

160°/16 mm.; n_D^{25} 1.6112. On redistillation, through a 30-cm. Fenske ring-packed column at a reflux ratio of 1:10, the product obtained possessed the following constants: b.p. 135–137°/4 mm.; n_D^{25} 1.6110; d_{25}^{25} 1.1040.

*2-Isopropylidene-3-pentenenitrile*⁹ (VIII). Acetone was condensed with 3-pentenenitrile in the same manner as described above for benzaldehyde. The product was distilled through a 76-cm. Nester spinning band column at a reflux ratio of 1:10. The liquid product melted at –8°. The compound added oxygen readily, and it was stored under nitrogen prior to analysis. Low results, particularly for carbon, were obtained until it was discovered that the analytical sample had to be burned very slowly.

The compound showed infrared absorption at 3.4 μ for saturated CH, 3.5 μ for unsaturated CH, 4.5 μ for conjugated nitrile, 6.17 μ for conjugated unsaturation, 7.25 μ for CH₃, and 10.45 μ for a *trans* internal double bond.

2-Isopropylidene-3-pentenenitrile proved difficult to hydrolyze. In contrast with 3-pentenenitrile, no acid or lactone formed when it was boiled with concentrated hydrochloric acid. The nitrile was hydrolyzed by boiling two days with 17% aqueous sodium hydroxide. On acidification and distillation, about 10% of 3-pentenoic acid and about 10% of crude liquid 2-isopropylidene-3-pentenoic acid were recovered. Following a procedure employed by Whyte and Cope¹⁰ to hydrolyze hindered nitriles, 48 g. of 2-isopropylidene-3-pentenenitrile was stirred 15 hr. at reflux temperature with a mixture of 45 g. of potassium hydroxide, 20 g. of water, and 100 ml. of diethylene glycol. After acidification and fractional distillation, 1.7 g. of a straw-colored liquid acid was recovered, n_D^{25} 1.4489, b.p. 82–90°/5 mm.

Anal. Calcd. for CH₃CH=CHC(COOH)=C(CH₃)₂: neut. equiv., 140. Found: neut. equiv., 137.3.

Some acetone was liberated, but most of the product was a solid polymer.

2-Isopropylidene-3-pentenenitrile was treated with two mole equivalents of bromine in chloroform at 3°, conditions employed by Craig¹¹ to prepare the tetrabromide of piperylene. From 4.4 g. of 2-isopropylidene-3-pentenenitrile there was obtained 6.1 g. of needles which were recrystallized from boiling heptane, m.p. 114–116°. No tetrabromide was formed.

(10) Whyte and Cope, *J. Am. Chem. Soc.*, **65**, 1999 (1943).

(11) Craig, *J. Am. Chem. Soc.*, **65**, 1011 (1943).

Anal. Calcd. for C₇H₁₁Br₂(CN): C, 34.20; H, 3.94; N, 4.99; Br, 56.95. Found: C, 34.26; H, 4.22; N, 5.06; Br, 56.95.

2-Isopropylidene-3-pentenenitrile, unlike 3-pentenenitrile, did not yield a solid *N-tert*-butylamide when reacted with *tert*-butyl alcohol and sulfuric acid in glacial acetic acid by the procedure used by Plaut and Ritter¹² to prepare amides from acrylonitrile.

There was no evidence of reaction when 2-isopropylidene-3-pentenenitrile was mixed with thioglycolic acid and hydrogen chloride in ethyl ether. Under these conditions, Shriner and Fuson¹³ indicate that unhindered nitriles form solid α -iminoalkyl mercaptoacetic acid hydrochlorides.

The other compounds listed in the table, II from furfuraldehyde, III from isobutyraldehyde, IV from acetaldehyde, V from crotonaldehyde, VI from *p*-methoxybenzaldehyde, VII from cyclohexanone, and IX from methyl ethyl ketone, were prepared by the same procedure using 32 mole per cent sodium ethoxide, based on 3-pentenenitrile, as the condensing agent. Erroneous carbon and hydrogen results were obtained unless the samples were burned slowly and carefully. These compounds also added oxygen readily, and it was necessary to store samples in an inert atmosphere prior to analysis.

Polymerization. A soft, tacky polymer was obtained by heating 2-benzylidene-3-pentenenitrile with 0.1% of its weight of hydroquinone under nitrogen in a sealed glass tube for 48 hr. at 175°. The resulting benzene-soluble polymer possessed an iodine number 14.7. X-ray diffraction measurements indicated it to be noncrystalline.

Treatment of 2-benzylidene-3-pentenenitrile under 7500 atmospheres pressure at 200° for 5 hr. produced a tough, transparent, red-brown polymer which was harder and less tacky than the polymer prepared by heating for 48 hr. at 175° under atmospheric pressure. It was soluble in benzene and chloroform, but insoluble in ethyl alcohol or acetic acid. The iodine number was 6.4. The molecular weight determined by elevation of the boiling point of a benzene solution was 440.

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(12) Plaut and Ritter, *J. Am. Chem. Soc.*, **73**, 4077 (1951).

(13) Shriner and Fuson, *Identification of Organic Compounds*, John Wiley & Sons, Inc., 1948, p. 205.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

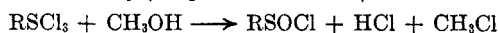
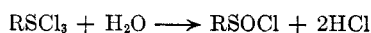
Some Reactions of Methanesulfinyl Chloride¹

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Methanesulfinyl chloride has been found to react with excess of alkanethiols to form mixtures of simple disulfides, with boiling alcohols to form alkyl chlorides, with benzene in the presence of anhydrous aluminum chloride to form methyl benzyl sulfone, and with aromatic amines to form methanesulfinamides.

The ease with which the alkanesulfinyl chlorides can be prepared by the controlled hydrolysis or alcoholysis of alkylsulfur trichlorides according to the equations:



(1) This work has been supported in part by the Office of Naval Research.

(2) Taken from the Master's thesis of Basil Said Farah.

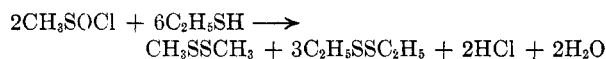
has made these compounds readily available³ and has led us to study certain reactions of methanesulfinyl chloride.

J. von Braun and Weisbach⁴ have reported that some of the lower alkanesulfinyl chlorides are con-

(3) I. B. Douglass and Donald Poole, *J. Org. Chem.*, **22**, 536 (1957).

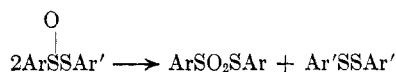
(4) J. von Braun and K. Weisbach, *Ber.*, **63B**, 2836 (1930).

verted to the corresponding thiosulfonate esters, RSO_2SR , by sodium mercaptides, dithiocarbamate salts, and mercaptans. In the present study no thiosulfonate esters were found among the reaction products when excess ethanethiol was treated with methanesulfinyl chloride. There was found instead, a mixture of the symmetrical methyl and ethyl disulfides in quantities indicated by the equation:



No fraction corresponding to the mixed disulfide was found. Further work will be necessary to indicate the successive stages of the reduction and to harmonize these results with those reported by von Braun and Weisbach.

Our experience has also confirmed the observation of Small, Bailey, and Cavallito⁵ that alkanethiosulfinate esters, RSOSR' , cannot be prepared by the action of mercaptans on alkanesulfinyl chlorides. Backer and Kloosterziel⁶ have prepared aromatic thiosulfinate esters by the action of thiophenols on aromatic sulfinyl chlorides but they indicate that the thiosulfinate esters readily disproportionate according to the equation:



Alcohols and alkanesulfinyl chlorides when brought together at low temperatures have been reported by Braun and Weisbach, and later by Meuwesen and Gebhardt⁷ to yield sulfinate esters. The present study indicates that when an alcohol and methanesulfinyl chloride are refluxed together the alcohol is converted in high yield to the alkyl chloride. In the case of benzyl alcohol, in addition to an 83% yield of α -chlorotoluene, an 8.3% yield of methyl benzyl sulfone was also recovered.

Attempts to prepare a sulfoxide by the reaction of methanesulfinyl chloride with benzene in the presence of anhydrous aluminum chloride were fruitless until the aluminum chloride was added in small portions to a mixture of benzene and the sulfinyl chloride. This procedure gave a 26% yield of methyl phenyl sulfoxide.

Methanesulfinyl chloride reacted readily with ether solutions of aniline and *p*-toluidine at the temperature of solid carbon dioxide. The resulting substituted methanesulfonamides could be isolated by the low-temperature evaporation of their ether solutions. They readily decomposed at higher temperatures, however, forming the corresponding sulfonamides and oily products. The decomposition was possibly a disproportionation according to the

following equation although the expected sulfen-

$$2\text{RSONHR}' \longrightarrow \text{RSO}_2\text{NHR}' + \text{RSNHR}'$$

amides were not identified among the oily by-products.

EXPERIMENTAL

Methanesulfinyl chloride was prepared by a method already described.³

Reaction of methanesulfinyl chloride with thiols. Sixteen grams (0.1 mole) of 2-naphthalenethiol was dissolved in 200 ml. of 3*N* sodium hydroxide solution and cooled at 0°. An equivalent amount of methanesulfinyl chloride was added dropwise with constant stirring. The solid which separated immediately, after recrystallizing from acetone, melted 143–144° and was shown to be 2-naphthyl disulfide by a mixed melting point with an authentic sample. The yield corresponded to 90.4% based on the 2-naphthalenethiol used.

In a similar manner, benzenethiol gave phenyl disulfide in 86% yield and α -toluenethiol gave benzyl disulfide in 38% yield.

In order to avoid the presence of moisture and to study the reaction more precisely, one mole of ethanethiol was placed in a three-neck flask surrounded by a Dry Ice bath and fitted with sealed stirrer and dropping funnel. The outlet of the reaction flask was connected in series with two traps cooled in Dry Ice and a third containing water for absorbing hydrogen chloride. The whole system was protected by a calcium chloride tube. One-half mole (49.5 g.) of pure methanesulfinyl chloride was added dropwise with constant stirring. When addition was complete the reaction flask was packed in Dry Ice and allowed to stand overnight.

When next examined, the reaction mixture had separated into two layers. An aliquot from the lower layer was titrated with standard alkali and another portion was allowed to stand with benzoyl chloride until the latter had been hydrolyzed to benzoic acid, thus proving the presence of water. The hydrogen chloride from the bottom layer, together with that absorbed in the water trap, corresponded to .383 mole or 76.5% of the chlorine in the sulfinyl chloride used.

The organic layer from the reaction flask was washed with water and sodium bicarbonate solution and then dried. Careful fractionation yielded 14.2 g. (0.13 mole) of methyl disulfide and 54 g. (0.442 mole) of ethyl disulfide.

Considering the 1:3 molar ratio of disulfides recovered from the experiment as indicative of the reacting proportions, 0.22 mole of methanesulfinyl chloride was caused to react with 0.66 mole of 1-butanethiol in a similar manner. The products isolated were 8.3 g. methyl disulfide (0.088 mole, 79%) and 46.3 g. of *n*-butyl disulfide (0.26 mole, 77%).

Reaction of methanesulfinyl chloride with alcohols. Seventeen grams of pure dried benzyl alcohol (0.16 mole) was refluxed with 9.85 g. methanesulfinyl chloride (0.10 mole) for 2.5 hr. On cooling, 1.40 g. of white crystals separated and were identified as methyl benzyl sulfone by mixed melting point with an authentic sample. The liquid portion of the reaction mixture was diluted with ether and extracted with sodium bicarbonate solution. From the ether layer 10.5 g. α -chlorotoluene was isolated and identified by its boiling point, refractive index, and molecular weight. The yield of methyl benzyl sulfone was 8.3% and that of α -chlorotoluene 83%, both based on the methanesulfinyl chloride used.

Twenty grams (0.22 mole) of methanesulfinyl chloride was treated dropwise with 9.2 g. (0.20 mole) of absolute ethanol in a reaction flask, attached to suitable traps for the absorption of hydrogen chloride and condensation of chloroethane, and refluxed for 6 hr. From the cold trap there was obtained 6.3 g. of colorless liquid which was identified as chloroethane (49% yield) by its boiling point, molecular weight and by the formation of ethyl mercuric chloride melting at 192–193°.

(5) La V. D. Small, J. H. Bailey, and C. J. Cavallito, *J. Am. Chem. Soc.*, **69**, 1710 (1947).

(6) H. J. Backer and H. Kloosterziel, *Rec. trav. chim.*, **73**, 129 (1954).

(7) A. Meuwesen and H. Gebhardt, *Ber.*, **69B**, 937 (1936).

The residue in the reaction flask was diluted with ether and extracted with sodium bicarbonate solution. On boiling the bicarbonate extract with α -chlorotoluene there was obtained 25.5 g. of methyl benzyl sulfone (68% yield), indicating that the aqueous extract had contained sodium methanesulfinate.

The acid found in the hydrogen chloride trap corresponded to only 7% of the original chlorine.

Reaction of methanesulfinyl chloride with benzene. One-half mole of methanesulfinyl chloride (49.25 g.) and 300 ml. dry benzene were placed in a three-neck flask fitted with sealed stirrer and reflux condenser. To the third neck was attached, by means of a large-diameter rubber tubing, a 125-ml. Erlenmeyer flask containing 135 g. (1.00 mole) of powdered anhydrous aluminum chloride. While maintaining the liquid reactants at 0° the aluminum chloride was added in small portions over a period of 30 min. and the reactants were then refluxed on the steam bath overnight. After working up the reaction mixture in the usual manner there was obtained 21 g. of colorless methyl phenyl sulfoxide boiling at 115° (2 mm.), having n_D^{25} 1.5880 and showing strong infrared absorption in the vicinity of 1040 cm^{-1} . This liquid solidified when placed in the refrigerator overnight but melted on warming to room temperature. Oxidation of the product gave a solid melting 86–88° and unchanged when mixed with an authentic sample of methyl phenyl sulfone. Methyl phenyl sulfoxide is reported to have n_D^{25} 1.5885, to melt at 30.0–30.5°, to boil at 104° (0.7 mm.)⁸ or 140–142° (13 mm.)⁹ when absolutely dry and to show

infrared absorption, when a liquid, at 1044 cm^{-1} .¹⁰ The yield corresponded to 26%, based on the sulfinyl chloride used.

The method described, of adding anhydrous aluminum chloride to the mixture of sulfinyl chloride and benzene, proved superior to the usual method of adding the chloride to a mixture of benzene and aluminum chloride. Numerous attempts to follow the latter procedure, using a variety of reactants, yielded only tars.

Reaction of methanesulfinyl chloride with aromatic amines. Nine and three-tenths grams of redistilled aniline (0.10 mole), dissolved in 100 ml. of anhydrous ether, was added dropwise with constant stirring to a solution of 4.95 g. methanesulfinyl chloride (0.05 mole) in 100 ml. ether cooled to –40 or –50°. After the reaction mixture had stood overnight, aniline hydrochloride was filtered out in quantitative yield. The ethereal solution was washed repeatedly with water and sodium bicarbonate solution, dried over calcium chloride, and evaporated either under vacuum or by blowing through it a stream of cold air. Decomposition always occurred when the ether solutions were evaporated by heating.

As the solvent was removed, crude methanesulfinanilide crystallized. Repeated recrystallization from anhydrous ether, washing with petroleum ether and with carbon tetrachloride gave a 71% yield of pure methanesulfinanilide melting at 86.88°.

Anal. Calcd. for $\text{C}_7\text{H}_9\text{ONS}$: N, 9.02. Found: N, 8.87.

Methanesulfin-p-toluidide, obtained in the same manner, melted at 96–98°, with decomposition occurring 103–106°.

Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{ONS}$: N, 8.28. Found: N, 8.05.

ORONO, ME.

(8) C. C. Price and J. J. Hydock, *J. Am. Chem. Soc.*, **74**, 1943 (1952).

(9) L. Horner and C. Belzel, *Ann.*, **579**, 175–192 (1953).

(10) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

Acetylenic Reactions of 2-(Phenylethynyl)tetrahydropyran¹

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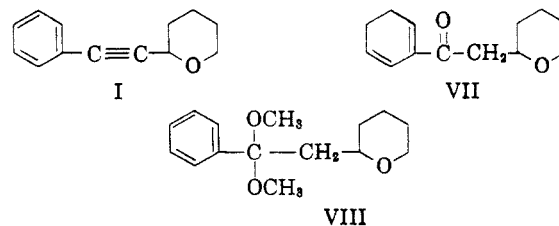
2-(Phenylethynyl)tetrahydropyran (I) was hydrogenated to 2-(2-phenylethyl)- and 2-(2-cyclohexylethyl)-tetrahydropyran. Addition of bromine and iodine to I yielded crystalline dihalides, hydration gave α -(2-tetrahydropyranyl)acetophenone, and addition of methanol formed α -(2-tetrahydropyranyl) acetophenone dimethylacetal.

In parallel with the glucosylation of acetylene and phenylacetylene by coupling of alkynylmetal compounds with tetraacetyl- α -D-glucopyranosyl bromide,³ racemic 2-(phenylethynyl)tetrahydropyran (I) was prepared as a model compound and examined in some reactions intended for its carbonyl hydrate counterpart.

Like the glycosyl halides, 2-halotetrahydropyrans show the characteristic reactivity of alpha halogen ethers toward organometallic compounds. For example, a series of 2-alkynyl-3-chlorotetrahydropyrans⁴ has been prepared from 1-alkynylmagnesium halides and 2,3-dichlorotetrahydro-

pyran. It is not unlikely that organolithium would yield similar products.⁵

The racemic 2-(phenylethynyl)tetrahydropyran (I) was obtained in 66% yield from 2-chlorotetrahydropyran and phenylethynylmagnesium bromide. It very easily formed peroxides upon exposure to air.



(1) The financial assistance of the Research Corp. is gratefully acknowledged.

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(3) R. Zelinski and R. Meyer, *J. Org. Chem.*, **23**, 810 (1958).

(4) O. Riobe, *Compt. rend.*, **231**, 1312 (1950); **236**, 2073 (1953).

(5) L. Summers and M. L. Larson, *J. Am. Chem. Soc.*, **74**, 4498 (1952).