Reactions of Substituted Methylenemalononitriles and Their Derivatives[1]

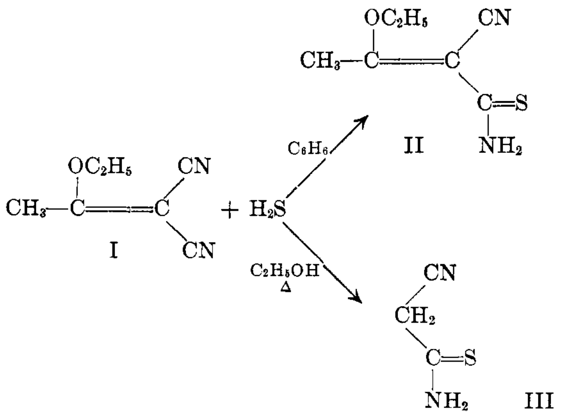
MARVIN A. MCCALL

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

Received December 26, 1961

1-Ethoxyethylidenemalononitrile was found to react with hydrogen sulfide to give different products depending on the solvent used. When benzene was the solvent, 2-cyano-3-ethoxythiocrotonamide was the product. When ethyl alcohol was the solvent, 2-cyanothioacetamide and ethyl thionoacetate were found. A possible mechanism accounting for the products obtained when ethyl alcohol was used as the solvent is that 2-cyano-3-ethoxythiocrotonamide is first formed, and it then reacts with excess hydrogen sulfide to form 2-cyanothioacetamide and ethyl thionoacetate. 2-Cyano-3-ethoxythiocrotonamide is so slightly soluble in benzene that it precipitates before it can react with the hydrogen sulfide. Several 2-cyano-3-alkoxy-2-alkenthioamides were prepared and their reactions were studied. The alkoxy group of these compounds was easily removed by mild hydrolysis to produce 2-cyano-3-hydroxy-2-alkenthioamides. The alkoxy group was also replaced by amines and ammonia. Mild oxidation of 2-cyano-3-hydroxythiocrotonamide with iodine in potassium iodide gave 3,3′-dithiobis[2-(1-hydroxyethylidene)-3-iminopropionitrile]. Surprisingly, this same product was also obtained when 2-cyano-3-ethoxythiocrotonamide was treated with iodine in potassium iodide under the same conditions.

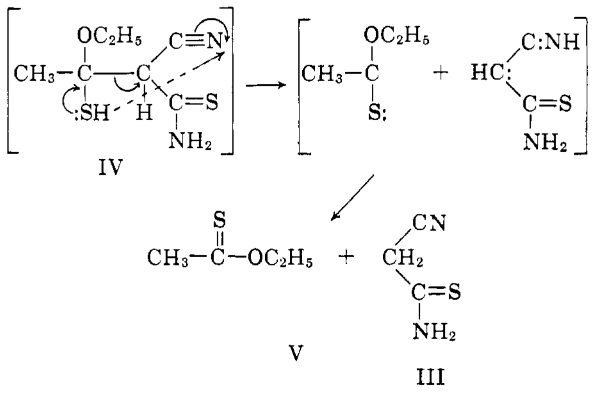
In a study of the reactions of methylenemalononitriles, 1-ethoxyethylidenemalononitrile (I) was found to react with hydrogen sulfide to give different products depending on the solvent used. When benzene was the solvent, 2-cyano-3-ethoxythiocrotonamide (II) was the product. When ethyl alcohol was the solvent, 2-cyanothioacetamide (III) was the product. This paper concerns the determination of the chemistry involved in the formation of II and III and a study of the reactions of II and other 2-cyano-3-ethoxy-2-alkenthioamides.



The structural assignment of II was supported by spectral data and was confirmed by the identification of the compound as the product obtained by synthesis from triethyl orthoacetate and 2-cyanothioacetamide.

The structural assignment of III was supported by spectral data and was confirmed by the identification of the compound as the product obtained by synthesis from malononitrile and hydrogen sulfide.[2]

A possible mechanism for the formation of III from I in ethyl alcohol is that II is first formed. Since II is soluble in dry ethyl alcohol to the extent of 0.5% at reflux temperature, it could react with the hydrogen sulfide to give the postulated intermediate addition product IV. IV would then break down under the reaction conditions to give the observed III and ethyl thionoacetate (V).



This proposed mechanism was tested by treating II with hydrogen sulfide in ethyl alcohol. III, V, and dithiomalonamide[3,4] (VI) were identified in the product. V was identified by gas chromatography and by mass spectrometry. Further evidence for the identity of V was obtained by synthesis of ethyl thionoacetate from ethyl acetimidate and hydrogen sulfide.[5] This authentic sample was found to have the same retention time on the gas chromatographic column as V, and the mass spectrum obtained on this sample was also identical with that of V. Other products identified by gas chromatography from the reaction of II with hydrogen sulfide in alcohol were hydrogen sulfide, ethyl

$$\mathrm{II} + H_2S + C_2H_5OH \longrightarrow \mathrm{III} + \mathrm{V} + \underset{\mathrm{VI}}{CH_2(CSNH_2)_2}$$

---

[1] Presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September 3–8, 1961.

[2] E. G. Howard, Jr., U.S. Patent 2,733,260 (1956).

[3] H. Lehr, W. Guex, and H. Erlenmeyer, *Helv. Chim. Acta*, **27**, 970 (1944).

[4] W. E. Hanford and P. Lawrence, U.S. Patent 2,280,578 (1942).

[5] S. A. Karjala and S. M. McElvain, *J. Am. Chem. Soc.*, **55**, 2966 (1933); *Chem. Abstr.*, **21**, 2458 (1927).

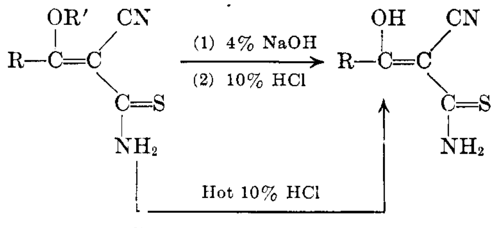
alcohol, and small quantities of ethyl acetate. The ethyl acetate probably resulted from hydrolysis or from oxidative exchange of the ethyl thionoacetate with air since thiono esters are noted for the ease with which the sulfur atom is removed.[6] In some preparations, sulfur was isolated. It was also demonstrated by infrared and gas chromatographic analyses that ethyl thionoacetate is converted in the presence of air to ethyl acetate.

The failure of a similar addition reaction of hydrogen sulfide to the double bond of II in benzene may be explained by the very low solubility of II in benzene (0.1% in refluxing benzene). II would precipitate as fast as it was formed in benzene and thus could not react further with hydrogen sulfide; however, since II is soluble to a limited extent in benzene, a small amount of III would be expected to be found if the reaction was carried out with a large excess of benzene over a long period. Small amounts of III as well as VI were identified in the infrared spectrum of the product obtained from a reaction carried out under these conditions.

Mechanisms involving the formation of thioacetic acid or ethanethiol were eliminated since no trace of these materials could be found in the reaction mixtures from I or II and hydrogen sulfide in the presence of ethyl alcohol. Simple hydrolysis with water was also ruled out since II could be recrystallized without hydrolysis from hot water; however, there is some question concerning the stability of II in a mixture of ethyl alcohol and water. In one experiment, II was decomposed and no identifiable products were obtained after II was stirred overnight in a mixture of alcohol and water with a catalytic amount of triethylamine. A similar experiment showed that II was stable in ethyl alcohol alone.

Another mechanism, involving first the alcoholysis of I or II in the presence of hydrogen sulfide as catalyst, was considered. It was demonstrated that V and trace quantities of ethyl acetate were obtained from triethyl orthoacetate and hydrogen sulfide; thus all the observed by-products from the reaction of hydrogen sulfide and ethyl alcohol with I or II could be accounted for. However, I reacted with hydrogen sulfide in dimethylformamide solution to form dithiomalonamide (VI), ethyl thionoacetate (V), and ethyl acetate. Alcohol, therefore, is not a necessary reactant in the cleavage, making the alcoholysis step unnecessary in explaining the mechanism for the formation of III from I in ethyl alcohol.

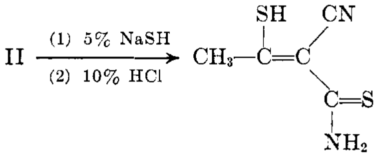
Other reactions of II were studied and several compounds of this type were prepared and characterized. It was found that the alkoxy group was easily removed by mild hydrolysis. When II was dissolved at room temperature with 4 to 5% sodium hydroxide solution and then cold, dilute (10%) hydrochloric acid solution was added, 2-cyano-3-hydroxythiocrotonamide (IX) was formed. This same compound was also prepared by simply heating II with 10% hydrochloric acid solution at steam bath temperatures for approximately ten minutes. These reactions were generally applicable to 2-cyano-3-alkoxy-2-alkenthioamides.



II. R = CH_3, R′ = C_2H_5
VII. R = CH_3, R′ = CH_3
VIII. R = C_2H_5, R′ = C_2H_5

IX. R = CH_3
X. R = C_2H_5

An attempt to prepare the mercapto derivative by replacing the 4% sodium hydroxide solution with dilute sodium hydrosulfide gave a product which had an infrared spectrum consistent with the proposed structure XI.



XI

The replacement of the ethoxy group probably results from a 1,4-attack of the sodium hydroxide or hydrosulfide on the conjugated system involving the nitrile or thioamide group and the carbon-carbon double bond followed by loss of sodium alkoxide.

The mercapto derivative XI was less stable than the hydroxy derivative IX and slowly decomposed during the analysis and on standing. The products of the decomposition were not identified.

The hydroxy and mercapto derivatives (IX, X, and XI) were acidic in aqueous solution. The hydroxy derivative IX was titrated with 0.5 *N* base and a neutralization equivalent of 146 (theor. 142) was obtained. It was stable to further attack with hydrogen sulfide in ethyl alcohol even though it was quite soluble in the alcohol; therefore, the hydroxy derivative IX was ruled out as a possible intermediate in the formation of III from the reaction of hydrogen sulfide and ethyl alcohol with I or II.

Attempts to form the corresponding hydroxy derivative from the reaction of I with dilute base followed by addition of acid failed to yield the expected product.

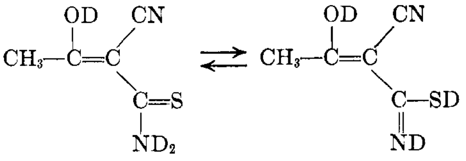
NMR studies did not verify the presence of the hydroxy proton in IX; however, infrared studies of deuterated IX confirmed the presence of the hydroxy group by an observed shift on deuteration from the normal absorption for ν(OH) at 3.13 μ

---

(6) R. Connor, "Organic Sulfur Compounds" in Henry Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 930, 937.

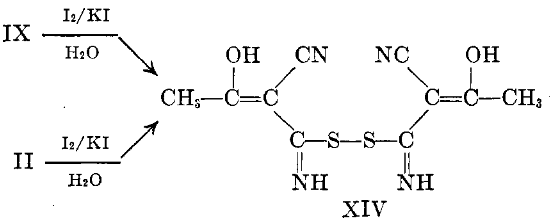
to 4.22 μ for ν(OD). The hydroxy bending vibration δ(OH) was observed at 7.0 μ. The presence of an isomeric ketonic structure was ruled out since there was no carbonyl absorption observed in the infrared spectrum. Also, IX failed to form a 2,4-dinitrophenylhydrazine derivative in either alcoholic or aqueous solution. The presence of an isomeric epoxy structure was ruled out since an oxirane analysis of IX was negative.

The amide nitrogen of IX was also deuterated and the observed shifts to the longer wavelengths as a result of deuteration were from 2.97 $\mu[\nu_a$(NH)] and 3.03 $\mu[\nu_s$(NH)] to 3.97 $\mu[\nu_a$(ND)] and 4.10 $\mu[\nu_s$(ND)]. There was also spectral evidence for considerable contribution from tautomeric structures XII and XIII. The enol ν(SH) absorption band at 3.8 μ was shifted to 5.5 $\mu[\nu$(SD)] in the deuterated compound.



A solid S-methyl derivative (methyl 2-cyano-3-hydroxythiocrotonimidate) of the enol structure of IX was obtained by treating II with methyl iodide in 4% sodium hydroxide solution. The ethyl group of II was lost during this alkylation reaction.

Upon mild oxidation of IX with iodine in potassium iodide, a disulfide, which was characterized as 3,3′-dithiobis[2-(1-hydroxyethylidene)-3-iminopropionitrile](XIV), was formed. It was surprising to find that if II was mildly oxidized in the same manner with iodine in potassium iodide the ethyl group was lost and the same product was formed. The absence of hydrogen iodide salt formation was demonstrated by a negative halogen analysis.



The stability of XIV was somewhat surprising since simpler disulfides of this type are usually unstable; for example, 1,1′-dithiodiformamidine has not been obtained except in the form of a salt with hydrogen halides.[7] Recently 1,1′-dithiobis-[N-phenylformamidine]dihydrobromide dihydrate was prepared from phenylthiourea.[8] It is also known that thioacetamide reacts with iodine in water to give oxidation products such as ammonium iodide, hydrogen iodide, and sulfur and that no disulfide is formed.[9] The additional resonance possibilities provided by the unsaturated, negatively substituted disulfide XIV probably accounts for its stability as compared with the marked unstable nature of the simpler members of this class of compounds.

Reaction of II with dimethylamine was found to yield 2-cyano-3-dimethylaminothiocrotonamide, in which the alkoxy group of II is replaced with the dialkylamino group. The ethoxy group was also replaced by anhydrous ammonia to form 3-amino-2-cyanothiocrotonamide. These alkoxy replacement reactions are consistent with reported reactions of diethyl ethoxymethylenemalonate to form the aminomethylenemalonic ester.[10]

Other derivatives of substituted methylenemalononitriles prepared were 2-cyano-3-phenylthioacrylamide, 2-cyano-3-(2-thienyl)thioacrylamide, and 2-cyano-3-(2-furyl)thioacrylamide.

Experimental

All melting points were determined using a Hoover-Thomas Unimelt apparatus and are uncorrected.

The infrared spectra were determined using a Baird, Model AB-2, double beam recording spectrophotometer and a Beckman, Model IR-5 recording spectrophotometer. Infrared absorption in the 12.5–25-μ range was obtained with a Perkin-Elmer Infracord, Model 137-B, with potassium bromide optics.

Two gas chromatographic columns were used in this work: Column No. 1 was made from 6-ft. × 1/4-in. aluminum tubing packed with 20% Carbowax 20M on 40–60 mesh regular Chromosorb (Johns-Manville). The carrier gas was hydrogen and the rate was 61 ml./min. The column temperature was 70° and the vaporizer temperature was 203°. Column No. 2 was made from 12-ft. × 1/4-in. aluminum tubing packed with 20% 400-Carbowax oil on 80–100 mesh specially prepared Celite 545. The carrier gas was hydrogen at the rate of 45 ml./min. The column temperature was 73° and the vaporizer temperature was 170°.

1-Ethoxyethylidenemalononitrile (I).—Triethyl orthoacetate (97 g., 0.6 mole), malononitrile (33 g., 0.5 mole), and glacial acetic acid (1.5 g.) were placed in a 1-l. flask equipped with a stirrer, thermometer, dropping funnel, and a Vigreux column (20 × 1 in.). The reaction mixture was heated and alcohol began to distil when the temperature of the reaction mixture was about 86–90°. After about 35 min., the temperature of the reaction mixture had reached 140°. The reaction mixture was then distilled under 30 mm. pressure, and 1-ethoxyethylidenemalononitrile was obtained as a fraction boiling at 163–165° at 10 mm. After crystallization from ethyl alcohol, 66.5 g. of 1-ethoxyethylidenemalononitrile (I) was obtained, m.p. 93–94°. In some preparations the low-boiling materials were vacuum-stripped and the residue recrystallized from ethyl alcohol to yield a product which melted at 90–92°.

2-Cyano-3-ethoxythiocrotonamide (II) **from** I.—1-Ethoxyethylidenemalononitrile (I, 13.6 g., 0.1 mole, m.p. 90–91°) was dissolved in 125 ml. of dry benzene and triethylamine (a few drops) was added as catalyst. The mixture was stirred with a magnetic stirrer, and hydrogen sulfide was bubbled into this solution until a solid formed. After a considerable amount of the solid had accumulated, it was removed by filtration and the filtrate was treated

---

[7] E. A. Werner, *J. Chem. Soc.*, 2168 (1912); E. Fromm, *Ann.*, **348**, 144 (1906).

[8] F. Kurzer and P. M. Sanderson, *J. Chem. Soc.*, 1058 (1959).

[9] P. C. Ray and M. L. Dey, *J. Chem. Soc.*, **109**, 698–701 (1916).

[10] L. Claisen and E. Haase, *Ann.*, **297**, 77 (1897).

again with hydrogen sulfide. This procedure was repeated several times. The total solid amounted to 12.3 g. (72.4%), m.p. 166–167°. On recrystallization from ethyl alcohol, the product melted at 173–174°. After recrystallization from hot water, a small sample of this material melted at 165–168°. The infrared spectra of these two recrystallized materials, however, were identical.

Useful bands in the infrared spectrum were at 2.93 μ and 3.03 $\mu[\nu(NH_2)]$, 4.52 $\mu[\nu(CN)]$, 6.43 $\mu[\nu(C{=}S)]$, 6.27 $\mu[\delta(NH_2)]$, 8.40 $\mu[\nu(C{-}O{-}C)]$, and 7.19 $\mu[\delta(CH_3)]$. Ultraviolet absorption bands in methanol were observed at 274 mμ and 311 mμ.

Anal. Calcd. for $C_7H_{10}N_2OS$: C, 49.39; H, 5.92; N, 16.46; S, 18.83. Found: C, 49.53; H, 6.11; N, 16.12; S, 18.53.

The solubility of this compound in boiling ethyl alcohol was approximately 0.5%. This solubility value was obtained by saturating a boiling absolute ethyl alcohol solution and weighing the precipitate obtained after evaporating the solvent.

The solubility of 2-cyano-3-ethoxythiocrotonamide in dry benzene, determined by the method used with ethyl alcohol, was approximately 0.1%.

II from Triethyl Orthoacetate and 2-Cyanothioacetamide.—A mixture of triethyl orthoacetate (16.2 g., 0.1 mole), 2-cyanothioacetamide (10.0 g., 0.1 mole), and 5 or 6 ml. of glacial acetic acid was heated on a steam bath for 10–15 min. During this time the solid starting material appeared to discolor and a new solid precipitate formed. The solution turned dark orange and was allowed to stand for approximately 10 min. It was then cooled and filtered to obtain 11.0 g. of product melting at 169–170°. On recrystallization from ethyl alcohol, the product melted at 172–173°. The melting point of a mixture with the product obtained from the reaction of I with hydrogen sulfide in alcohol was not depressed, and the infrared spectra of the two materials were identical.

2-Cyanothioacetamide (III) from I.—1-Ethoxyethylidenemalononitrile (I, 13.6 g., 0.1 mole, m.p. 90–92°) was dissolved in 150 ml. of ethyl alcohol containing 5 drops of triethylamine. This solution was heated on the steam bath and stirred with a magnetic stirrer while hydrogen sulfide was bubbled into the mixture for 4 hr. The mixture was allowed to stand for 24 hr. and then saturated again with hydrogen sulfide for 30 min. The reaction flask was equipped with a cold water condenser and a cold trap containing ice and salt to trap any volatile products that might be swept over with the excess hydrogen sulfide.

A small sample of solid was isolated by freezing the solution in Dry Ice and acetone, m.p. 111–113°. Most of the solvent (130 g.) was then removed by distillation at atmospheric pressure through a 6-in. packed column. The temperature of the reaction mixture was kept below 90°. The solid product was obtained by cooling and filtering the small volume (15–20 ml.) of liquid remaining after distillation. This solid was washed with a little cold ethyl alcohol and then with ethyl ether. The yield was 6.5 g., m.p. 100–110°. This product was recrystallized from ethyl alcohol to obtain 4.5 g. of crystalline solid, m.p. 115–117°. The melting point of a mixture with authentic 2-cyanothioacetamide prepared from malononitrile and hydrogen sulfide was not depressed. The infrared spectrum of this product was identical with that of the sample prepared from malononitrile and hydrogen sulfide.

The liquid distillate and liquid collected in a cold trap on the reaction flask were combined and found by gas chromatography, using column No. 1, to contain hydrogen sulfide (1.0%, retention time 0.87 min.), ethyl acetate (<0.1%, retention time 5 min.), ethyl alcohol (95.1%, retention time 6 min.), and ethyl thionoacetate (3.8%, retention time 15 min.). Water was found to have the same retention time as ethyl thionoacetate on this column; therefore, column No. 2 was also used. With column No. 2, the following were found: hydrogen sulfide (1.0%, retention time 2.5 min.), ethyl acetate (0.1%, retention time 6.5 min.), ethyl alcohol (95.1%, retention time 10.5 min.), ethyl thionoacetate (3.6%, retention time 14.5 min.), and water (0.2%, retention time 27.5 min.).

Ethyl thionoacetate (V) was collected in a small Dry Ice-cooled trap attached to the chromatographic column and examined by mass spectrographic analysis. It was found to have a maximum mass peak at 104. No other peaks were observed at a higher mass; therefore, the molecular weight was interpreted as being 104. The mass spectrum was identical with that obtained from an authentic sample of ethyl thionoacetate.

III from Malononitrile and Hydrogen Sulfide.[2]—Malononitrile (66.0 g., 1 mole) was dissolved in ethyl alcohol (200 ml.) and triethylamine (6 or 8 drops) was added as catalyst. The mixture was stirred while hydrogen sulfide was bubbled into the solution for 3 to 4 hr. Three crops of crystals, all of which melted at 114–120°, were isolated by filtration. These were combined and recrystallized from ethyl alcohol, m.p. 116–117°. This product was titratable[11] with base and had a neutralization equivalent of 99.4 (theor. 100) and a molecular weight of 97 (determined by boiling point elevation in acetone). Useful absorption bands in the infrared spectrum of III were at 3.05 and 3.14$\mu[\nu(NH_2)]$, 3.24 $\mu[\nu(CH_2)]$, 4.5 $\mu[\nu(C{\equiv}N)]$, 6.21 $\mu[\delta(NH_2)]$, 6.91 $\mu[\delta\text{-}(CH_2)]$, 7.82 $\mu[\nu(C{=}S)]$, and 13.34 $\mu[\delta(CH_2)]$. Very weak absorption peaks at 3.95 μ and at 15.14 μ were interpreted as evidence for the presence of the tautomeric enol form of the thioamide.

III from II in Ethyl Alcohol.—2-Cyano-3-ethoxythiocrotonamide (II, 5.0 g., m.p. 172–173.5°) was placed in 100 ml. of ethyl alcohol containing 5 drops of triethylamine. This reaction mixture was heated on the steam bath and stirred with a magnetic stirrer while hydrogen sulfide was bubbled into the mixture for 6 hr. The mixture was allowed to stand for 24 hr. and then saturated again with hydrogen sulfide for 30 min. All materials which were carried over with the excess hydrogen sulfide gas were collected in a trap cooled with ice and salt. Most of the alcohol was distilled at atmospheric pressure through a 6-in. Vigreux column. A solid product was obtained by cooling and filtering the small volume (20–25 ml.) of liquid remaining after distillation. This solid was recrystallized from hot water, m.p. 115–117°. The melting point of a mixture with authentic 2-cyanothioacetamide prepared from malononitrile and hydrogen sulfide or with the 2-cyanothioacetamide obtained from I was not depressed. Its infrared spectrum was identical with that of authentic 2-cyanothioacetamide and with that obtained from I.

The liquid distillate and the liquid caught in the ice-salt trap were combined and found by gas chromatography to contain the same components as were obtained from the reaction of I with hydrogen sulfide in alcohol. The retention times on columns No. 1 and 2 for by-product V were the same as those for authentic ethyl thionoacetate. The mass spectrum of V was also identical with that of authentic ethyl thionoacetate.

In some repeat experiments using 1.7 g. of II in 350 ml. of ethyl alcohol with hydrogen sulfide bubbling into the mixture for 15 hr., a solid (0.18 g.) decomposing at 190° was obtained. This solid was recrystallized from water and gave a product decomposing at 214–216°. The decomposition point recorded[3] for dithiomalonamide is 212°. Infrared and NMR data supported the dithiomalonamide structure. Characteristic absorption bands in the infrared spectrum were at 3.1 $\mu[\nu(NH)]$, 3.28 $\mu[\nu(CH_2)]$, 6.21 μ $[\nu(C{=}N)$ and $\delta(NH_2)]$, and 7.0 μ and 13.48 $\mu[\delta(CH_2)]$. Absorption peaks indicating the presence of the enol form of the thioamide were found at 3.9 $\mu[\nu(SH)]$ and 15.15 μ $[\nu(CS)]$. Another by-product was often found in these reactions and was identified by X-ray diffraction measurements as sulfur.

III from II in Benzene.—2-Cyano-3-ethoxythiocrotonamide (II, 1.7 g., 0.1 mole, m.p. 172–173.5°) was suspended in 350 ml. of dry benzene containing 20 drops of triethylamine, and hydrogen sulfide was bubbled into this suspension for 15 hr. at room temperature. An insoluble material (0.9 g.) was obtained by filtration. There was evidence from the infrared spectrum that this material was primarily starting material with possibly some 2-cyanothioacetamide. This material was extracted with 25–30 ml. of hot ethyl alcohol. The insoluble portion (0.45 g., m.p. 165–167°) had an infrared spectrum identical to that of the starting material. The filtrate was concentrated and 0.4 g. of solid was obtained. From the infrared spectrum this solid appeared to be a mixture of starting material and a small amount of dithiomalonamide.

On evaporation of the benzene filtrate from the reaction mixture, approximately 0.3 g. of a solid was obtained, m.p. 102–104°. This material was identified by the infrared spectrum as impure 2-cyanothioacetamide (III); however, it was never obtained in the pure state.

Ethyl Thionoacetate.—An excess of 20% sodium hydroxide solution was added to 107.57 g. (1.0 mole) of ethyl acetimidate hydrochloride (prepared by a published method[12]) dispersed in dry ethyl ether (500 ml.). The solid imido ether hydrochloride dissolved rapidly in the sodium hydroxide solution, and the ether layer became slightly colored. The ether and aqueous phases were intimately mixed in a separatory funnel, and the ether layer was separated and dried for 5–10 min. over anhydrous sodium sulfate. The ether solution was then placed in a flask equipped with a water-cooled condenser and a magnetic stirrer. Hydrogen sulfide was bubbled into the ether solution for 5 hr. The reaction mixture was cooled externally with an ice–salt bath. The mixture was allowed to stand for 15 hr., then filtered, and the ether removed under reduced pressure. The remaining oil was dried over anhydrous sodium sulfate. This product was found to be > 99.9% pure based on gas chromatographic analysis. The retention time on column No. 1 was 15 min. A very small additional peak (<0.01%) was observed at 5-min. retention time. The retention time for ethyl acetate was found to be 5 min. on this column. No other peaks were observed. On column No. 2 the retention time was 14.5 min. and the ethyl acetate peak (<0.01%) was 6.5 min. The retention times on these two columns for this known ethyl thionoacetate were found to be the same as those obtained for the by-product V obtained from the reaction of I or II with hydrogen sulfide in alcohol.

The mass spectrographic analysis of this compound showed a peak at mass 104. No other peaks were observed at a higher mass; therefore, the molecular weight was interpreted as being 104. The mass spectrum was identical with that obtained from isolated by-product V obtained from the reaction of I or II with hydrogen sulfide in ethyl alcohol.

The ethyl thionoacetate was distilled at atmospheric pressure under nitrogen, b.p. 106–107°, n^{20}_D 1.4640. The mass spectrum was unchanged.

The ethyl thionoacetate was changed rapidly to ethyl acetate on exposure to air. The vapor of pure ethyl thionoacetate in air showed no carbonyl absorption in the infrared spectrum when checked immediately after the mixture was prepared; however, after 45 min. a small absorption band was observed for the carbonyl function. When the vapor was allowed to remain in contact with air for 63 hr., the spectrum was found to be identical with that of ethyl acetate.

The conversion of ethyl thionoacetate to ethyl acetate after exposure to air was also observed by gas chromatographic studies.

Thioacetic Acid and Ethanethiol.—The retention time for thioacetic acid (Eastman technical grade) on column No. 1 was found to be 19 min. This retention time did not correspond to any observed retention time obtained for the reaction products from I or II with hydrogen sulfide in ethyl alcohol.

Thioacetic acid was allowed to react with hydrogen sulfide in the presence of excess ethyl alcohol for 8 hr. The products were identified by their retention times as hydrogen sulfide (1.6%), ethyl acetate (0.1%), ethyl alcohol (97.5%), and thioacetic acid (0.8%).

Ethyl *p*-toluenesulfonate (20 g.) was treated with sodium hydrosulfide (10 g.) in ethyl alcohol. The volatile ethanethiol was removed from the reaction mixture by distillation, b.p. 34–36° at atmospheric pressure. It was found to have a retention time of 1.8 min. on column No. 1. This retention time did not correspond to any observed retention time for products obtained from the reaction of I or II with hydrogen sulfide in ethyl alcohol.

Reaction of II with Ethyl Alcohol and Water.—2-Cyano-3-ethoxythiocrotonamide (II, 1.7 g., 0.1 mole) was stirred for 15 hr. with a mixture of 117 ml. of water, 234 ml. of ethyl alcohol, and 20 drops of triethylamine. The material dissolved readily in this alcohol–water mixture. The solvent was removed by evaporation. The product was a dark sticky oil which was not identified.

Attempted Reaction of II with Ethyl Alcohol.—2-Cyano-3-ethoxythiocrotonamide (II, 1 g., m.p. 173–174°) was refluxed in 25 ml. of absolute ethyl alcohol for 8 hr. The alcohol was concentrated by evaporation and 0.75 g. of solid was recovered, m.p. 173–175°. Infrared analysis indicated that this material was the starting material.

Reaction of Triethyl Orthoacetate with Hydrogen Sulfide and Ethyl Alcohol.—Triethyl orthoacetate (50 ml., Eastman chemical P-2851) was mixed with 100 ml. of absolute ethyl alcohol. Hydrogen sulfide was bubbled into this mixture for about 11 hr. The products were identified by retention time on gas chromatographic columns No. 1 and 2. The products identified were hydrogen sulfide (0.4%), ethyl acetate (3.4%), ethyl alcohol (84.9%), and ethyl thionoacetate (11.3%). These were the same products obtained when II was treated with hydrogen sulfide in ethyl alcohol.

Dithiomalonamide (VI) from I in Dimethylformamide.—1-Ethoxyethylidenemalononitrile (I, 10 g.) was dissolved in 100 ml. of dimethylformamide containing 6 drops of triethylamine. The mixture was heated to 75–80° while hydrogen sulfide was bubbled into the solution for 8 hr. The mixture was then allowed to remain at 70–75° for 15 hr. and then saturated again with hydrogen sulfide. Approximately 50% of the dimethylformamide was then removed under reduced pressure. The concentrate was then diluted with cold water until a precipitate formed. This solid was filtered to obtain 6.7 g. of material which melted with decomposition at 185–190°. After recrystallization from hot water it decomposed at 201–202°. The infrared spectrum of this product was identical with that of dithiomalonamide (VI) obtained from the reaction of II with hydrogen sulfide in ethyl alcohol. Ethyl thionoacetate (V) and ethyl acetate were identified as by-products of this reaction.

2-Cyano-3-methoxythiocrotonamide (VII).—This compound was prepared from 14.4 g. (0.12 mole) of trimethyl orthoacetate, 10 g. (0.1 mole) of 2-cyanothioacetamide, and 2 ml. of glacial acetic acid by the same general procedure used for preparing II from triethyl orthoacetate and 2-cyanothioacetamide. The solid product was washed with ethyl ether and recrystallized from methanol, m.p. 230° with decomposition. The infrared spectrum was consistent with the proposed formula.

Anal. Calcd. for $C_6H_8N_2OS$: C, 46.13; H, 5.16; N, 17.93; S, 20.52. Found: C, 46.38; H, 5.18; N, 18.18; S, 20.61.

2-Cyano-3-ethoxythio-2-pentenamide (VIII).—Triethyl orthopropionate (21.1 g., 0.12 mole), 2-cyanothioacetamide (10.0 g., 0.1 mole), and glacial acetic acid (6 ml.) were heated on a steam bath for approximately 8 min. A dark red solution formed and the reaction mixture was set aside

---

[11] J. S. Fritz, *Anal. Chem.*, **24**, 674 (1952).

[12] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., New York, N. Y., 1948, p. 284.

to crystallize. The orange crystals obtained after filtering the mixture were recrystallized from ethyl alcohol to yield yellow crystals, m.p. 130–132.5°.

Anal. Calcd. for $C_8H_{12}N_2OS$: C, 52.14; H, 6.57; N, 15.21; S, 17.40. Found: C, 51.88; H, 6.84; N, 15.27; S, 17.12.

The infrared spectrum was consistent with the proposed structure. The net yield of recrystallized material was only 4 g.; however, several grams of unchanged 2-cyanothioacetamide was recovered, showing that the reaction had not gone to completion.

2-Cyano-3-hydroxythiocrotonamide (IX).—2-Cyano-3-ethoxythiocrotonamide (26.0 g., 0.153 mole) was dissolved in 150 ml. of 4% sodium hydroxide solution. The solution was filtered and the product then precipitated by the addition of 10% hydrochloric acid solution. The solid precipitate was filtered, washed with a little water, and dried. The solid (20.3 g.) was recrystallized from ethyl alcohol to give a product melting at 146–148°.

Anal. Calcd. for $C_5H_{11}N_2OS$: C, 42.24; H, 4.26; N, 19.70; S, 22.52. Found: C, 42.16; H, 4.09; N, 19.77; S, 23.63. An oxygen analysis by a modified Ünterzacher method was found to be 11.13 (calcd. 11.25).

The product was also recrystallized from water and no change in melting point or in the infrared spectrum was observed. The product was acidic in aqueous solution and failed to form a 2,4-dinitrophenylhydrazone in alcohol or aqueous solution.

The same product was also obtained from 2-cyano-3-methoxythiocrotonamide on similar treatment with base and acid.

2-Cyano-3-hydroxythiocrotonamide was also obtained in good yield by simply heating a sample of 2-cyano-3-ethoxythiocrotonamide with 10% hydrochloric acid solution on a steam bath for 10 min. The melting point of a mixture of this product with the product obtained when both base and acid were used was not depressed and the infrared spectra of the two products were identical.

NMR studies showed that the ethoxy group was not present; however, an absorption band assignable to the hydroxy proton was not found.

The neutralization equivalent as determined by iodine titration was 141 (theor. 142.17); analysis for oxirane oxygen indicated that none was present.

A deuterated sample was obtained by carrying out the above reactions with dilute base and acid in deuterium oxide instead of water. The melting point of this deuterated sample was 148–149°. Shifts observed in the infrared absorption spectrum due to deuteration were as follows: 2.97 $\mu[\nu_a(\mathrm{NH})]$ to 3.97 $\mu[\nu_a(\mathrm{ND})]$, 3.03 $\mu[\nu_s(\mathrm{NH})]$ to 4.10 $\mu[\nu_s(\mathrm{ND})]$, 3.13 $\mu[\nu(\mathrm{OH})]$ to 4.22 $\mu[\nu(\mathrm{OD})]$, enol 3.8 $\mu[\nu(\mathrm{SH})]$ to 5.5 $\mu[\nu(\mathrm{SD})]$. Other useful bands were 6.5 $\mu[\nu(\mathrm{C{=}S})]$, 7.7 $\mu[\nu(\mathrm{COH})]$, 6.41 $\mu[\delta(\mathrm{NH_2})]$, and 7.0 $\mu[\delta(\mathrm{OH})]$.

2-Cyano-3-hydroxythio-2-pentenamide (X).—2-Cyano-3-ethoxythio-2-pentenamide (0.75 g., m.p. 130–132.5°) was dissolved in 25 ml. of cold 4% sodium hydroxide solution. The solution was filtered and the product then precipitated by the addition of 10% hydrochloric acid solution. The solid product was isolated by filtration, washed with a little cold water, and dried, m.p. 84–85°.

Anal. Calcd. for $C_6H_8N_2OS$: C, 46.13; H, 5.16; N, 17.93. Found: C, 46.21; H, 5.08; N, 17.98.

2-Cyano-3-mercaptothiocrotonamide (XI).—2-Cyano-3-ethoxythiocrotonamide (1.7 g., 0.1 mole) was dissolved in 25 ml. of a 5% solution of sodium hydrosulfide (Fisher Chemical Co.). The mixture was filtered and cooled with ice and then acidified with 10% hydrochloric acid solution. The orange precipitate was collected by filtration and washed with a small quantity of ice water. The dried product (approx. 1.0 g.) began to shrink at 99° and melted at 102–106°.

Anal. Calcd. for $C_5H_6N_2S_2$: C, 37.94; H, 3.82; S, 40.52. Found: C, 38.49; H, 3.50; S, 42.70.

Attempts to recrystallize the product from alcohol and water mixture failed. A small amount was successfully recrystallized from hot water; however, considerable decomposition occurred. Dilute aqueous solutions of this compound were acidic. On standing, the product turned dark and apparently decomposed.

Useful bands in the infrared spectrum were at 4.1 $\mu[\nu(\mathrm{SH})]$, 4.52 $\mu[\nu(\mathrm{C{\equiv}N})]$, 6.18 $\mu[\delta(\mathrm{NH_2})]$, 6.55 $\mu[\nu(\mathrm{C{=}S})]$, and 12.22 $\mu[\delta(\mathrm{SH})]$.

Methyl 2-Cyano-3-hydroxythiocrotonimidate.—2-Cyano-3-ethoxythiocrotonamide (II, 1.7 g., 0.01 mole) was dissolved in 4% sodium hydroxide solution. This solution was then placed in a glass-stoppered flask containing 1.4 g. (0.01 mole) of methyl iodide and shaken vigorously for 10 min. A yellow solid was formed and was isolated by filtration, m.p. 234–236°. This material was recrystallized from hot water, m.p. 234–236°. The infrared spectrum indicated that the ethoxy group had been replaced with a hydroxy group. Characteristic absorption bands in the infrared spectrum were 3.1 $\mu[\nu(\mathrm{NH})]$, 4.61 $\mu[\nu(\mathrm{C{\equiv}N})]$, 6.35 $\mu[\nu(\mathrm{C{=}N})]$, 7.05 $\mu[\delta(\mathrm{CH_3})]$, and 14.98 $\mu[\nu(\mathrm{CSC})]$.

Anal. Calcd. for $C_6H_8N_2OS$: C, 46.13; H, 5.16; S, 20.52. Found: C, 46.06; H, 5.36; S, 20.53.

3,3′-Dithiobis[2-(1-hydroxyethylidene)-3-iminopropionitrile] (XIV) from IX.—2-Cyano-3-hydroxythiocrotonamide (IX, 7.15 g., 0.05 mole) was dissolved in 250 ml. of ethyl alcohol. To this solution was slowly added 270 ml. of iodine solution (0.1847 *N* iodine in potassium iodide; calculated that 0.05 atom of iodine was needed). A small amount of crushed ice was added to the alcoholic solution and the reaction flask was also externally cooled with crushed ice. As soon as the theoretical quantity of iodine had been added, the mixture was stirred for an additional 5 min. and a few milliliters of excess iodine solution was added. The mixture was then filtered, washed with cold water, then with alcohol, and dried to yield 7.0 g. (theor. 7.0 g.), m.p. 158.5° (began to turn dark 5° or 10° before melting). Useful bands in the infrared spectrum were 3.0 $\mu[\nu(\mathrm{OH})]$, 3.05 $\mu[\nu(\mathrm{NH})]$, 4.45 $\mu[\nu(\mathrm{C{\equiv}N})]$, 6.25 $\mu[\nu(\mathrm{C{=}N})]$, 6.10 $\mu[\nu(\mathrm{C{=}C})]$, 7.25 $\mu[\delta(\mathrm{CH_3})]$, 8.00 $\mu[\delta(\mathrm{OH})]$, 15.10 $\mu[\nu(\mathrm{C{-}S})]$, and 18.7 $\mu[\nu(\mathrm{C{-}S{-}S{-}C})]$. Ultraviolet absorption spectra of this compound in methanol and in dimethylformamidine showed strong absorption bands at 255 and 316 mμ.

Small samples recrystallized from dimethylformamide and washed with ethyl alcohol melted at 144–145°. A mixture of this material with unrecrystallized material melted at 145°. The infrared absorption spectrum of the recrystallized material was identical with that of the unrecrystallized material. When the unrecrystallized sample was washed with more water and hot alcohol, a sample which melted at 167–168° was obtained. Qualitative analysis for halogen was negative.

Anal. Calcd. for $C_{10}H_{10}N_4O_2S_2$: C, 42.54; H, 3.57; N, 19.85; S, 22.71. Found: C, 42.42; H, 3.80; N, 19.68; S, 22.63.

XIV from II.—This material was prepared by the same procedure described in preparing XIV from IX except that 2-cyano-3-ethoxythiocrotonamide (II) was used as the starting material rather than 2-cyano-3-hydroxythiocrotonamide (IX). The solvent was dimethylformamide. The melting point of the product was 148–150°. The melting point of a mixture with recrystallized product from IX was not depressed. The infrared spectrum of this material was identical with that of the product obtained from IX.

2-Cyano-3-aminothiocrotonamide.—2-Cyano-3-ethoxythiocrotonamide (1.7 g., 0.1 mole) was placed in 350 ml. of absolute ethyl alcohol and stirred with a magnetic stirrer while anhydrous ammonia was bubbled into the suspension. The solid dissolved after about 30 min., and after 1.5 hr. the mixture became warm (35–40°). This reaction mixture was then poured into an open beaker and allowed to evaporate in the hood over a 72-hr. period. The solid recovered weighed 1.55 g., m.p. 175–180°. This solid was treated with Darco G-60 during recrystallization from hot water.

The recrystallized product weighed 1.1 g., m.p. 179–180°. Infrared absorption bands noted were 3.01 $\mu[\nu(NH_2)]$ and 3.1 $\mu[\nu(CH)]$.

Anal. Calcd. for $C_5H_7N_3S$: C, 42.53; H, 5.00; S, 22.71. Found: C, 42.35; H, 5.08; S, 22.53.

2-Cyano-3-dimethylaminothiocrotonamide.—2-Cyano-3-methoxythiocrotonamide (0.75 g.) was suspended in a mixture of benzene and ethyl ether. Anhydrous dimethylamine was bubbled into the suspension until most of the solid had dissolved. This solution was filtered and evaporated to dryness. The residue was then recrystallized from methanol. Analytical data indicated that this material was not pure.

This material was then recrystallized from methanol and found to melt at 152–154° (softened at 150°). The infrared spectrum was in agreement with the structure given.

Anal. Calcd. for $C_7H_{11}N_3S$: C, 49.68; H, 6.55; N, 24.82. Found: C, 49.63; H, 6.24; N, 24.57.

2-Cyano-3-phenylthioacrylamide.—2-Cyanothioacetamide (1.0 g., 0.01 mole) was mixed with 1.06 g. (0.01 mole) of benzaldehyde in 10 ml. of ethyl alcohol containing 2 drops of piperidine. The mixture was stirred, and the reaction was noted to be slightly exothermic. The reaction mixture was then placed on the steam bath for 5 min. and then set aside overnight. The solvent had evaporated by the next morning. The sticky residue was washed with hexane then with ethyl ether and dried, m.p. 140–190°. This crude product was recrystallized from ethyl alcohol and water to obtain a yellow solid, m.p. 149–150°. The infrared spectrum was in agreement with the proposed structure.

Anal. Calcd. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.89. Found: C, 63.22; H, 4.33; N, 14.41.

2-Cyano-3-(2-thienyl)thioacrylamide.—(2-Thienylmethylene)malononitrile (5.0 g., 0.03 mole) was dissolved in benzene and 3 drops of triethylamine was added. Hydrogen sulfide was bubbled into the mixture until most of the solvent was evaporated. The resulting solid was treated with Darco G-60 and recrystallized from benzene to obtain a yellow solid, m.p. 169–171°. The molecular weight, determined by boiling point elevation in benzene, was 229. The theoretical molecular weight was 193.19. The infrared spectrum was in agreement with the proposed structure.

Anal. Calcd. for $C_8H_6N_2S_2$: C, 49.46; H, 3.11; N, 14.42; S, 33.00. Found: C, 49.54; H, 3.38; N, 14.34; S, 32.29.

2-Cyano-3-(2-furyl)thioacrylamide.—(2-Furylmethylene)-malononitrile (7.20 g., 0.05 mole, m.p. 72.5–73°) was dissolved in 50 ml. of dry benzene and 3 drops of triethylamine was added to the mixture. The mixture was stirred with a magnetic stirrer, and hydrogen sulfide was bubbled into this solution until most of the benzene was evaporated. The resulting solid was filtered, treated with Darco G-60, and recrystallized from benzene. The product (6.3 g.) melted at 155–156°.

Anal. Calcd. for $C_8H_6N_2OS$: C, 53.94; H, 3.39; N, 15.72; S, 17.99. Found: C, 54.07; H, 3.39; N, 15.70; S, 17.76.

Acknowledgment.—The author is indebted to Dr. H. W. Coover and Dr. N. H. Shearer for helpful discussions and suggestions throughout this study. Thanks are also due Mr. M. V. Otis for infrared analyses, Dr. V. W. Goodlett for NMR studies, Mr. C. L. Harrison for gas chromatographic analyses, and Mr. J. S. Lewis for mass spectrometric analyses.

Organic Sulfur Compounds. VII. Some Addition and Co-oxidation Reactions of Thiols with 2,5-Dimethyl-2,4-hexadiene

Alexis A. Oswald,[1a] B. E. Hudson, Jr.,[1b] George Rodgers,[2] and Fernand Noel[3]

Esso Research and Engineering Company, Linden, New Jersey

Received January 12, 1962

Aromatic and aliphatic thiols were added to 2,5-dimethyl-2,4-hexadiene by a radical mechanism to yield the 1,2-monoadducts in better than 80% yield. On low temperature co-oxidation of aromatic thiols and 2,5-dimethyl-2,4-hexadiene by molecular oxygen, crystalline 2,5-dimethyl-5-arylmercapto-3-hexen-2-yl hydroperoxides were obtained according to a 1,4-radical mechanism. In the addition reaction, the hydrogen of the mercaptan is abstracted predominantly at the more reactive, secondary carbon of the allylic radical intermediate. In the co-oxidation reaction, most of the product is derived from the tertiary resonance form which contributes more than the secondary to the structure of the allylic radical intermediate. Co-oxidation reactions, important in the chemistry of fuel instability, also occur in severely cracked naphtha of high diene content with added aromatic thiols.

A previous paper of this series reported that an aromatic thiol (4-chlorobenzenethiol) can be selectively added to the more reactive double bond of some unconjugated diolefins (dicyclopentadienes, Aldrin).[4a] The same thiol and diolefins could also be co-oxidized by oxygen in hydrocarbon solutions. Again only the more reactive double bond was affected and unsaturated hydroperoxides containing sulfur were formed. These unsaturated hydroperoxides rearranged to substituted 2-hydroxyethyl sulfoxides, as did the hydroperoxide derived from monoölefin–thiol co-oxidation[4a,5] according to the following reaction equation:

$$\mathrm{RSH} + \mathrm{CR_2'{=}CR_2''} + \mathrm{O_2} \longrightarrow \mathrm{R{-}S{-}CR_2'{-}CR_2''{-}O_2H} \longrightarrow \mathrm{R{-}SO{-}CR_2'{-}CR_2''{-}OH}$$

---

[1] Esso Research and Engineering Co., (a) Central Basic Research Laboratory, P.O. Box 45, Linden, New Jersey; (b) Analytical Research Division, P.O. Box 121, Linden, New Jersey.

[2] Present address: 56 Sigwin Circle, Wallingford, Connecticut.

[3] Imperial Oil Ltd., Research Department, P.O. Box 3022, Sarnia, Ontario, Canada.

[4] A. A. Oswald and F. Noel, (a) *J. Org. Chem.*, **26**, 3948 (1961); (b) *Chem. Eng. Data*, **6**, 294 (1961).

[5] A. A. Oswald, *J. Org. Chem.*, **24**, 443 (1959); **26**, 842 (1961).