[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Triphenylvinyl Mercaptan

BY C. F. KOELSCH AND GLENN ULLYOT

Thiophenols may be obtained, often in good yields, by the action of sulfur on arylmagnesium halides.[1] Triphenylvinylmagnesium bromide reacts with sulfur in an analogous manner, giving the corresponding thiol, $(C_6H_5)C{=}C(SH)C_6H_5$.

A few thiols have been described in which the sulfhydryl group is attached to an unsaturated aliphatic carbon atom,[2] but the carbonyl group which each of these compounds contains probably influences the behavior of the sulfhydryl group. On alkylation, these substances give S-ethers,[3] and on treatment with phenylhydrazine or with hydroxylamine they evolve hydrogen sulfide with the formation of phenylhydrazones or oximes, indicating that they react in the tautomeric forms C=C—SH and CH—C=S.

In contrast, triphenylvinyl mercaptan appears to react in only the enol form. It dissolves readily in aqueous sodium hydroxide, slowly in boiling aqueous sodium carbonate; carbon dioxide precipitates the mercaptan from these solutions. Methyl sulfate and alkali give a S-methyl ether, and benzoylation by the Schotten–Baumann reaction gives a benzoate. Boiling with alcoholic hydroxylamine acetate gives bis-triphenylvinyl disulfide, which may also be obtained by oxidizing the mercaptan with permanganate. Acid hydrolysis of the mercaptan yields diphenylacetophenone.

Diphenylacetophenone, the O-analog of triphenylvinyl mercaptan, was for a long time considered as triphenylvinyl alcohol, since it could be acetylated and since it supposedly did not form an oxime.[4] At the present time, however, it is given the ketonic formula, Kohler having shown that under the proper conditions it forms an oxime and adds alkylmagnesium halides.[5] Furthermore, diphenylacetophenone is insoluble in alkalies, while the closely related 9-benzoylfluorene is known in a keto and an enol form, the latter of which is readily soluble in aqueous alcoholic alkali, while the former is slowly soluble, solution being accompanied by enolization.[6] The present results indicate that sulfur has little tendency to form a double bond with carbon, a conclusion which may also be drawn from the readiness with which aliphatic thioaldehydes and ketones polymerize, and from the reactivity and color of the aromatic thioketones.

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(1) Taboury, *Bull. soc. chim.*, [3] **33**, 836 (1905).

(2) $C_6H_5CH{=}C(SH)COOH$, Granacher, *Helv. Chim. Acta.*, **5**, 610 (1922); $CH_3C(SH){=}CHCOOC_2H_5$, Scheibler and Bube, *Ber.*, **48**, 1451 (1915).

(3) Mitra, *J. Indian Chem. Soc.*, **10, 71** (1933).

(4) Biltz, *Ber.*, **32**, 650 (1899).

(5) Kohler, *Am. Chem. J.*, **36**, 191 (1906).

(6) Meyer and Gottlieb-Billroth, *Ber.*, **54**, 575 (1921); *cf.* Ley and Manecke, *ibid.*, **56**, 777 (1923).

Experimental

Triphenylvinyl Mercaptan.—To a solution of triphenylvinylmagnesium bromide containing two grams of magnesium[7] is added 2.2 g. of sulfur, and the mixture is refluxed for two hours. The magnesium compound is hydrolyzed with iced sulfuric acid, the ether is removed, and the sirupy residue is crystallized from benzene and then from ligroin; yield, 12 g. The compound forms faintly yellow needles that melt at 110–111°.

Anal. Calcd. for $C_{20}H_{16}S$: C, 83.3; H, 5.6. Found: C, 83.5; H, 5.5. *Mol. wt.* Calcd.: 288. Found: (Rast) 275.

Triphenylvinyl mercaptan dissolves in warm aqueous sodium hydroxide, giving a yellow solution which deposits the white difficultly soluble salt on cooling. On boiling with sodium carbonate solution, the mercaptan slowly dissolves; carbon dioxide passed into a warm solution of the sodium salt precipitates the mercaptan.

When a solution of 1 g. of the mercaptan in 30 ml. of acetic acid is acidified with a few drops of sulfuric acid and then boiled, hydrogen sulfide is evolved. On cooling this solution, diphenylacetophenone crystallizes in a nearly theoretical yield. The product melts at 134.5–135° alone or mixed with an authentic sample, and gives the characteristic green color on heating with concd. sulfuric acid.

The methyl ether is obtained by shaking a solution of 1 g. of the mercaptan and 2 g. of sodium hydroxide in 40 ml. of water with 3 ml. of methyl sulfate for twelve hours. The product, crystallized from methanol, forms orange-yellow prisms (0.8 g.) that melt at 109.5–110°. The methyl ether is insoluble in hot sodium hydroxide solution, but very easily soluble in the common organic solvents including petroleum ether; a mixture with triphenylvinyl mercaptan melts at 86–89°. On boiling the methyl ether with acetic acid containing a little sulfuric acid, methyl mercaptan is evolved.

Anal. Calcd. for $C_{21}H_{18}S$: C, 83.4; H, 6.0. Found: C, 83.3; H, 6.0.

The benzoate, prepared by the Schotten–Baumann reaction and crystallized from acetic acid, forms colorless needles that melt at 192–193°. Concordant analytical results were difficult to obtain.

Anal. Calcd. for $C_{27}H_{20}OS$: C, 82.5; H, 5.1. Found: C, 81.6; H, 5.2.

Bis-triphenylvinyl Disulfide.—To a solution of 1 g. of triphenylvinyl mercaptan in hot sodium hydroxide is added 1 g. of potassium permanganate. The mixture is made faintly acid and filtered. The solid is dried and extracted repeatedly with hot ligroin (b. p. 90–110°). The disulfide is obtained by concentrating and cooling the combined extracts. On recrystallization from acetic acid there is obtained about 0.4 g. of yellow prisms that melt at 179.5–180.5° and give a qualitative test for sulfur.

Anal. Calcd. for $C_{40}H_{30}S_2$: C, 83.6; H, 5.3. Found: C, 83.8; H, 5.7. *Mol. wt.* (Rast). Calcd. 574. Found: 585.

The disulfide is obtained when a solution of the mercaptan in alcohol is boiled for four hours with an excess of hydroxylamine hydrochloride and sodium acetate.

Summary

Triphenylvinyl mercaptan, obtained from triphenylvinylmagnesium bromide and sulfur, behaves as an enolic substance, in contrast to its O-analog, diphenylacetophenone.

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[7] Koelsch, THIS JOURNAL, **54**, 2047 (1932).