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Synthetic Studies of the Derivatives of Acetylene. I. Reactions of 5-Bromopent-3-en-1-yne[1]

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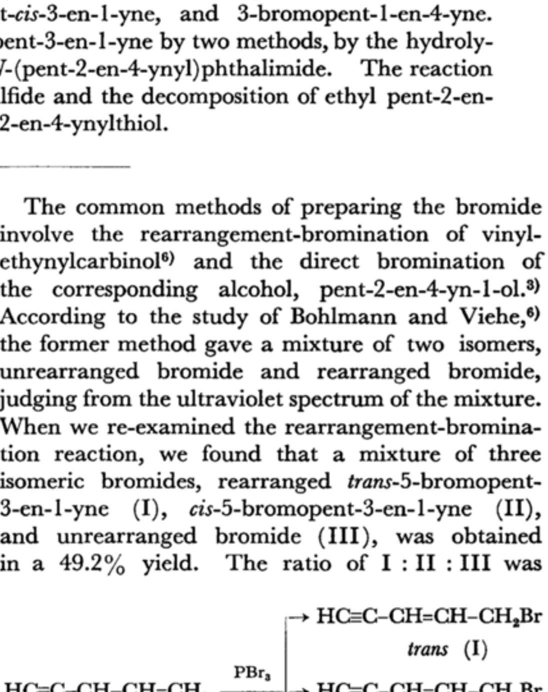
The preparation of pent-2-en-4-ynylamine and pent-2-en-4-ynylthiol and their derivatives from 5-bromopent-3-en-1-yne was studied. Moreover, in connection with the preparation of the bromide, the rearrangement-bromination of vinylethynylcarbinol was found to give three isomeric bromides, 5-bromopent-*trans*-3-en-1-yne, 5-bromopent-*cis*-3-en-1-yne, and 3-bromopent-1-en-4-yne. Pent-2-en-4-ynylamine was obtained from 5-bromopent-3-en-1-yne by two methods, by the hydrolysis of the hexaminium salt and by the cleavage of *N*-(pent-2-en-4-ynyl)phthalimide. The reaction of 5-bromopent-3-en-1-yne with potassium hydrosulfide and the decomposition of ethyl pent-2-en-4-ynylxanthate by alcoholic ammonia gave pent-2-en-4-ynylthiol.

In previous papers, it was reported that propargyl bromide could be converted to propargylamine and propargyl mercaptan and their derivatives.[2a—c] These studies have now been extended to such a vinylogous bromide as 5-bromopent-3-en-1-yne (I). Compound I may be expected to be useful for some synthetic reactions because it has two different functional groups. It is well known that the bromine atom has so enhanced a reactivity that it undergoes Reformatskii reaction with carbonyl compounds,[3] but there have been only a few other studies, such as those of the reactions with potassium acetate,[4] ethyl acetoacetate,[5] potassium cyanide,[6] and diethylamine.[7] In the present study we examined various substitution reactions of I in order not only to synthesize the conjugated vinylacetylenic amine, thiol, and their derivatives, but also to investigate the difference in the reactivity of the bromine atom between I and propargyl bomide. Almost all of the reaction products prepared were new substances.

The common methods of preparing the bromide involve the rearrangement-bromination of vinylethynylcarbinol[6] and the direct bromination of the corresponding alcohol, pent-2-en-4-yn-1-ol.[3] According to the study of Bohlmann and Viehe,[6] the former method gave a mixture of two isomers, unrearranged bromide and rearranged bromide, judging from the ultraviolet spectrum of the mixture. When we re-examined the rearrangement-bromination reaction, we found that a mixture of three isomeric bromides, rearranged *trans*-5-bromopent-3-en-1-yne (I), *cis*-5-bromopent-3-en-1-yne (II), and unrearranged bromide (III), was obtained in a 49.2% yield. The ratio of I : II : III was found to be about 2 : 1 : 1 by gas chromatography. The structures of these three isomers were confirmed by their infrared, ultraviolet, and NMR spectra, and by microanalyses of their hexaminium salts. Compound III was identified by its ultraviolet spectrum, which showed no absorption maximum. However, the final confirmation of *cis*- and *trans*-isomers depended on their NMR and ultraviolet spectra. The coupling constants of the olefinic protons of the two isomers are 10.5 and 17.0 Hz values which are characteristic of *cis*- and *trans*-olefinic protons respectively. Moreover, the absorption peaks of the ultraviolet spectra are



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[1] This investigation was presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

[2] a) K. Sato, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **76**, 1404 (1955). b) K. Sato and O. Miyamoto, *ibid.*, **77**, 1409 (1956). c) K. Sato, *ibid.*, **77**, 1411 (1956).

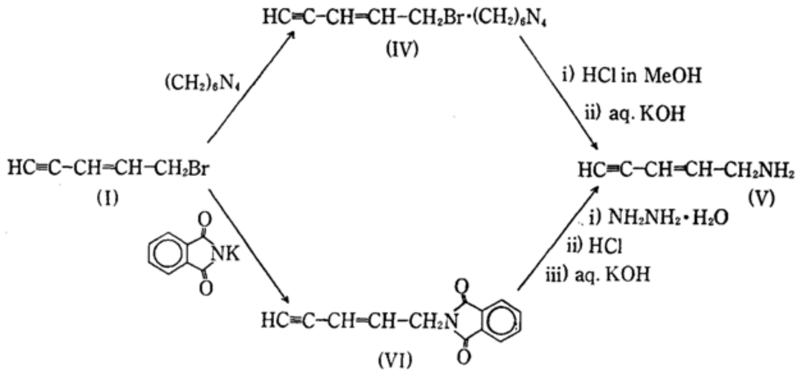
[3] H. B. Henbest, E. R. H. Jones and I. M. S. Walls, *J. Chem. Soc.*, **1950**, 3646.

[4] I. M. Heilbron, E. R. H. Jones, R. N. Lacey, J. T. McCombie and R. Raphael, *ibid.*, **1945**, 77.

[5] L. Crombie, S. H. Harper and D. Tompson, *ibid.*, **1951**, 2906.

[6] F. Bohlmann and H. G. Viehe, *Chem. Ber.*, **87**, 712 (1954).

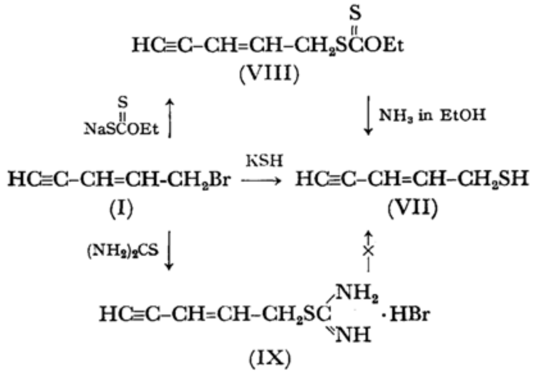
[7] R. H. Jones, R. N. Lacey and P. Smith, *J. Chem. Soc.*, **1946**, 940.



$238.5\ \mathrm{m}\mu$ ($\varepsilon=11400$) and $238\ \mathrm{m}\mu$ ($\varepsilon=14400$); these values are also complete agreement with the *cis*- and *trans*-structures of the conjugated vinylacetylenic system.[8] Although vinylethynylcarbinol was obtained in a good yield, it is very troublesome to separate the three isomers formed in the following rearrangement-bromination reaction, as will be described in the Experimental section. Therefore, we were obliged to prepare the bromide I by the other direct bromination method[3] of pent-2-en-4-yn-1-ol, which had been obtained in the pure *trans*-form from sodium acetylide and epichlorohydrin.[4]

Allylamine and propargylamine derivatives were prepared from the corresponding halides by Delépine and Gabriel reactions but conjugated vinylacetylenic amines such as V have not been prepared. 5-Bromopent-3-en-1-yne reacted with hexamine in methanol to give the hexaminium salt (IV), which was warmed with concentrated hydrochloric acid to give brown crystals. When the crystals were treated with aqueous potassium hydroxide, pent-2-en-4-ynylamine (V) was obtained as a colorless liquid. On the other hand, the reaction of I with potassium phthalimide gave *N*-(pent-2-en-4-ynyl)phthalimide (VI) in a 92% yield. This result is interesting, for it contrasts with the fact that *N*-propargylphthalimide was obtained in only a 10% yield in a similar reaction.[2a] Compound VI was refluxed with hydrazine hydrate in ethanol and then treated with hydrochloric acid to yield pale brown crystals. The treatment of the crystals with aqueous potassium hydroxide gave the corresponding amine, V, in a 32% yield. Compound V was identified from its infrared and ultraviolet spectra and by the microanalyses of its derivatives. Especially, the location of the absorption maximum in the ultraviolet spectrum indicated that V had the expected conjugated vinylacetylenic structure. Compound V reacted normally with benzoyl chloride, sodium cyanate, phenyl isocyanate, and carbon disulfide to give the corresponding derivatives.

No report has also been found concerning the preparation of such vinylacetylenic thiols as VII. We found that VII could be obtained by two methods, the reaction of I with potassium hydrosulfide and the decomposition of the ethyl xanthate, though VII was not obtained by the hydrolysis of the isothiuronium bromide (IX). Compound I reacted with potassium hydrosulfide in acetone-water to give VII in a 47% yield, and ethyl pent-2-en-4-ynylxanthate (VIII), prepared in a 59.7% yield by the reaction of I with sodium xanthate, was decomposed by alcoholic ammonia also to yield VII in a 55% yield. However, VII could not be obtained by the hydrolysis of *S*-(pent-2-en-4-ynyl)isothiuronium bromide (IX) (itself obtained in a high yield by the reaction of I with thiourea) by aqueous sodium hydroxide because of the resinification of the reaction mixture upon distillation. *p*-Tolyl pent-2-en-4-ynyl sulfide (X) and pent-2-en-4-ynylthioacetic acid (XI) were prepared by the reaction of I with *p*-thiocresol and thioglycolic acid respectively.



From these results, the present authors conclude that compound I behaves almost like allyl bromide in the substitution reactions presented above, while I also shows a characteristic property with propargyl bromide in such reactions with carbonyl compounds as the Reformatskii reaction.

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[8] I. Bell, E.R.H. Jones and H.C. Whiting, *J. Chem. Soc.*, **1957**, 2597.

Experimental[9)]

Materials. Vinylethynylcarbinol was obtained by the method of Bohlmann and Viehe.[6)] 5-Bromopent-3-en-1-yne was prepared by the bromination of pent-2-en-4-yn-1-ol,[3)] which had itself been obtained from sodium acetylide and epichlorohydrin.[4)] The other materials were obtained from commercial sources.

Bromination of Vinylethynylcarbinol. The bromination was carried out by a slight modification of the method of Bohlmann and Viehe.[6)] A solution of phosphorus tribromide (35.0 g) (0.13 mol) in 50 m*l* of dry ether was stirred, drop by drop and at 10±2°C, into a mixture of vinylethynylcarbinol (24.6 g) (0.3 mol) in 100 m*l* of dry ether containing 2.5 g of pyridine. After the mixture had been heated for 2.5 hr under reflux, the resulting mixture was chilled, poured over ice water, and extracted with ether. The ether was washed with water and saturated aqueous sodium bicarbonate, dried over sodium sulfate, and evaporated. The residue was distilled, giving mixed isomers (21.4 g) (49.2%) of a pale yellow liquid, bp 66—76°C/84 mmHg. The gas chromatography showed three peaks, and the ratio of I : II : III was 0.48 : 0.25 : 0.26. This mixture was distilled into three fractions through a 30 cm column.

Fraction 1 was 3-bromopent-1-en-4-yne (III) (6.3 g) (14.5%); bp 70—74°C/124 mmHg, n_D^{20} 1.5102; ν_{max}^{film} 3270, 2100, 1632, and 890 cm^{-1} (C=CH$_2$); and NMR peaks at δ 2.74 (the acetylenic proton), 4.98 (–CHBr–), 5.18 and 5.49 (terminal olefinic protons *cis* and *trans* to the vicinal olefinic proton respectively), and 6.09 ppm (the last olefinic proton). The ultraviolet spectrum had no absorption peak.

Fraction 2 was 5-bromopent-*cis*-3-en-1-yne (II) (3.5 g) (8.1%); bp 83—84°C/124 mmHg, n_D^{20} 1.5319; ν_{max}^{film} 3280, 2100, 1610, and 765 cm^{-1} (*cis* CH=CH); λ_{max}^{EtOH} 238.5 mμ (ε=11400); NMR peaks at δ 3.23 (the acetylenic proton), 4.11 (bromomethyl protons), 5.51 (the olefinic proton adjacent to the triple bond), and 6.19 ppm (the last olefinic proton); $J_{CH=CH}$=10.5 Hz. Moreover, it was identified as hexaminium bromide; mp 176—177.5°C (Found: N, 19.83%. Calcd for $C_{11}H_{17}N_4Br$: N, 19.64%).

Fraction 3 was 5-bromopent-*trans*-3-en-1-yne (I) (5.6 g) (12.9%); bp 85—87°C/124 mmHg, n_D^{20} 1.5422 (lit.[3)] n_D^{17} 1.5430); ν_{max}^{film} 3300, 2080, 1620, and 955 cm^{-1} (*trans* CH=CH); λ_{max}^{EtOH} 238 mμ (ε=14400); NMR peaks at δ 2.90 (the acetylenic proton), 3.93 (bromomethyl protons), 5.65 (the olefinic proton adjacent to the triple bond), and 6.31 ppm (the last olefinic proton); $J_{CH=CH}$=17.0 Hz. These characteristic absorption peaks were in complete accord with those of *trans* authentic bromide prepared according to the method of Henbest and his co-workers.[3)]

5-Bromopent-3-en-1-yne-hexamethylenetetramine (IV). A solution of 5-bromopent-3-en-1-yne (36.1 g) (0.25 mol) in 110 m*l* of ether was added, portion by portion, to a hot solution of hexamine (35.2 g) (0.25 mol) in 350 m*l* of methanol. After the solution had been refluxed for 10 min and then left to stand overnight, pale yellow crystals precipitated (54.7 g, mp 183—184°C (dec.)); from the filtrate, after the removal of the solvent, 6.4 more grams of crystal were obtained, mp 179—181°C (dec.). The yield was 86.0%. Recrystallization from methanol gave the pure IV; mp 184—185°C (dec.), ν_{max}^{KBr} 3180, 2080, 1630, and 945 cm^{-1}; λ_{max}^{EtOH} 219 (ε=12000), 228 (ε=15400), and 237 mμ (ε=12000). Found: C, 46.03; H, 6.28%. Calcd for $C_{11}H_{17}N_4Br$: C, 46.33; H, 6.01%.

***N*-(Pent-2-en-4-ynyl)phthalimide (VI).** A mixture of 5-bromopent-3-en-1-yne (4.4 g) (0.03 mol), potassium phthalimide (5.6 g) (0.03 mol), and 30 m*l* of ethanol was stirred for 12 hr under reflux. The removal of ethanol, followed by treatment with dilute aqueous potassium hydroxide, gave white crystals (5.8 g) (92.1%), mp 119—120.5°C. Recrystallization from ethanol provided the pure VI, mp 125—126°C; ν_{max}^{KBr} 3250, 2070, 1770, 955, 800, and 720 cm^{-1}. Found: C, 73.93; H, 4.62%. Calcd for $C_{13}H_9O_2N$: C, 73.92; H, 4.30%.

Pent-2-en-4-ynylamine (V). *A) From 5-Bromopent-3-en-1-yne-hexamethylenetetramine.* To a hot solution of 5-bromopent-3-en-1-yne-hexamethylenetetramine (28.5 g) (0.1 mol) in 330 m*l* of methanol, a 50 m*l* portion of concentrated hydrochloric acid was added, portion by portion, the mixture was then heated for 20 min under reflux. After the mixture had stood overnight, the precipitated ammonium chloride was filtered out; the removal of the solvent from the resulting filtrate gave brown crystals. Recrystallization from methanol gave 14.5 g of pale brown crystals, mp above 250°C; ν_{max}^{KBr} 3220, 3100—2900, 2070, 1600, 1565, 1490, and 955 cm^{-1}.

To a solution of the crystals (8.0 g) in 10 m*l* of water, a solution of potassium hydroxide (4.5 g) in 20 m*l* of water was added at 0—5°C; the resulting solution was extracted with ether. After drying over potassium hydroxide and evaporating, the distillation of the residue gave 1.8 g (40.3% based on hexaminium salt) of a liquid, bp 51°C/20 mmHg, n_D^{20} 1.5078; ν_{max}^{film} 3400—3150, 3300, 2080, 1590, 955, and 850 cm^{-1}; λ_{max}^{EtOH} 226 mμ (ε=14500).

B) From N-(Pent-2-en-4-ynyl)phthalimide. *N*-(Pent-2-en-4-ynyl)phthalimide (4.2 g) (0.02 mol) was treated for 1.5 hr with 80% aqueous hydrazine (1.4 g) (0.02 mol) in 60 m*l* of boiling 95% ethanol. Concentrated hydrochloric acid (3.5 m*l*) was added to the resulting mixture, which was then heated for 20 min under reflux. After the reaction mixture had then cooled and been filtered, the concentration of the filtrate gave 2.1 g (89.2%) of pale brown crystals, mp above 250°C. The infrared spectrum of this crystal was in complete accord with that of the hydrochloride salt obtained by passing hydrogen chloride into an ethereal solution of pent-2-en-4-ynylamine.

These crystals (5.9 g) (0.05 mol) were treated with aqueous potassium hydroxide such as in method A to yield 1.3 g (32.2%) of V, bp 55—56°C/28 mmHg.

This amine gave the following derivatives. Reaction with benzoyl chloride gave *N*-benzoylpent-2-en-4-ynylamine, mp 107—107.5°C (dil. MeOH); Found: C, 77.74; H, 6.05%. Calcd for $C_{12}H_{11}ON$: C, 77.81;

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9) All melting points and boiling points are uncorrected and all distillations were carried out in a nitrogen atmosphere. Infrared and ultraviolet spectra were recorded on a Hitachi Model EPI-S2 spectrometer and Hitachi Model EPS-3T spectrometer, respectively. Gas chromatographic analyses were carried out on a Shimadzu Model GC-1C chromatograph and NMR spectra were taken on a JEOL C-60H instrument with tetramethylsilane as an internal reference.

H, 5.99%. Treatment with sodium cyanate and phenyl isocyanate afforded *N*-pent-2-en-4-ynylurea, mp 103—104°C (EtOH); Found: C, 57.49; H, 6.64%. Calcd for $C_6H_8ON_2$: C, 58.05; H, 6.50%, and *N*-phenyl-*N′*-pent-2-en-4-ynylurea, mp 137—137.5°C (EtOH); Found: C, 71.81; H, 6.33%. Calcd for $C_{12}H_{12}ON_2$: C, 71.98; H, 6.04%, respectively. Reaction with carbon disulfide gave pent-2-en-4-ynylammonium pent-2-en-4-ynyldithiocarbamate, mp 89—90°C; Found: C, 55.19; H, 6.21%. Calcd for $C_{11}H_{14}N_2S_2$: C, 55.43; H, 5.92%.

Ethyl Pent-2-en-4-ynylxanthate (VIII). 5-Bromopent-3-en-1-yne (14.5 g) (0.1 mol) was added at 5—8°C to a solution of sodium ethylxanthate in 60 m*l* of ethanol. After the mixture had been stirred for 1.5 hr at room temperature, sodium chloride was filtered out and the filtrate was concentrated *in vacuo*. The residue was distilled to give 11.1 g (59.7%) of a pale yellow liquid, bp 82—84°C/0.3 mmHg, n_D^{20} 1.5880; ν_{max}^{film} 3260, 2100, 1625, 1050 ($-S-\overset{S}{\overset{\|}{C}}-O-$),[10] and 950 cm^{-1}; λ_{max}^{EtOH} 227.5 (ε=21500) and 282.5 mμ (ε=12800).[10] Found: C, 50.78; H, 5.71%. Calcd for $C_8H_{10}OS_2$: C, 51.58; H, 5.41%.

***S*-Pent-2-en-4-ynylisothiuronium Bromide (IX).** 5-Bromopent-3-en-1-yne (14.5 g) (0.1 mol) was added, portion by portion, to a hot solution of thiourea (7.6 g) (0.1 mol) in 180 m*l* of ethanol. After the mixture had been warmed for 3 hr at 50°C, the ethanol was evaporated to give white crystals (25.7 g) (97.0%), mp 142—144°C. Recrystallization from ethanol-isopropyl ether gave the pure IX, mp 146.5—147°C; ν_{max}^{KBr} 3300, 3100, 2100, and 958 cm^{-1}; λ_{max}^{EtOH} 229 mμ (ε=21600). Found: C, 32.63; H, 4.35%. Calcd for $C_6H_9N_2OBr$: C, 32.59; H, 4.10%.

Pent-2-en-4-ynylthiol (VII). *A) Reaction of 5-Bromopent-3-en-1-yne with Potassium Hydrosulfide.* A solution of 5-bromopent-3-en-1-yne (7.5 g) (0.05 mol) in 5 m*l* of acetone was added at room temperature for 30 min to aqueous potassium hydrosulfide prepared by the passage of hydrogen sulfide into a solution of potassium hydroxide (2.8 g) (0.05 mol) in 10 m*l* of water. After the mixture had been stirred for an additional hour, the resulting mixture was extracted with ether. The ether was dried over anhydrous sodium sulfate; the concentrate was distilled *in vacuo* to give 2.3 g (47.0%) of a colorless liquid, bp 46—47°C/15 mmHg, n_D^{20} 1.5580; ν_{max}^{film} 3300, 2550, 2050 ,1625, and 955 cm^{-1}; λ_{max}^{EtOH} 229 mμ (ε=9700).

Reaction with 2,4-dinitrochlorobenzene gave the 2,4-dinitrophenyl sulfide, mp 106.5—107.5°C (EtOH). Found: C, 49.68; H, 3.42%. Calcd for $C_{11}H_8O_4N_2S$: C, 50.00; H, 3.30%.

B) From Ethyl Pent-2-en-4-ynylxanthate. A saturated ammonia solution in 16 g of ethanol was stirred, drop by drop, into pent-2-en-4-ynylxanthate (4.2 g) (0.02 mol) at 55—60°C, then the mixture was stirred for 1.5 hr. The residue obtained after evaporating the solvent was distilled to give 1.1 g (55.0%) of a colorless liquid, bp 48—49°C/16 mmHg. The infrared spectrum of the product was in complete accord with that of the VII prepared by method A.

p-Tolyl Pent-2-en-4-ynyl Sulfide (X). 5-Bromopent-3-en-1-yne (7.1 g) (0.05 mol) was added at room temperature to a solution of *p*-thiocresol (6.2 g) (0.05 mol) and sodium ethoxide, prepared from sodium (1.2 g) (0.05 mol) and 35 m*l* of ethanol. After the mixture had been warmed for 1 hr, the precipitated sodium bromide was filtered; after the ethanol had been evaporated, the filtrate was extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated. The residue was distilled, giving 7.3 g (77.7%) of a liquid, bp 91—93°C/0.3 mmHg, n_D^{20} 1.5944; ν_{max}^{film} 3300, 2050, 1625, 1600, 1495, 955, and 800 cm^{-1}; λ_{max}^{EtOH} 227 mμ (ε=20700). Found: C, 75.92; H, 6.65%. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42%.

Pent-2-en-4-ynylthioacetic Acid (XI). 5-Bromopent-3-en-1-yne (15.2 g) (0.11 mol) was added at room temperature to a solution of sodium hydroxide (8.0 g) (0.2 mol) and thioglycolic acid (9.2 g) (0.1 mol) in 200 m*l* of water, after which the mixture was stirred for 20 hr at room temperature. The reaction mixture extracted with ether to remove the unreacted bromide. The water layer was acidified with 20% dilute sulfuric acid and extracted with ether. The ethereal extract, after being washed with water, dried over calcium chloride, and evaporated, was distilled to give 5.3 g (34.0%) of pale yellow liquid, bp 111—113°C/0.3 mmHg, n_D^{20} 1.5537; ν_{max}^{film} 3250, 3100—2900, 2070, 1710, and 955 cm^{-1}; λ_{max}^{EtOH} 229 mμ (ε=12200). Mol; Found by alkali titration: 157.1. Calcd for $C_7H_8O_2S$: 156.2.

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[10] E. Klein, J. K. Bosarbe and I. Norman, *J. Phys. Chem.*, **64**, 1666 (1960).