

TABLE I
 X-RAY-INDUCED ADDITION OF HYDROGEN SULFIDE TO ACETYLENES

RC≡CR'		Moles H ₂ S/moles RC≡CR'	Dosage, e.v./g. × 10 ⁻¹⁹	Mole RC≡CR' reacted	G _{RC≡CR'}	Product distribution, %			
R	R'					II	III	IV	V
CH ₃	H	2.2/1.1	26	0.15	~ 270	32	35	^a	33
CH ₃	CH ₃	0.9/0.5	26	.017	~ 70	24	41	..	35
CF ₃	H	0.7/0.2	30	.022	~ 100	73	~20	~5	..
CF ₃	CF ₃	2.0/0.6	28	.025	~ 35	60		^b	
C ₆ H ₅	H	0.6/0.18	22	.14	~1900	8	..	47	45

^a Possible trace of IV mixed with III. ^b The higher-boiling compounds were not separated.

is a doublet (J 11.1 c.p.s.), while the other is a doublet split to quadruplets (J doublet = 11.7 c.p.s., J quad. = 4.2 c.p.s.). The vinyl hydrogen resonances are complex but consistent with the presence of two isomeric 3,3,3-trifluoropropene-1-thiols (II, R = CF₃, R' = H). The F¹⁹ n.m.r. spectrum likewise shows the presence of the two stereoisomers in the reaction product. It consists of two resonances in an integrated intensity ratio of about 60:40, centered at -176 c.p.s. and at -376 c.p.s. The splitting pattern of each resonance is doublets split to doublets. The larger resonance has J -values of 8.6 and 4.2 c.p.s., while the minor resonance has J -values of 7.7 and 2.7 c.p.s.

The proton n.m.r. spectrum of the methylacetylene-H₂S adduct (1-propene-1-thiol) indicates that it is also a mixture of *cis* and *trans* isomers. The spectrum consists of two resonances in the CH₃ region at τ 8.38 and 8.28, two in the SH region at τ 7.32 and 7.2, and a multiline resonance in the vinyl proton region centered at approximately τ 4.2. The possibility that the product might be a mixture of 1-propene-1-thiol and 1-propene-2-thiol was ruled out by hydrolyzing the 1:1 adduct in the presence of 2,4-dinitrophenylhydrazine. Only propionaldehyde 2,4-DNP was obtained, in confirmation of the 1-propene-1-thiol structure.

The structure of the vinylthiol from phenylacetylene has been inferred from the fact that bis-(β -phenylvinyl) sulfide is the major reaction product.

The free-radical chain nature of the reactions is evidenced not only by the magnitude of the G -values observed and by the analogy of these reactions to thiol additions to acetylenes but by the further observation that azo catalysts will effect the addition of hydrogen sulfide to phenylacetylene and to methylacetylene. In both cases, high conversions were obtained, but no trace of vinylthiol could be found. The absence of vinylthiols in these reaction products is undoubtedly associated with their instability at the higher temperatures necessary for reactions using azo initiators.

Experimental

Reaction of Methylacetylene with Hydrogen Sulfide (X-Rays).

—A mixture of 42 g. (1.1 moles) of methylacetylene and 75 g. (2.2 moles) of hydrogen sulfide in a 300-ml. stainless-steel cylinder was irradiated with X-rays for 3.5 hours at an average dose rate of approximately 20,000 rads/minute.⁹ After the excess reactants were bled off there remained 16 g. of pale yellow liquid. The combined product from three such runs was distilled under vacuum, and the following fractions obtained: (1) b.p. ~28° (165 mm.), 10.5 g., n_D^{20} 1.481; (2) b.p. 35° (10 mm.) 16.5 g., n_D^{20} 1.524; (3) residue, 10.5 g.

Fraction 1 was shown to be 1-propene-1-thiol. Its infrared spectrum included —SH absorption at 2564 cm.⁻¹ and —C=C— absorption at 1613 cm.⁻¹.

Anal. Calcd. for C₃H₆S: C, 48.6; H, 8.16; S, 43.2. Found: C, 48.3; H, 8.08; S, 42.8.

A 0.47-g. (6.5 mmoles) sample of fraction 1 mixed with 1.3 g. (6.5 mmoles) of 2,4-dinitrophenylhydrazine and 0.9 g. of concd. sulfuric acid in 40 ml. of ethyl alcohol was refluxed until hydrogen sulfide evolution ceased. The solution was diluted with water

and cooled, whereupon approximately 1.0 g. of orange crystals separated (m.p. 130–140°). Attempts to purify this material by recrystallization were unsuccessful. Accordingly, a sample was chromatographed on silica gel, and a *single* 2,4-dinitrophenylhydrazine was obtained at an eluent volume corresponding to that of propionaldehyde 2,4-dinitrophenylhydrazone. The derivative was isolated by evaporation of the eluent solvent and sublimed. It melted at 152–154° and showed no depression of the melting point in a mixture with authentic propionaldehyde 2,4-DNP. Its infrared spectrum was identical with that of an authentic sample.

2,4-Dinitrophenyl 1-Propenyl Disulfide.—A sample (0.16 g., 2.1 mmoles) of freshly prepared 1-propene-1-thiol was mixed with 0.44 g. (1.9 mmoles) of recrystallized 2,4-dinitrobenzenesulfonyl chloride in 25 ml. of anhydrous ether and allowed to stand at room temperature for 24 hours. Evaporation of the ether left a yellow solid, which was recrystallized from a mixture of heptane and benzene. After several recrystallizations it melted at 74–77°.

Anal. Calcd. for C₉H₈N₂O₄S₂: N, 10.3; S, 23.5. Found: N, 10.5; S, 23.2.

Fraction 2 was shown to be impure propane-1,2-dithiol¹⁰ on the basis of analysis, infrared absorption and derivative preparation with 2,4-dinitrobenzenesulfonyl chloride. The infrared spectrum showed SH absorption at 2564 cm.⁻¹, which was much more intense than that shown by 1-propene-1-thiol (fraction 1), but there was still some absorption at 1613 cm.⁻¹ (C=C), suggestive of possible contamination with dipropenyl sulfide.

Anal. Calcd. for C₃H₆S₂: C, 33.3; H, 7.84; S, 59.2. Found: C, 36.5; H, 7.46; S, 56.8.

1,2-Bis-(2,4-dinitrophenylthio)-propane.—A 0.30-g. (3 mmoles) sample of fraction 2 was mixed with 1.2 g. (5 mmoles) of recrystallized 2,4-dinitrobenzenesulfonyl chloride in 45 ml. of anhydrous ether. After standing for 2 days at room temperature, there was obtained 1.1 g. of a yellow crystalline precipitate, which melted at 135–136° after recrystallization from benzene-cyclohexane.

Anal. Calcd. for C₁₅H₁₂N₄O₈S₄: N, 11.1; S, 25.4. Found: N, 11.2; S, 25.5.

Fraction 3.—Attempted distillation of the residue gave a small amount of a product, boiling at 52–53° (2 mm.) (n_D^{20} 1.532), which appears to be a tetramer of the propenethiol.

Anal. Calcd. for (C₃H₆S)₄: C, 48.6; H, 8.16; S, 43.2; mol. wt., 296. Found: C, 48.7; H, 8.33; S, 43.2; mol. wt., 292, 286.

The remainder of this fraction was apparently polymeric.

X-Ray-induced Addition of Hydrogen Sulfide to Phenylacetylene.—A mixture of 18 g. (0.18 mole) of redistilled phenylacetylene and 22 g. (0.65 mole) of hydrogen sulfide in a 100-ml. stainless-steel pressure vessel was irradiated with X-rays for 3 hours at an average dose rate of ~20,000 rads/minute. Volatiles were bled off, and the product, a mixture of oil and crystals, was rinsed out with petroleum ether. The crystalline product was only sparingly soluble and was filtered off (wt. = 7.8 g.). After recrystallization from cyclohexane, it melted at 96–96.5°. It was shown to be bis-(β -phenylvinyl) sulfide on the basis of its analysis and infrared spectrum, including the near infrared region.

Anal. Calcd. for C₁₆H₁₄S: C, 80.6; H, 5.92; S, 13.4; mol. wt., 238. Found: C, 81.2; H, 5.91; S, 13.6; mol. wt., 241.

The near infrared absorption at 6135 cm.⁻¹ of a 3% solution in CCl₄ was compared with that of similar solutions of α -methylstyrene and of *p*-methoxy- β -methylstyrene. The optical densities of the sulfide and *p*-methoxy- β -methylstyrene were similar (0.23 vs. 0.11), while that of the α -methylstyrene was much higher (1.44). This is clear evidence for the bis-(β -phenylvinyl) sulfide structure rather than the alternative α,α' - or α,β' -diphenylvinyl sulfide structure.

Distillation of the liquid portion (10 g.) of the reaction product gave 1.5 g. of material boiling at 48–51° (0.25 mm.), identified as β -phenylvinylthiol, on the basis of its analysis and infrared spectrum.

(9) The X-rays were generated by impinging electrons from a 3-Mev. van de Graaff generator onto a water-cooled gold target. Dose rates were determined by ferrous sulfate dosimetry.

(10) S. M. Iqbal and L. N. Owen, *J. Chem. Soc.*, 1030 (1960).

Anal. Calcd. for C_8H_8S : C, 70.5; H, 5.92; S, 23.5. Found: C, 70.1; H, 5.71; S, 23.2.

The infrared spectrum included absorption bands at 2564 cm^{-1} (SH) and 1613 cm^{-1} (C=C), as well as the usual aromatic and monosubstituted benzene absorptions. An attempt to prepare a derivative by reaction with 2,4-dinitrobenzenesulfonyl chloride gave a gum that failed to crystallize.

Oxidation of Bis-(β -phenylvinyl) Sulfide to Bis-(β -phenylvinyl) Sulfone.—Bis-(β -phenylvinyl) sulfide (3.5 g.) was stirred with 16 ml. each of glacial acetic acid and acetic anhydride. The mixture was cooled to 0–5° while 5 ml. of 30% hydrogen peroxide was added dropwise during 20 minutes, and the reaction mixture was then allowed to warm up slowly. After standing overnight, the mixture was poured into ice-water and the crystalline sulfone filtered off (3.1 g., 78% yield). Recrystallization from methanol gave white needles, m.p. 90–91°. The infrared spectrum included the expected absorptions at 1613 cm^{-1} (—C=C—) and at 1316 and 1124 cm^{-1} (SO_2).

Anal. Calcd. for $C_{16}H_{14}SO_2$: C, 71.1; H, 5.22; S, 12.8. Found: C, 71.4; H, 5.30; S, 12.8.

The X-Ray-induced Addition of Hydrogen Sulfide to 3,3,3-Trifluoropropyne.—A mixture of trifluoropropyne (20 g., 0.21 mole) and hydrogen sulfide (25 g., 0.73 mole) in a stainless-steel pressure vessel was irradiated with X-rays for 4 hours at an average dose rate of $\sim 20,000$ rads/minute. After the excess volatiles were bled off, there remained 3.1 g. of a vile-smelling, yellow liquid.

The products from several such runs were combined (19 g.) and distilled through a low-temperature, helices-packed column. Two major fractions were obtained; the first (9.5 g.) appeared to boil at 6–8° (70 mm.) (n^{25}_D 1.3879–1.3931). The higher-boiling fraction (5 g.) was pumped over into a trap under oil-pump vacuum (~ 0.25 mm.) without an accurate boiling point being recorded (n^{25}_D 1.4408).

Redistillation of the lower-boiling fraction through a spinning-band column gave a center cut (4 g.) boiling at 21–22° (138 mm.) (n^{25}_D 1.3889–1.3899). The infrared spectrum included the expected absorptions for 3,3,3-trifluoropropenethiol; viz., 2564 cm^{-1} (SH), 3125–3030 cm^{-1} (CH), 1639 cm^{-1} (C=C) and 1430–1100 cm^{-1} region (CF_3).

Anal. Calcd. for $C_3H_3SF_3$: F, 44.5; S, 25.0. Found: F, 44.2; S, 25.0.

The higher-boiling product included decreased but significant C=C absorption (1639 cm^{-1}), together with increased CH (2940 cm^{-1}) and SH (2564 cm^{-1}) absorptions in the infrared. Redistillation gave as the principal fraction 1.7 g. boiling at 33° (15 mm.). Its infrared spectrum was essentially the same as that of the crude material.

Anal. Calcd. for $C_3H_3S_2F_3$ (2:1): S, 39.4; F, 35.2; mol. wt., 161. Calcd. for $C_3H_4SF_6$ (1:2): S, 14.4; F, 51.3; mol. wt., 222. Found: S, 36.0; F, 37.3; mol. wt., 173.

The analysis and infrared spectrum suggest a mixture of the 2:1 adduct, probably $CF_3CH(SH)CH_2SH$, and the 1:2 adduct ($CF_3CH=CH$) $_2S$ in a ratio of about 85:15. The data calculated for such a mixture are: S, 35.6; F, 37.6; mol. wt., 171.

X-Ray-induced Addition of Hydrogen Sulfide to Hexafluoro-2-butyne.—A mixture of hexafluoro-2-butyne (96.0 g.) and hydrogen sulfide (62 g., 1.8 moles) was irradiated with X-rays for 5 hours at an average dose rate of about 15,000 rads/minute. Volatiles were bled off, collected in a -80° trap, and subsequently reirradiated. The liquid product from four such runs (20 g.) was distilled through a spinning-band column to give 9.5 g. of hexafluoro-2-butene-2-thiol (b.p. 57–58°, n^{25}_D 1.339).

Anal. Calcd. for $C_4F_6H_2S$: S, 16.4; F, 58.1. Found: S, 16.3; F, 58.1.

There was also obtained a small fraction (2 g.) of material boiling over the range 58° (90 mm.) to 53° (45 mm.) (n^{25}_D 1.360), which is probably a mixture of hexafluorobutanedithiol and bis-(hexafluorobutenyl) sulfide. There remained, following removal of this material, about 5 g. of viscous, oily residue.

Addition of Hydrogen Sulfide to Dimethylacetylene.—A mixture of 28 g. (0.52 mole) of dimethylacetylene and 29 g. (0.85 mole) of hydrogen sulfide in a 300-ml. stainless-steel cylinder was irradiated with X-rays for 3.5 hours at an average dose rate of about 20,000 rads/minute. Volatiles were bled off by immersing the cylinder in warm water (35–40°). There remained 3.8 g. of pale yellow liquid. The products from two runs were combined and distilled through an 8 in. Vigreux column. After removing dissolved dimethylacetylene, the following fractions were obtained.

1, $\sim 25^\circ$ (65 mm.)	0.7 g.	n^{25}_D 1.4782
2, 45–46° (12 mm.)	1.2 g.	1.5182
3, 37° (~ 1 mm.)	0.6 g.	1.5189
4, Residue	~ 1.0 g.	1.556

The infrared spectrum of 1 included the expected bands for a 1:1 adduct, $CH_3C(SH)=CHCH_3$; viz., 2564 cm^{-1} (SH) and 1639–1613 cm^{-1} (C=C; doublet), in addition to the usual C—H absorptions.

Anal. Calcd. for C_4H_8S : C, 54.5; H, 9.15; S, 36.3. Found: C, 56.5; H, 9.34; S, 34.8.

Fraction 2 was shown to be butane-2,3-dithiol¹⁰ by its infrared spectrum (strong SH absorption and no C=C absorption) and by preparation of a derivative with 2,4-dinitrobenzenesulfonyl chloride. A mixture of 0.2 g. of the dithiol and 0.8 g. of 2,4-dinitrobenzenesulfonyl chloride in 60 ml. of anhydrous ether on standing for 15 hours gave 0.4 g. (40% yield) of the bis-disulfide derivative. It was recrystallized from benzene to a constant melting point of 169–170°.

Anal. Calcd. for $C_{16}H_{14}N_4O_8S_4$: N, 10.8; S, 24.7. Found: N, 10.8; S, 24.9.

Nuclear Magnetic Resonance Spectra.—Proton spectra were obtained with an A-60 nuclear magnetic resonance spectrometer manufactured by Varian Associates, Palo Alto, Calif. The standard was tetramethylsilane. F^{19} spectra (56.4 Mc.) were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates. The standard was *sym*-1,2-difluoro-tetrachloroethane.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Stereochemistry of Allylic Rearrangements. XIII. The Racemization, Carboxyl-oxygen Equilibration and Solvolysis of *trans*- α,γ -Dimethylallyl *p*-Nitrobenzoate in Aqueous Acetone¹

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Rate constants for the following four first-order processes associated with the solvolysis of optically active *trans*- α,γ -dimethylallyl *p*-nitrobenzoate (I) in 60% aqueous acetone have been determined: (a) racemization of the unsolvolyzed ester (k_{rac} eq. 1), (b) solvolysis of the ester (k_t), (c) equilibration of the carboxyl-oxygen atoms in the unsolvolyzed ester (k_{eq} eq. 2) and (d) scrambling of carboxyl-oxygen atoms in each enantiomer starting with discretely ¹⁸O-labeled optically pure I (k_s eq. 3). Comparison of these constants with those reported earlier (ref. 3) for 90% acetone shows that solvent effects are consistent with the view that racemization and oxygen equilibration result from reformation of substrate (racemic and oxygen-equilibrated) by internal return from an internal ion-pair intermediate (II); $k_{rac} = k_{sq}$ for both solvents. The rate at which the oxygen atoms in the enantiomers become scrambled (k_s) relative to the rate of interconversion of the enantiomers ($k_{rac}/2$) provides information concerning the nature of the ion-pair intermediate II.

Introduction

Internal return associated with the solvolysis of optically active and ¹⁸O-labeled *trans*- α,γ -dimethylallyl *p*-

nitrobenzoate (I) in aqueous acetone results in the following first-order changes in the unsolvolyzed ester.³ In these equations R represents the *trans*- α,γ -dimeth-

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(3) H. L. Goering and M. M. Pombo, *J. Am. Chem. Soc.*, **82**, 2515 (1960).