[Contribution from the Department of Chemistry, Purdue University]

Acetylenic Sulfur Compounds. I. Preparation and Characterization of *p*-Tolymercaptoacetylene and 1-Phenyl-2-phenylmercaptoacetylene

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p-Tolylmercaptoacetylene and 1-phenyl-2-phenylmercaptoacetylene and its sulfone have been prepared and characterized. Benzenesulfenyl chloride adds to phenylacetylene to give β-chloro-α-phenylmercaptostyrene.

In contrast to the scarcity of information about compounds having but one sulfur atom directly attached to an acetylenic group,[1,2,2a] there are known several compounds having a sulfur group attached to each carbon of an acetylenic function, *e.g.*, bis-(ethylmercapto)-,[3] bis-(2-methyl-2-propylmercapto)-,[4] bis-(*p*-tolylmercapto)-,[5] bis-(benzylmercapto)-[6] and bis-(2-nitrophenylmercapto)-acetylene.[6] This paper concerns the preparation and characterization of *p*-tolylmercaptoacetylene (I), 1-phenyl-2-phenylmercaptoacetylene (II) and its sulfone (III), all of which contain but one sulfur grouping. Added interest in such compounds stems from the hypothesis that *p*-tolylmercaptoacetylene is an intermediate in the conversion of *cis*-dichloroethylene to *cis*-bis-(*p*-tolylmercapto)-ethylene.[7]

The route employed for preparing *p*-tolylmercaptoacetylene (I) was similar to that used for the synthesis of the bis-(arylmercapto)-acetylenes.[3-6] *p*-Tolylmercaptoethylene, prepared by the sealed tube reaction of vinyl bromide with sodium *p*-toluenethiolate, was brominated and the resulting dibromide was doubly dehydrobrominated. The product had infrared absorption bands at 3.08 μ (≡C—H) and 4.90 μ (—C≡C—), the latter band being shifted from the 4.67–4.76 μ region reported for dialkyl acetylenes.[8-10] Compound I was readily converted to the corresponding and sharp-melting mercuric acetylide.

$$CH_2{=}CHBr \xrightarrow{C_7H_7SNa}$$

$$C_7H_7SCH{=}CH_2 \xrightarrow[2,\ KOH]{1,\ Br_2} \underset{\text{I}}{C_7H_7SC{\equiv}CH}$$

Traces of *p*-tolylmercaptoacetylene (I) were also detected in the reaction of chloroacetylene with sodium *p*-toluenethiolate, compound I being formed presumably by the dehydrohalogenation of an initial stereospecific *trans* nucleophilic addition product, *cis*-1-chloro-2-(*p*-tolylmercapto)-ethylene.[7] In fact, when this last compound is treated with alkaline mercuric iodide reagent, mercuric bis-(*p*-tolylmercaptoacetylide) is obtained.[7,10a]

1-Phenyl-2-phenylmercaptoacetylene (II) was prepared by treating benzenesulfenyl chloride with the Grignard reagent of phenylacetylene. It was also obtained by treating 1-phenyl-2-phenylmercaptoethylene (prepared by the addition of benzenethiol to the phenylacetylene) with bromine followed by alcoholic potassium hydroxide. The samples of II obtained by these two routes gave the same sulfone III through oxidation with hydrogen peroxide. This sulfone had approximately the same melting point as *trans*-1-phenyl-2-(phenylsulfonyl)-ethylene, and the mixture melting points were approximately the same. However, their infrared spectra were distinctly different and sulfone III had a strong infrared absorption band at 4.80 μ, this region being characteristic of the carbon–carbon triple bond.[8-10] Hydrogenation of III over palladium-on-charcoal gave the known phenyl β-phenylethyl sulfone (IV).

$$\left.\begin{array}{r} C_6H_5SCl + C_6H_5C{\equiv}CMgBr \xrightarrow{\qquad\quad} \\ C_6H_5SCH{=}CHC_6H_5 \xrightarrow[2,\ KOH]{1,\ Br_2} \end{array}\right\} \underset{\text{II}}{C_6H_5SC{\equiv}CC_6H_5}$$

$$\text{II} + H_2O_2(HOAc) \longrightarrow \underset{\text{III}}{C_6H_5SO_2C{\equiv}CC_6H_5}$$

$$\text{III} + H_2 \xrightarrow{Pd(C)} \underset{\text{IV}}{C_6H_5SO_2CH_2CH_2C_6H_5}$$

Several other approaches to the acetylenes II and III or their homologs were unsuccessful. One of these involved adding benzenesulfenyl chloride to phenylacetylene with a contemplated subsequent dehydrohalogenation. However, the direction of addition [$C_6H_5C(SC_6H_5){=}CHCl$] was apparently opposite to that expected considering the reaction product obtained from styrene ($C_6H_5CHClCH_2SC_6H_5$).[11] The orientation of the product from phenylacetylene was established by hydrolysis of its sulfone to benzyl phenyl sulfone, presumably by way of α-(phenylsulfonyl)-phenylacetaldehyde.

Also unsuccessful were additional attempts to prepare compounds II and III, *e.g.*, by the reaction of phenylethynylmagnesium bromide with diphenyl disulfide and benzenesulfonyl fluoride, respectively.

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(1) C. S. Rondestvedt, Jr., This Journal, **76**, 1926 (1954).

(2) F. Krafft and G. Heizmann, *Ber.*, **33**, 3588 (1900); C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 175.

(2a) W. E. Parham and P. L. Stright (Dallas, Texas, Meeting of American Chemical Society, April, 1956) obtained phenylmercaptoacetylene by treating *cis*- and *trans*-bis-(phenylmercapto)ethylene with butyllithium.

(3) H. Baganz and W. Triebsch, *Naturwissenschaften*, **42**, 155 (1955).

(4) H. J. Backer and J. Strating, *Rec. trav. chim.*, **73**, 565 (1954); H. J. Backer, J. Strating and J. F. A. Hazenburg, *ibid.*, **72**, 813 (1953).

(5) E. Fromm and E. Siebert, *Ber.*, **55**, 1014 (1922).

(6) E. Fromm, H. Benzinger and F. Schafer, *Ann.*, **394**, 325 (1912).

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

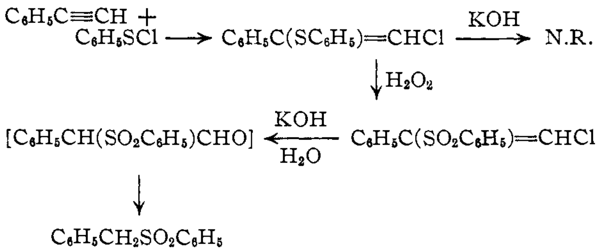
(8) F. A. Miller in H. Gilman's "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 144.

(9) J. H. Wotiz and F. A. Miller, This Journal, **71**, 3441 (1949).

(10) V. Z. Williams, *Rev. Sci. Instr.*, **19**, 143 (1948).

(10a) *trans*-1-Chloro-2-(*p*-tolylmercapto)-ethylene, which was prepared from acetylene and *p*-toluenesulfenyl chloride, when treated likewise, did not form this mercury derivative; W. E. Truce and M. M. Boudakian, This Journal, **78**, 2748 (1956).

(11) W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).



$$\begin{tikzcd}
\mathrm{C_6H_5C{\equiv}CH} + \mathrm{C_6H_5SCl} \arrow[r] & \mathrm{C_6H_5C(SC_6H_5){=}CHCl} \arrow[r, "\mathrm{KOH}"] \arrow[d, "\mathrm{H_2O_2}"] & \mathrm{N.R.} \\
{[\mathrm{C_6H_5CH(SO_2C_6H_5)CHO}]} \arrow[d] & \mathrm{C_6H_5C(SO_2C_6H_5){=}CHCl} \arrow[l, "\mathrm{KOH}", "\mathrm{H_2O}"'] & \\
\mathrm{C_6H_5CH_2SO_2C_6H_5} & &
\end{tikzcd}$$

Experimental[12]

p-Tolylmercaptoethylene.[13]—Vinyl bromide (3.21 g., 2.11 ml., 0.03 mole, Matheson) was distilled into a Carius tube, to which was added 3.73 g. (0.03 mole) of *p*-toluenethiol, 0.76 g. (0.033 mole) of sodium and 0.1 g. of the polymerization inhibitor, diphenylamine, in 45 ml. of absolute ethanol. The reaction was run for 39 hr. at 125°. Sodium bromide (3.09 g.) was filtered off and washed with hot absolute ethanol. The filtrate was concentrated, diluted with water and extracted with petroleum ether (b.p. 30–60°). The ether extracts were dried over magnesium sulfate and evaporated to give 4.06 g. (88.3%) of an oil having b.p. 78.0° (4.0 mm.), n^{20}D 1.5727.

p-Tolylsulfonylethylene, prepared from 1.15 g. (0.0076 mole) of the sulfide, 4.0 g. of 30% hydrogen peroxide in 5.0 ml. of glacial acetic acid, weighed 0.97 g. (75.4%) and melted at 62.0–63.0°. Recrystallization from absolute ethanol raised the melting point to 65° (reported m.p. 66°,[14] 65–66°[15]).

Anal.[16] Calcd. for $C_9H_{10}O_2S$: C, 58.67; H, 5.74. Found: C, 59.28; H, 5.90.

p-Tolylmercaptoacetylene.—Bromine (51.9 g., 0.324 mole) in 200 ml. of chloroform was added over a 2-hr. period to a chilled (0°) solution of 48.7 g. (0.324 mole) of *p*-tolylmercaptoethylene in 400 ml. of chloroform. Toward the end of the reaction, the bromine was not decolorized. Stirring was continued for an additional hour. The reaction mixture was concentrated to a red-brown oil weighing 103.0 g. and representing a quantitative yield of 1,2-dibromo-1-(*p*-tolylmercapto)-ethane.

This oil (103.0 g., 0.324 mole) dissolved in 250 ml. of 95% ethanol was added dropwise over a 0.5 hr. period to 42.0 g. (0.648 mole) of potassium hydroxide in 450 ml. of 95% ethanol. After the initial exothermic reaction had subsided, the reaction mixture was heated to reflux for 12 hr. Potassium bromide (70.0 g., theoretical 77.2 g.) was filtered off, the filtrate was concentrated, water was added, and the reaction mixture was extracted with petroleum ether (30–60°). The ether extracts were dried over magnesium sulfate and evaporated to 61.0 g. of an oil which distilled at 78.5–80.5° (2.3 mm.), n^{20}D 1.5729; upon redistillation, b.p. 73.0–77.0° (2.5 mm.), n^{20}D 1.5721. The product gave a negative Beilstein test for halogen and weighed 22.8 g. (47.7% conversion to *p*-tolylmercaptoacetylene). *p*-Tolylmercaptoacetylene turns dark on standing, even at 0°. The infrared spectrum[17] (0.02 mm.) showed a terminal acetylene stretching frequency band at 3.08 μ (reported[8,9] 3.02–3.12 μ), and a deformation frequency band for a carbon-carbon triple bond at 4.90 μ (reported[8,10] 4.67 to 4.76 μ).

p-Tolylmercaptoacetylene was converted to its mercury derivative[18–20] by adding 1.0 g. (0.00675 mole) of it in 10 ml. of 95% ethanol with stirring to a chilled solution of alkaline mercuric iodide reagent (9.08 ml., 0.01350 equivalent). The reaction mixture was filtered, washed with cold 50% ethanol to give a solid, m.p. 144.5–145.5° (wt. 1.60 g., 95.8% yield). Recrystallization from 95% ethanol (Norite A) increased the melting point to 145.5–146.5°.

Anal.[21] Calcd. for $Hg(C_9H_7S)_2$: C, 43.65; H, 2.85; S, 12.96; Hg, 40.52. Found: C, 43.50; H, 2.87; S, 12.84; Hg, 40.47.

Upon standing at room temperature, mercuric bis-(*p*-tolylmercaptoacetylide) turns slightly brown.

1-Phenyl-2-phenylmercaptoacetylene.—Benzenesulfenyl chloride was prepared by the chlorination of 50.0 g. (0.229 mole) of diphenyl disulfide in carbon tetrachloride; b.p. 44.0–47.5° (1.0 mm.), weight 60.2 g. (91.0%).[22] To a Grignard reagent, prepared from 2.65 g. (0.109 mole) of magnesium and 11.9 g. (0.109 mole) of ethyl bromide in 50 ml. of anhydrous ether, 10.0 g. (0.098 mole) of phenylacetylene in 25 ml. of ether was added dropwise and the mixture was stirred and refluxed until no more ethane was evolved (1 hr.). Freshly prepared benzenesulfenyl chloride (14.2 g., 0.098 mole) in 75 ml. of anhydrous ether was added dropwise and the mixture was heated at reflux for 1 hr. and then allowed to stand overnight. The mixture was hydrolyzed by pouring onto a mixture of ice and hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were dried over Drierite, the ether was distilled off and the residual liquid was vacuum distilled to give 11.7 g. (57.0%) of 1-phenyl-2-phenylmercaptoacetylene, b.p. 155.0–170.0° (2.5 mm.), n^{25}D 1.6629–1.6644.

To a solution of 6.3 g. (0.03 mole) of this acetylenic sulfide in 100 ml. of glacial acetic acid, 13 ml. (0.13 mole) of 30% hydrogen peroxide was added dropwise with stirring. The mixture was allowed to stand overnight and then poured onto ice to give 2.8 g. of a solid sulfone, m.p. 70–72°. Concentration of the filtrate gave an additional 1.6 g. of sulfone, m.p. 69–71° (combined yield 61.0%). An analytical sample was crystallized twice from petroleum ether (b.p. 65–67°) and had m.p. 73.0–74.0°.

Anal. Calcd. for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16. Found: C, 69.70, 69.58; H, 4.28, 4.59.

This sulfone had an infrared deformation frequency band at 480 μ (2150 cm.$^{-1}$) (reported[8–10] for disubstituted acetylenes, 4.67 to 4.76 μ).

Mixture melting points of 1-phenyl-2-phenylsulfonylacetylene (m.p. 73–74°) and *trans*-1-phenyl-2-phenylsulfonylethylene (m.p. 73–74°)[23] showed only slight variations in melting point within the temperature range, 71.5–76.0°.

An alternate synthesis of 1-phenyl-2-phenylmercaptoacetylene was carried out by adding 27.5 g. (0.25 mole) of benzenethiol to 25.5 g. (0.25 mole) of phenylacetylene immersed in an ice-bath. After allowing the mixture to stand overnight at room temperature, it was distilled to give 41.3 g. (78% yield) of 1-phenyl-2-phenylmercaptoethylene, b.p. 146–147° (1 mm.).[15] The sulfide was dissolved in 150 ml. of carbon tetrachloride and an equimolar amount of bromine (31.2 g., 0.195 mole) in 100 ml. of carbon tetrachloride was added in portions, a considerable amount of hydrogen bromide being evolved. The bromine was not completely decolorized. The mixture was allowed to stand for 4 hr., was washed twice with sodium bicarbonate solution and was dried over anhydrous sodium sulfate.

The solvent was evaporated and the residual liquid was refluxed with 22 g. (0.39 mole) of potassium hydroxide in 500 ml. of 95% ethanol for 1 hr., the mixture was neutralized with hydrochloric acid and the insoluble salts were filtered off. The ethanol was evaporated, water was added to the residue and the mixture was extracted with ether. The ethereal extracts were dried over anhydrous sodium sulfate and distilled to give 22.0 g. (54%) of 1-phenyl-2-phenylmercaptoacetylene, b.p. 155.0–158.5° (2.0 mm.), n^{20}D 1.6593–1.6652.

This sulfide (1.0 g., 0.0048 mole) was dissolved in 10 ml. of 1:1 acetic acid–acetic anhydride solution, cooled in an

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(12) All boiling points and melting points are uncorrected.

(13) J. Loevenich, J. Losen and A. Dierichs, *Ber.*, **60**, 950 (1927); W. Reppe, E. Keyssner and F. Nicolai, German Patent 646,995; *C. A.*, **31**, 6258 (1937).

(14) G. D. Buckley, J. L. Charlish and J. D. Rose, *J. Chem. Soc.*, 1514 (1947).

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

(16) Except where noted, all microanalyses were performed by Dr. C. S. Yeh and Mrs. S. L. Margerum, Purdue Chemistry Microanalytical Laboratory.

(17) The infrared spectra were run by Mr. H. Susi, Mrs. L. Walsh and Mr. J. Stewart of the Purdue Chemistry Infrared Laboratory.

(18) J. R. Johnson and W. L. McEwen, THIS JOURNAL, **48**, 469 (1926).

(19) J. U. Nef, *Ann.*, **308**, 299 (1899).

(20) Refer to J. G. Hanna and S. Siggia, *Anal. Chem.*, **21**, 1469 (1949), for the quantitative determination of monosubstituted acetylenes as mercury derivatives.

(21) Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(22) H. Lecher, F. Holschneider, K. Koberle, W. Speer and P. Stocklin, *Ber.*, **58**, 409 (1925).

(23) W. E. Truce, J. A. Simms and H. E. Hill, THIS JOURNAL, **75**, 5411 (1953).

ice-bath, to which 2 ml. (*ca.* 0.02 mole) of 30% hydrogen peroxide was added. Two phases formed and the mixture was shaken occasionally until dissolution was complete. The mixture was allowed to stand at room temperature overnight and then poured onto ice to give a solid which was recrystallized from aqueous methanol, weight 0.70 g. (61%), m.p. 72–75°. Infrared analysis showed the presence of the acetylenic band at 4.80 μ and the complete absence of ethylenic bands.

Hydrogenation of 1-Phenyl-2-phenylsulfonylacetylene.—1-Phenyl-2-phenylsulfonylacetylene (1.0 g., 0.0413 mole) in 200 ml. of absolute ethanol was hydrogenated using 0.5 g. of a palladium-on-charcoal catalyst at 18 p.s.i. The catalyst was filtered off and the solvent evaporated. The residue was crystallized from 50% ethanol giving 0.44 g. (43%) of white crystals melting at 55.5–56.5° (reported[24] m.p. 58°). Attempts to elevate the melting point by further crystallization or treatment with permanganate in acetone were unsuccessful. A mixed melting point with an independently synthesized sample of phenyl β-phenylethyl sulfone (m.p. 58–59°) showed no depression (observed m.p. 56.5–58.0°).

Addition Product of Benzenesulfenyl Chloride and Phenylacetylene.—Phenylacetylene (10.2 g., 0.10 mole) and 14.5 g. (0.10 mole) of freshly prepared benzenesulfenyl chloride were mixed in 50 ml. of benzene. The exothermic reaction required cooling in an ice-bath. After standing overnight at room temperature, the reaction mixture was vacuum distilled to give 20.0 g. (81%) of pale yellow liquid boiling at 132–139° (1 mm.). A middle cut, obtained by redistillation and having b.p. 158–161° (2.5 mm.), $n^{25}\text{D}$ 1.6405, was submitted for analysis.

Anal. Calcd. for $C_{14}H_{11}SCl$: C, 68.14; H, 4.49. Found: C, 68.16; H, 4.74.

Refluxing 28.2 g. (0.114 mole) of this chlorovinyl sulfide with 6.7 g. (0.12 mole) of potassium hydroxide in 400 ml. of 95% ethanol, yielded only recovered starting material (60% recovery), $n^{20}\text{D}$ 1.6410–1.6433. When 7.0 g. (0.028 mole) of the chlorovinyl sulfide was refluxed with 35 ml. of γ-collidine for 7 hr., only 2% of the chloride ion was liberated (isolated as silver chloride).

The chlorovinyl sulfide (6.4 g., 0.026 mole) was dissolved in 30 ml. of 1:1 acetic acid–acetic anhydride, cooled in an ice-bath, and then 10 ml. (*ca.* 0.10 mole) of 30% hydrogen peroxide was added. Two layers formed and the mixture was shaken occasionally until dissolution had occurred. The bath was allowed to come to room temperature. After standing overnight the mixture was poured into water and the resulting liquid was extracted with ether. The ether solution was treated with 5% sodium bicarbonate solution to remove acetic acid and then was evaporated to give an oily residue. The residual oil was added to 100 ml. of 50% ethanol containing 3.1 g. (0.055 mole) of potassium hydroxide and the mixture was refluxed for 4 hr. Upon cooling there was deposited 3.51 g. of white crystals, m.p. 128–140°. After three crystallizations from absolute ethanol the product had m.p. 147–150°. A mixed m.p. with an authentic sample of phenyl benzyl sulfone[25] was not depressed.

Unsuccessful Attempts to Prepare 1-Phenyl-2-phenylmercaptoacetylene or Its Sulfone.—To ethylmagnesium bromide reagent, prepared from 2.65 g. (0.109 mole) of magnesium turnings, 11.9 g. (0.109 mole) of ethyl bromide and 50 ml. of ether, was added 10 g. (0.098 mole) of phenylacetylene dissolved in 50 ml. of anhydrous benzene. After the evolution of ethane had subsided, the reaction mixture was refluxed for approximately 2 hr. Di-*p*-tolyl disulfide (24.1 g., 0.098 mole), dissolved in 100 ml. of anhydrous benzene, was added to the Grignard reagent. The reaction mixture was refluxed for 4 hr., a yellow precipitate separating during this time. The reaction mixture was cooled and then filtered. The ether–benzene filtrate was poured onto 50 ml. of water and the ether and benzene were removed by steam distillation. The aqueous mixture was acidified with dilute hydrochloric acid to dissolve basic magnesium salts and the organic material was extracted with ether. The ether layer was evaporated and the residue was recrystallized from 95% ethanol. Only di-*p*-tolyl disulfide (12.8 g., 53% recovery) was obtained, m.p. and mixture m.p. 44–45°.

p-Toluenesulfonyl fluoride (65.3 g., m.p. 40.5–42.0°) was prepared[26] from 190 g. (1.0 mole) of *p*-toluenesulfonyl chloride and 120 ml. of a solution containing 141.2 g. (1.5 moles) of potassium fluoride dihydrate; 20 g. (0.115 mole) of this sulfonyl fluoride in 100 ml. of anhydrous benzene was added to a Grignard reagent prepared from 10 g. (0.098 mole) of phenylacetylene in the same manner as indicated previously. After refluxing the reaction mixture for 36 hr., it was cooled and 100 ml. of water was slowly added. No exothermic reaction was noted. The mixture was steam distilled to remove ether, benzene and *p*-toluenesulfonyl fluoride. The residue was extracted with ether and the ether was then evaporated. Attempts to crystallize this residue from ethanol were unsuccessful.

Phenylbromoacetylene was prepared by adding phenylacetylene (10 g., 0.098 mole) to a solution formed by adding 160 g. (1.0 mole) of bromine to 120 g. (3.0 moles) of sodium hydroxide dissolved in 250 ml. of water. The mixture was stirred for 2 hr. and was then extracted with ether. The ether layer was dried and distilled to yield 8.2 g. (46%) of phenylbromoacetylene, b.p. 87.5–88° (13 mm.). Phenylbromoacetylene (8.2 g., 0.045 mole) was added to a solution prepared from 1.04 g. (0.045 mole) of sodium, 100 ml. of absolute ethanol and 4.95 g. (0.045 mole) of thiophenol. The solution was refluxed for 48 hr. (after a few hours a precipitate had formed). The alcohol was removed by distillation and had a strong odor of phenylacetylene. The residue was treated with 100 ml. of water and was extracted with ether. The aqueous solution upon treatment with a small amount of 30% hydrogen peroxide yielded no diphenyl disulfide. The ether extract was evaporated and was then vacuum distilled. After a small forerun there was obtained 3.3 g. of liquid boiling at 190–192° (12 mm.), which solidified upon cooling. Upon recrystallization from methanol the solid melted at 59–61° (reported for diphenyl disulfide, m.p. 61–62°).

A solution of 8.5 g. (0.05 mole) of silver nitrate in a small amount of water was mixed with 100 ml. of 95% ethanol and then added to a solution of 5 g. (0.049 mole) of phenylacetylene in alcohol. The precipitate was filtered, washed with ethanol and then with ether. The silver phenylacetylide was mixed with 300 ml. of dimethylformamide in which most of it dissolved. A solution of 9.5 g. (0.05 mole) of *p*-toluenesulfonyl chloride in 100 ml. of dimethylformamide was added. There was an immediate reaction and when warmed the silver chloride coagulated. The solution was allowed to cool and the silver chloride was filtered off. The dimethylformamide was removed from the filtrate by vacuum distillation. The liquid remaining was recrystallized from benzene. White crystals were obtained which melted at 95.5–97.5°. The product was identified as *p*-toluenesulfonic acid, its S-benzylthiouronium salt melting at 180.5–182.5°.

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[24] T. Posner, *Ber.*, **38**, 651 (1905).

[25] R. L. Shriner, H. C. Struck and W. J. Jorison, THIS JOURNAL, **52**, 2060 (1930).

[26] W. Davies and J. H. Dick, *J. Chem. Soc.*, 2104 (1931).