried, evaporated, and the oily residue was dissolved in hot absolute ethanol; crystallization was effected by cooling in a Dry Ice–trichloroethylene-bath and scratching the sides of the beaker with a glass rod. A solid was isolated (0.2 g.) which melted at 36–40°. The infrared spectrum of this crude material was identical to that of an authentic sample of I.

(22) R. Mozingo, *Org. Syntheses*, **26**, 78 (1946).

(23) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

**Isomerization of *cis*-to *trans*-1-Mesityl-2-(mesitylsulfonyl)-ethene.**—Compound II (0.26 g., 0.00080 mole) was treated with 0.2 g. (0.0016 mole) of *p*-toluenethiol, 0.040 g. (0.0016 g. atom) of sodium in 40 ml. of absolute ethanol and heated at 140° for 5 days in a sealed tube. The crude product was fractionally recrystallized from 95% ethanol and the following fractions were obtained: (1) wt. 0.07 g., m.p. 114–115°, identified as VI by an undepressed mixture melting point with an authentic sample (m.p. 114–115°), and identical infrared spectra; (2) wt. 0.13 g., m.p. 181–183°. Its infrared spectrum was identical to that of the starting material I; (3) wt. 0.03 g., polymeric material.

Under the same conditions, VI (4.0 g.) gave an 85% recovery of starting materials and a small amount of a white crystalline solid, m.p. 185–186°, which analyzed correctly for the *p*-toluenethiol adduct of VI. Its infrared spectrum was different from that of II and depressed the melting point to 158–165°.

*Anal.* Calcd. for C<sub>27</sub>H<sub>32</sub>O<sub>2</sub>S<sub>2</sub>: C, 71.68; H, 7.08. Found: C, 71.59; H, 7.05.

**Mesityl Disulfide.**—Mesitylenethiol (15.2 g., 0.100 mole), prepared as previously described, was dissolved in a solution of 6.0 g. of sodium hydroxide in 200 ml. of water. While the temperature of the reaction mixture was maintained at 0°, 22 ml. of 30% hydrogen peroxide was added dropwise. Stirring was continued at this temperature for 2 hours, and then the mixture was allowed to warm up to room temperature. The disulfide was filtered off, washed with water, and then dried. The yield of mesityl disulfide was 14.6 g. (97.3%), melting at 123.5–125° (reported<sup>24</sup> m.p. 125°). The product was used directly without further purification.

**1-Mesityl-2-mesitylsulfonylacetylene (X).**—*n*-Butyllithium was prepared by the method of Gilman, *et al.*,<sup>25</sup> from 0.62 g. (0.090 g. atom) of lithium wire and 5.7 g. (0.042 mole) of *n*-butyl bromide in anhydrous ether. Mesitylacetylene (6.0 g., 0.042 mole) was added while the temperature was maintained at 10°. Stirring was continued at this temperature for an additional hour and then 10.6 g. (0.0350 mole) of mesityl disulfide dissolved in 75 ml. of ether was added. The mixture was heated at 30° for 1.5 hours, and then allowed to stand overnight. After pouring on crushed ice, the ether layer was separated, the aqueous layer was extracted with ether, the organic layers were combined and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was distilled under reduced pressure to give a main fraction (5.6 g.) boiling at 183–192° at 0.6 mm. The distillate partially solidified, and on fractional crystallization from absolute ethanol, 0.8 g. of mesityl disulfide, m.p. 123–125°, was isolated. The yield of crude acetylene was 48%.

A portion of the oily residue (1.0 g.) was dissolved in 10 ml. of a 1:1 acetic anhydride-glacial acetic acid mixture and treated with 8 ml. of 30% H<sub>2</sub>O<sub>2</sub>. The mixture was stirred overnight at room temperature, poured on crushed ice, and the crude sulfone was filtered off and dried. After recrystallizing from ethanol, 0.4 g. of X was obtained, m.p. 116°. Its infrared spectrum showed the following bands and intensities in Nujol mull: 3.43(s), 4.62(m), 6.20(w), 6.38(w), 6.85(s), 7.25(m), 7.53(s), 8.15(w), 8.41(w), 8.64(s), 9.30(w), 9.49(w), 9.67(w), 11.56(w), 11.80(w), 12.23(m) and 13.96(w)  $\mu$ .

*Anal.* Calcd. for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>S: C, 73.62; H, 6.75. Found: C, 73.41; H, 6.70.

**Attempted Synthesis of *cis*-1-Mesityl-2-(mesitylsulfonyl)-ethene by the Catalytic Reduction of X.**—1-Mesityl-2-mesitylsulfonylacetylene was hydrogenated in the presence of a 5% palladium-on-charcoal catalyst. The reduction did not stop at the olefin stage, but the saturated compound VII, m.p. 183–185°, was obtained in a 67% yield. The infrared spectrum of this compound was superimposable with that of an authentic sample, and gave a mixture melting point of 183–186° with a sample of VII, m.p. 186–187°. Reduction of 0.18 g. of X in the presence of freshly prepared Lindlar catalyst<sup>10</sup> and quinoline gave only recovered starting material (0.08 g.), m.p. 113–115°. Its infrared spectrum was superimposable with that of X.

**Synthesis of *trans*-1-Mesityl-2-(mesitylsulfonyl)-ethene by the Sodium Borohydride Reduction of X.**—1-Mesityl-2-mesitylsulfonylacetylene (0.08 g., 0.0003 mole) was added

to a solution of 0.02 g. (0.0005 mole) of sodium borohydride in 25 ml. of diglyme cooled in an ice-bath. The mixture was stirred at 0° for 3.5 hours, and then allowed to warm up to room temperature. After an additional hour at room temperature, the mixture was poured on crushed ice which was acidified with a few drops of concentrated sulfuric acid, and then cooled in a refrigerator for 48 hours. The solid was filtered off, dried and recrystallized from 95% ethanol to give 0.03 g. of *trans*-1-mesityl-2-(mesitylsulfonyl)-ethene, m.p. 114–114.5°. The infrared spectrum of this product was identical to that of an authentic sample of VI. Their mixture melting point was 114–115°.

**Peroxide-catalyzed Addition of *p*-Toluenethiol to Phenylacetylene.**—A mixture of 12.5 g. (0.100 mole) of *p*-toluenethiol, 10.2 g. (0.100 mole) of phenylacetylene and 0.4 g. of benzoyl peroxide dissolved in 50 ml. of cyclohexane was refluxed for 10 hours, cooled, and then washed with dilute aqueous sodium hydroxide. The organic layer was evaporated, and the oily solid was dissolved in boiling petroleum ether (b.p. 30–60°), and then cooled in a refrigerator. The crude solid was filtered off to give 9.4 g. of *cis*-1-phenyl-2-(*p*-tolylmercapto)-ethene, m.p. 59–63°. After several recrystallizations from methanol, the melting point rose to 63.5–64.5° (reported<sup>12</sup> m.p. 65°). A mixture melting point determination with an authentic sample of this compound, m.p. 63.5–64.5°, was undepressed.

The filtrate was evaporated and the residual oil was distilled to give 10.2 g. of *trans*-1-phenyl-2-(*p*-tolylmercapto)-ethene, b.p. 158–164° at 1 mm., *n*<sub>D</sub><sup>25</sup> 1.6524–1.6544. The infrared spectrum of this product was identical with that of the *trans* isomer prepared by the addition of *p*-toluenethiol to phenylacetylene in the absence of a solvent and added peroxide; b.p. 152–152.2° at 0.65 mm., melting point when solidified 44–45°, *n*<sub>D</sub><sup>25</sup> 1.6549 (reported<sup>12</sup> m.p. 44°).

**Peroxide-catalyzed Addition of Mesitylenethiol to Mesitylacetylene.**—A mixture of 6.1 g. (0.040 mole) of mesitylenethiol, 5.8 g. (0.040 mole) of mesitylacetylene and 0.2 g. of benzoyl peroxide dissolved in 40 ml. of cyclohexane was refluxed for 12 hours, cooled, and then washed with dilute aqueous sodium hydroxide. The organic layer was dried over anhydrous magnesium sulfate and evaporated. The oily residue could not be solidified, but was distilled under reduced pressure to give 5.2 g. of product, b.p. 162–169° at 0.25 mm., *n*<sub>D</sub><sup>25</sup> 1.5933–1.5947. The distillate partially solidified on standing. Its infrared spectrum was identical with that of *cis*-1-mesityl-2-(mesitylmercapto)-ethene. The distillation pot contained a small amount of polymeric material.

To the basic washings was added a few ml. of 30% hydrogen peroxide and the mixture was allowed to stand at room temperature for a few days. The solid was filtered off and recrystallized from absolute ethanol to give 1.3 g. of mesityl disulfide, m.p. 123.5–125°. The yield of I based on recovered starting material was 55%.

**Model Compounds for N.m.r. Study.**—*cis*-1-Phenyl-2-(phenylsulfonyl)-ethene, m.p. 64–65°, was prepared by oxidation of the addition product of sodium benzenethiolate and phenylacetylene.<sup>26</sup>

*trans*-1-Phenyl-2-(phenylsulfonyl)-ethene, m.p. 73.5–75°, was prepared by the method of Smith and Davis.<sup>27,28</sup>

*cis*- and *trans*-1-phenyl-2-(*p*-tolylsulfonyl)-ethenes, m.p. 76–77° and 121.5–122°, respectively, were prepared by the procedure of Kohler and Potter.<sup>12,29</sup>

**N.m.r. Method of Analysis.**<sup>30</sup>—All spectra were obtained with a Varian model 4311 high-resolution spectrometer, operating at an average frequency of 56 Mc. and measured by standard audio-side band technique.<sup>31</sup> The samples were dissolved in deuterated chloroform in about a 10% solution, and analyzed.

(26) Unpublished results from this Laboratory.

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

(28) This sulfone was assigned the *trans* configuration, since it was previously prepared by the Friedel-Crafts reaction of *trans*- $\omega$ -styrenesulfonyl chloride with benzene [W. E. Truce, J. A. Simms, and H. E. Hill, *J. Am. Chem. Soc.*, **75**, 5411 (1953)].

(29) The assignment of configuration to these compounds were reported in ref. 4.

(30) The authors wish to express their gratitude to Mr. William Baitinger of this Laboratory for the determination of the n.m.r. spectra and the calculations of the coupling constants.

(31) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(24) A. Holtmeyer, *Z. Chem.*, 688 (1867).

(25) H. Gilman, *et al.*, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

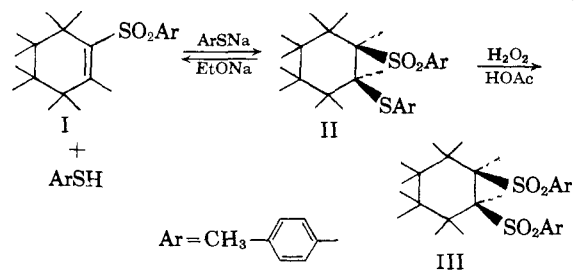
## The Stereochemistry of the Nucleophilic Addition of *p*-Toluenethiol to 1-*p*-Tolylsulfonyl-cyclohexene<sup>1</sup>

BY WILLIAM E. TRUCE AND ALAN J. LEVY

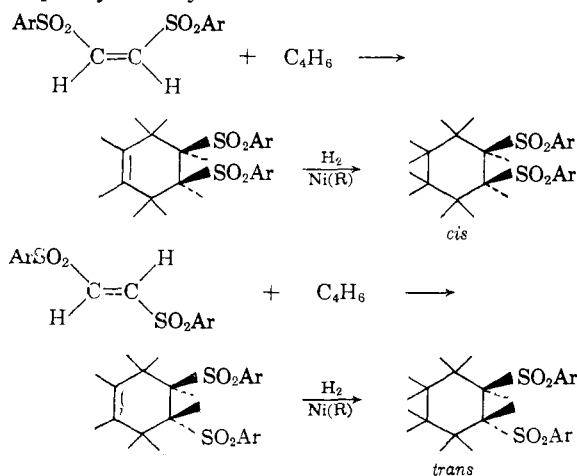
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*p*-Toluenethiol adds to 1-*p*-tolylsulfonyl-cyclohexene, under mildly basic conditions, in a *trans* manner giving *cis*-2-*p*-tolylmercapto-1-*p*-tolylsulfonylcyclohexane. The stereochemistry of the adduct was confirmed by independent synthesis and supported by n.m.r. spectra. A mechanism for the addition is proposed and evidence presented to support it.

Having demonstrated<sup>2-4</sup> that thiols under basic conditions add to acetylenes in a *trans* manner, we undertook the study of the stereochemistry of like additions to olefins. 1-*p*-Tolylsulfonyl-cyclohexene (I)<sup>5</sup> was selected for initial study because the double bond is activated and the system lends itself to a facile structure proof. The adduct II from the addition of alcoholic sodium *p*-toluenethiolate to the olefin I was oxidized to its disulfone III. Both the *cis* and *trans* isomers of 1,2-bis(*p*-



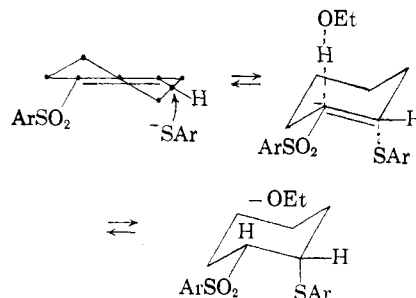
tolylsulfonyl)-cyclohexane (III) were independently synthesized from the known<sup>6,7</sup> *cis*- and *trans*-1,2-bis-*p*-tolylsulfonylethenes.



The independently prepared *trans*-disulfone was different from III, while the independently prepared *cis*-disulfone was shown to be identical with III, thus establishing that the nucleophilic addition had proceeded in a *trans* manner. The assignment of a *cis* configuration to II is further supported by n.m.r. spectra; *vide infra*.

Under the conditions of the reaction (0.1 molar equivalent of base) the addition of the nucleophile to the olefin was found to be reversible; with a full equivalent of base the adduct dissociates almost completely to olefin and thiolate. However, regardless of the reaction time, only the *cis* isomer was found.

It is well established<sup>8,9</sup> that for cyclohexane compounds substituted in the 1,2-positions the *trans* isomer is thermodynamically more stable. Therefore, the stereoselective addition leading *exclusively* to the less stable isomer can best be explained by a reaction mechanism involving a virtually concerted process.



Nucleophilic attack *via* the least hindered path corresponds to the axial direction<sup>10a-c</sup> in the transition state. If it is assumed that the bonds about the carbon atom developing a partial negative charge become tetrahedral,<sup>11a-c</sup> and that

(8) W. G. Dauben and K. S. Pitzer in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 19.

(9) *cis*-2-(Phenylsulfonyl)-methylcyclohexane was completely isomerized to its *trans* isomer by heating in a basic medium; F. G. Bordwell and W. A. Hewitt, *J. Am. Chem. Soc.*, **79**, 3493 (1957).

(10) This is analogous to the proposed direction of attack on cyclohexenyl systems by free radicals: (a) H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952); (b) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955); (c) J. C. D. Brand and I. D. R. Stevens, *J. Chem. Soc.*, 629 (1958).

(11) (a) G. Cilento, *Chem. Revs.*, **60**, 147 (1960); (b) E. J. Corey and E. T. Kaiser, *J. Am. Chem. Soc.*, **83**, 490 (1961); (c) H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2565 (1960).

(1) Presented at the 17th National Organic Chemistry Symposium of the American Chemical Society, June 29, 1961, Bloomington, Ind.

(2) W. E. Truce, J. A. Simms and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 695 (1956).

(3) W. E. Truce and J. A. Simms, *ibid.*, **78**, 2756 (1956).

(4) W. E. Truce and R. F. Heine, *ibid.*, **81**, 592 (1959).

(5) F. G. Bordwell and R. J. Kern, *ibid.*, **77**, 1141 (1955).

(6) W. E. Truce and R. J. McManis, *ibid.*, **76**, 5745 (1954).

(7) W. E. Truce, *et al.*, *ibid.*, **78**, 2743 (1956).