tracted with three 125-ml. portions of chloroform. The extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield, after two recrystallizations from ethanol-water, 0.94 g. (94%) of 3,4-dihydro-4-phenylcarbostyril, m.p. 177-178°, lit.[4] m.p. 177-178°.

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[4] E. F. M. Stephenson, *J. Chem. Soc.*, 2557 (1956).

Dicyanomethylene-1,3-dithietane

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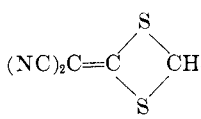
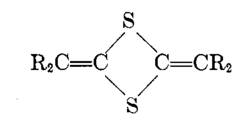
Dicyanomethylene-1,3-dithietane (I) is akin to the desaurins (II)[1] but differs from them in having only one exocyclic methylene group and in being much more reactive.

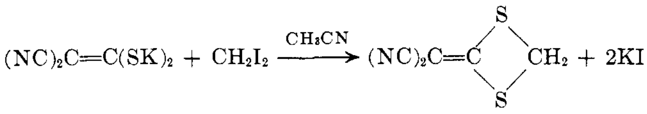


I



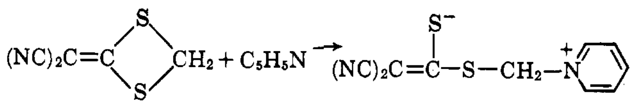
II

This new dithietane is prepared in yields of 65% from dipotassio-1,1-dimercapto-2,2-dicyanoethylene and excess diiodomethane in refluxing acetonitrile. These conditions are similar to those used in the preparation of simple dialkyl derivatives.[2] The dithietane must be handled with great care because it causes severe itching and skin lesions.

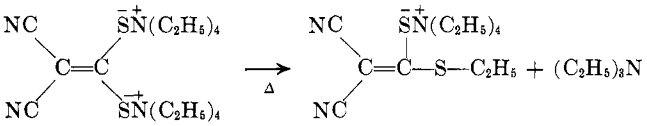


Conceivably, the methylene hydrogens of I might be acidic, especially since a 6-π-electron system could result on loss of a proton. In accordance with this hypothesis, a nearly quantitative yield of hydrogen is obtained when I reacts with sodium hydride in dimethoxyethane; however, dithietane was not recovered upon acidification. A stable sodium salt could not be isolated nor could any alkylation products be observed under these conditions. No deuterium exchange occurred when dithietane was heated in refluxing deuterium oxide. It appears that the anion of I forms only with strong base and, if it possesses unusual stability,[3] it is at the same time very reactive.

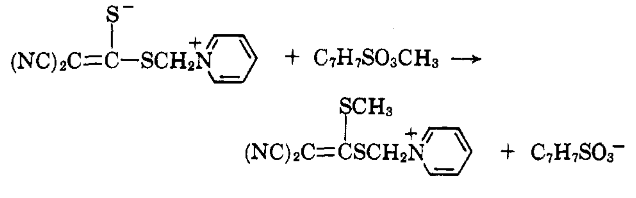
Ring-Opening with Pyridine.—The ring itself proved to be remarkably labile, being opened by nucleophilic reagents.[4] When the dithietane in hot benzene is treated with pyridine, the initially clear solution rapidly becomes turbid, and a pyridinium zwitterion is obtained in 80% yield.



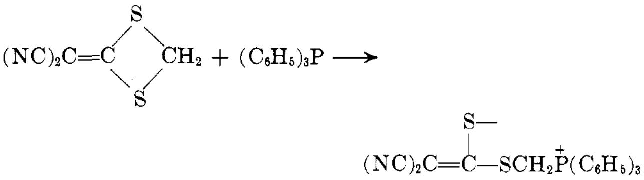
Elemental analysis, molecular weight, proton magnetic resonance, and ultraviolet spectral data were in agreement with the zwitterion structure. The ultraviolet spectrum of the pyridinium zwitterion, λ_{max} 338 mμ (ϵ 19,300) and 263 (9860), compares favorably with that of tetraethylammonium 2,2-dicyano-1-ethylthioethylene-1-thiolate, λ_{max} 342 mμ (ϵ 21,800) and 285 (10,000), prepared by the pyrolysis of bis(tetraethylammonium) 2,2-dicyanoethylene-1,1-dithiolate.



Treatment of the pyridinium zwitterion with methyl *p*-toluenesulfonate gave an S-methyl derivative whose ultraviolet spectrum is virtually identical with that of 1,1-dicyano-2,2-bis(methylthio)ethylene when allowance is made for the pyridinium and *p*-toluenesulfonate absorptions.



Ring-Opening with Triphenylphosphine.—Triphenylphosphine does not remove sulfur from the dithietane ring as it does readily with episulfides[5] and slowly with thietanes.[6] The reaction of I with triphenylphosphine opens the dithietane ring to give a phosphonium zwitterion. No reaction was observed with the weaker nucleophile triphenylarsine. Elemental analysis, molecular weight determination, and spectral data again supported the zwitterionic structure.



Experimental

Dipotassio-1,1-dimercapto-2,2-dicyanoethylene was prepared from carbon disulfide, malononitrile, and 2 moles of potassium hydroxide.[7] The salt was prepared earlier by Kendall and Edwards but was not isolated.[2]

Bis(tetraethylammonium) 2,2-Dicyanoethylene-1,1-dithiolate.—Dipotassio-1,1-dimercapto-2,2-dicyanoethylene (56 g., 0.26 mole) was dissolved in 290 ml. of methanol. Tetraethylammonium chloride (100 g., 0.6 mole) in 135 ml. of methanol was added. The reaction mixture was stirred for 15 min. and filtered to remove 31 g. of potassium chloride. The filtrate was evaporated on a rotary evaporator, and the yellow solid which remained was dried in a vacuum oven at 50° (18 mm.). The crude tetraethyl-

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[1] P. Yates and D. R. Moore, *J. Am. Chem. Soc.*, **80**, 5577 (1958), references cited therein; A. Schönberg, L. Vargha, and H. Kaltschmitt, *Ber.*, **64**, 2581 (1931); A. Schönberg, A. Stephenson, H. Kaltschmitt, E. Petersen, and H. Schulten, *ibid.*, **66**, 243 (1933).

[2] H. D. Edwards and J. D. Kendall, U. S. Patents 2,533,233 and 2,493,071 (1950).

[3] The methylene protons in the diethylmercaptal of formaldehyde are acidic enough to give an anion which can be alkylated: J. F. Arens, M. Fröhling, and A. Fröhling, *Rec. trav. chim.*, **78**, 663 (1959).

[4] Cyclic acetals of dicyanoketene are attacked by nucleophilic reagents to give ring-opened products: W. J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958).

[5] R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958); C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

[6] S. M. Kotin, Ph.D. thesis, University of Pennsylvania, 1963.

[7] W. R. Hatchard, to be published.

ammonium salt (109 g.) recrystallized from ethanol–tetrahydrofuran as yellow crystals, m.p. 180° dec.

Anal. Calcd. for $C_{20}H_{40}N_4S_2$: C, 59.94; H, 10.06; N, 13.98; S, 16.01. Found: C, 60.47; H, 10.14; N, 14.12; S, 16.26.

The ultraviolet spectrum in ethanol had absorption at 340 mμ (ε 21,300) and 272 (14,500). The infrared spectrum had absorption at 2160, 2140, 2050, and 1440 cm.$^{-1}$.

Tetraethylammonium 2,2-Dicyano-1-ethylthioethylene-1-thiolate.—Bis(tetraethylammonium) 2,2-dicyanoethylene-1,1-dithiolate (20.0 g., 0.05 mole) was heated to 180° (20 mm.) in a flask connected to a trap cooled to −80°. The triethylamine evolved was collected and converted to its hydrochloride, m.p. 254–256°, in 95% yield (6.5 g.). The pyrolysis residue crystallized on cooling and was recrystallized from methanol as yellow crystals, m.p. 52–54°, in 85% yield (13.55 g.). The ultraviolet spectrum had absorption at 342 mμ (ε 21,800) and 285 (10,000).

Anal. Calcd. for $C_{14}H_{25}N_2S_2$: N, 15.38. Found: N, 15.43.

The salt was readily converted to known 1,1-dicyano-2,2-bis(ethylthio)ethylene,[2] with ethyl bromide in ethyl acetate.

Dicyanomethylene-1,3-dithietane.—Dipotassio-1,1-dimercapto-2,2-dicyanoethylene (109 g., 0.5 mole) was suspended in 1 l. of acetonitrile (Union Carbide commercial grade, not dried). Diiodomethane (267 g., 1.0 mole) was added, and the reaction mixture was stirred vigorously with a mechanical stirrer and was refluxed for 23 hr. A gray solid (136 g.), presumably potassium iodide, was separated by filtration from the dark brown solution. The acetonitrile filtrate was evaporated on a rotary evaporator. Then the residue was extracted with 500 ml. of water to remove any potassium iodide and was dissolved in about 1 l. of hot benzene. The brown benzene solution was partly decolorized with charcoal and a filter aid (Celite). Yellow-brown crystals, m.p. 145–149° (49.9 g., 65%), were obtained when the benzene solution was concentrated and cooled. Additional crystals, m.p. 146–150° (8.5 g.), were obtained by concentration of the mother liquors. The product can be purified further by sublimation, which is tedious, or by recrystallization from benzene or benzene–hexane. The infrared spectrum had absorptions at 3058, 2976, 1493, and 1425 cm.$^{-1}$, and the ultraviolet spectrum exhibited maxima at 303 mμ (ε 15,500) and 253 (5100).

Bis(tetraethylammonium) 2,2-dicyanoethylene-1,1-dithiolate could be used instead of the dipotassium salt, but the yields were not improved.

The dithietane is soluble at room temperature in glacial acetic acid, chloroform, dichloromethane, dimethyl sulfoxide, acetonitrile, dioxane, dimethylformamide, and acetone. It is somewhat less soluble in benzene, ethanol, methanol, water, and ethyl acetate and is insoluble in carbon tetrachloride, hexane, ether, and carbon disulfide.

Anal. Calcd. for $C_5H_2N_2S_2$: C, 38.93; H, 1.31; S, 41.58; mol. wt., 154. Found: C, 38.83; H, 1.55; S, 41.18; mol. wt., 166.

1,1-Dicyano-2-(S,N-methylpyridinium)mercaptoethylene-2-thiolate.—Pyridine (12 g., 0.15 mole) was added to a solution of dicyanomethylene-1,3-dithietane (7.7 g., 0.5 mole) in 150 ml. of hot benzene. The clear solution became turbid within 5 min. and was refluxed for 22 hr. At the end of this time there was considerable solid in the flask, and the solution was dark brown. The solid was removed by filtration and washed with benzene. The yield was 9.4 g. (81%). The tan solid was recrystallized three times from water–acetonitrile to give white to pale yellow crystals, m.p. 193–194° dec.

Anal. Calcd. for $C_{10}H_7N_3S_2$: C, 51.48; H, 3.03; N, 18.04; S, 27.49; mol. wt., 233. Found: C, 51.79; H, 3.06; N, 18.02; S, 27.86; mol. wt. (boiling point elevation of acetone), 235 and 250.

The infrared spectrum had absorption at 2260, 2240, 1650, and 1500 cm.$^{-1}$. The ultraviolet spectrum in acetonitrile showed absorption at 338 mμ (ε 19,300) and 263 (9860). The proton magnetic resonance spectrum in dimethyl sulfoxide (60 Mc., tetramethylsilane as internal reference) showed absorption at 455, 420, 395, and 294 c.p.s. The ratio of the total area of absorption at 455, 420, and 395 c.p.s. to the area of the absorption at 294 c.p.s. was 5:2.

The pyridinium zwitterion was soluble in dimethyl sulfoxide, acetonitrile, dimethylformamide, hot acetic acid, and hot methanol. It had low solubility in ethanol, benzene, chloroform, dioxane, tetrahydrofuran and carbon tetrachloride. A deep wine red color develops when the zwitterion in dimethyl sulfoxide is treated with basic reagents such as sodium carbonate, sodium methoxide, or sodium azide. It is not clear whether this color is due to the anion formed by removing a methylene proton or to a thiophene derivative formed by cyclization.[8]

1,1-Dicyano-2(S,N-methylpyridinium)mercapto-2-methylmercaptoethylene *p*-Toluenesulfonate.—The pyridinium zwitterion (6.9 g., 0.03 mole) was heated with 25 ml. of methyl *p*-toluenesulfonate. After about 12 hr. a buff solid (9.8 g.) was removed by filtration and washed with benzene. It was recrystallized three times from acetonitrile to yield white crystals, m.p. 175.6–176.0°.

Anal. Calcd. for $C_{18}H_{17}N_3O_3S_3$: C, 51.53; H, 4.09; N, 10.02; S, 22.93. Found: C, 51.79; H, 4.19; N, 10.18; S, 22.94.

The infrared spectrum had absorption at 2200, 1650, 1500 cm.$^{-1}$. The ultraviolet spectrum in acetonitrile had absorption at 332 mμ (ε 11,500), 263 (5770), and 219 (9860). The ultraviolet spectrum of 1,1-dicyano-2,2-bis(methylthio)ethylene had maxima at 330 mμ (ε 13,300), 290 (6850), and 220 (2995).

The proton magnetic resonance spectrum in deuterium oxide (60 Mc., tetramethylsilane as internal reference) showed a complex multiplet, poorly resolved, centered at 495, a singlet at 386, and two singlets at 183 and 172 c.p.s. The relative areas were, respectively, 9:2:3:3.

The compound was soluble in water and partially soluble in acetonitrile, ethanol, and chloroform. It was insoluble in methylene chloride and dioxane.

1,1-Dicyano-2-(S-methyltriphenylphosphonium)mercaptoethylene-2-thiolate.—Dicyanomethylene-1,3-dithietane (15.4 g., 0.10 mole) was dissolved in 350 ml. of hot benzene, and triphenylphosphine (34.3 g., 0.15 mole) in 150 ml. of benzene was added in one portion. Within 2 min. the clear solution became turbid and was refluxed for 20 min. The tan solid (27.4 g., 66%) was removed by filtration and washed three times with benzene. The filtrate was returned to the reaction flask and refluxed for 6 hr. more to give an additional 9.7 g. of tan solid. The over-all yield of crude material, m.p. 245–246° dec., was 89%.

The solid was recrystallized from acetonitrile as nearly white crystals, m.p. 245–246° dec. The crystals darkened above 230°.

Anal. Calcd. for $C_{23}H_{17}N_2PS_2$: C, 66.32; H, 4.12; N, 6.73; S, 15.40; P, 7.45; mol. wt., 417. Found: C, 66.62; H, 4.23; N, 6.59; S, 15.85; P, 7.60; mol. wt. (boiling point elevation of acetone), 465 and 483.

The infrared spectrum had absorption at 2200, 2180, 1575, and 1490 cm.$^{-1}$. The ultraviolet spectrum in acetonitrile had maxima at 342 mμ (ε 18,300) and 275 (9940). The proton magnetic resonance spectrum (60 Mc., tetramethylsilane as internal reference) in dimethyl sulfoxide showed absorption at 470, 443, and 347 c.p.s. The latter was a doublet (J = 8 c.p.s.). The ratio of the combined areas of the absorption at 470 and 443 c.p.s. to the absorption at 347 c.p.s. was 15:2.

The phosphonium zwitterion was soluble in dimethyl sulfoxide, acetone, acetonitrile, hot chloroform, and nitromethane. It was slightly soluble in ether, dioxane, and ethyl actetate, and it was insoluble in water, acetic acid, benzene, and ethanol.

Acknowledgment.—We wish to thank Dr. Owen Webster and Dr. B. C. McKusick for helpful discussions.

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[8] R. Gompper and E. Kutter, *Angew. Chem. Intern. Ed. Engl.*, **1**, 216 (1962).

2,4-*p*-Menthadiene. A New Monoterpene from Valencia Orange Oil

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During an investigation of the constituents of cold-pressed orange oil, a new terpene hydrocarbon was isolated. Catalytic reduction yielded *cis-* and *trans-*