methyl), 1.36 (C-methyl), 2.25 (N-methyl), and 4.65 (benzylic hydrogen), and multiplets (phenyl ring) centered at 7.25 and 7.55 ppm with relative areas of 3, 3, 6, 1, 3, and 2, respectively.[30] The nmr spectrum in 75% trifluoroacetic acid possessed singlets at 1.68 (C-methyl), 3.04, and 5.42 ppm with relative areas of 6, 6, and 1, respectively. The infrared spectrum showed no absorption corresponding to N–H or C=O groups. An ethanol solution showed a low intensity band with λ_{max} 255 mμ.

Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.52; H, 8.31; N, 12.84. Found: C, 71.59; H, 8.31; N, 12.98.

Registry No.—**1**, 15451-12-4; **2**, 15451-13-5; **3**, 15451-14-6; **4**, 15451-15-7; **5**, 15451-16-8; **5** HCl, 15451-17-9; **7**, 15451-18-0; **7** HBr, 15451-19-1; **8**, 15451-20-4; **9**, 15451-21-5; **10**, 15451-22-6; **11**, 15451-23-7; **11** picrate, 15451-24-8; **12**, 15451-25-9; **12** picrate, 15451-26-0; **13**, 15451-27-1; **14**, 15451-28-2; **15**, 15451-29-3; **16**, 15451-30-6; 1,1-dimethyl-2-phenylethene, 768-49-0.

---

[30] Separation of the phenyl hydrogen absorption into three- and two-proton multiplets was also observed in the spectrum of 4,4-dimethyl-2-phenyl-1-pyrroline.[1]

Syntheses of Dicyanoacetylene

ENGELBERT CIGANEK AND CARL G. KRESPAN

Contribution No. 1379 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received September 25, 1967

Thermal decomposition of dicyanodiazomethane at 220° gave tetracyanoethylene, cyanogen, and dicyanoacetylene. The two latter products were also formed in the pyrolysis of tetracyanoethylene at 700°. Thermolysis of the easily accessible 4,5-dicyano-1,3-dithiol-2-one (**5**) was found to provide a convenient synthesis of dicyanoacetylene.

Dicyanoacetylene (**1**) was first prepared by Moureu and Bongrand[1] almost 60 years ago by the dehydration of the bisamide of acetylenedicarboxylic acid. While its physical properties have been studied in great detail,[2,3] investigations of its chemical reactions have been hampered by lack of a satisfactory synthesis; despite its unusually high reactivity, only relatively few papers on this subject have appeared so far.[4,5] The original synthesis[1] of dicyanoacetylene proceeds with acceptable yields (30–40%) only on a small scale; attempts to modify it have met with little success.[5e,l] The gas phase pyrolysis of 1,2-dichloro-1,2-dicyanoethylene[6] affords dicyanoacetylene and chlorine in good yields, but the products recombine so rapidly at low temperatures that they must be separated immediately in order to obtain acceptable conversions. The two other reported syntheses of dicyanoacetylene are the retrodiene cleavage of dimethyl 5,6-dicyanooxabicyclo[2.2.1]hepta-2,5-dienedicarboxylate[7] and the reaction of carbon with nitrogen at or above 2500°.[8] We have found that dicyanoacetylene is formed on gas phase pyrolysis of tetracyanoethylene (**2**), 4,5-dicyano-1,3-dithiol-2-one (**5**), and 4,5-dicyano-1,3-dithiol-2-thione (**6**).[9] Pyrolysis of **5** is believed to be the best and most convenient synthetic method for the preparation of dicyanoacetylene presently available.

Results and Discussion

As part of our investigations of the chemistry of dicyanocarbene,[10] we were interested in the reactions of this species in the absence of added carbene acceptors. To this purpose, solid dicyanodiazomethane (**4**)[11] was pyrolyzed in a stream of helium at 220° [12] in the preheater of a gas chromatograph. The products were separated by gas chromatography and identified by their mass spectra. In addition to nitrogen and tetracyanoethylene (30–40% yield), cyanogen (**3**) and dicyanoacetylene (**1**) were formed in considerable but undeter-

---

[1] C. Moureu and J. C. Bongrand, *Bull. Soc. Chim. France*, 846 (1909); *Ann. Chim.* (Paris), [9] **14**, 5 (1920); *Compt. Rend.*, **170**, 1025 (1920).

[2] The following physical data have been published: crystal structure,[3a] heat of combustion and formation,[3b] flame temperatures,[3f] heat of vaporization and vapor pressure,[3c] molecular orbital calculations,[3d] resonance energy,[3e] thermodynamic functions,[3m] ultraviolet spectrum,[3g] infrared spectrum,[3h,n] Raman spectrum,[3h,m] mass spectrum,[3i] molecular refraction,[1,3j] molecular polarizability,[3m] magneto-optical properties,[3k] melting point curves with maleonitrile and fumaronitrile,[3j] lifetime in space,[3o] and toxicity.[3l]

[3] (a) R. B. Hannan and R. L. Collin, *Acta Cryst.*, **6**, 350 (1953); (b) G. T. Armstrong and S. Marantz, *J. Phys. Chem.*, **64**, 1776 (1960); (c) A. J. Saggiomo, *J. Org. Chem.*, **22**, 1171 (1957); (d) J. B. Moffat, *Can. J. Chem.*, **42**, 1323 (1964); (e) M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1608 (1959); (f) A. D. Kirshenbaum and A. V. Grosse, *ibid.*, **78**, 2020 (1956); A. V. Grosse and C. S. Stokes, U. S. Department of Commerce, Office of Technical Services, P. B. Report 171, 460 (1960); *Chem. Abstr.*, **52**, 8696 (1962); (g) F. A. Miller and R. B. Hannan, Jr., *Spectrochim. Acta*, **12**, 321 (1958); (h) F. A. Miller and R. B. Hannan, Jr., *J. Chem. Phys.*, **21**, 110 (1953); F. A. Miller, R. B. Hannan, Jr., and L. R. Cousins, *ibid.*, **23**, 2127 (1955); (i) V. H. Dibeler, R. M. Reese, and J. L. Franklin, *J. Am. Chem. Soc.*, **83**, 1813 (1961); (j) H. Mommaerts, *Bull. Soc. Chim. Belges*, **52**, 79 (1943); (k) A. Turpin and D. Voigt, *Compt. Rend.*, **256**, 1712 (1963); F. Galais and J. F. Labarre, *J. Chim. Phys.*, **61**, 717 (1964); (l) A. Desgret, *Compt. Rend.*, **152**, 1707 (1911); (m) C. Nagarjan, E. R. Lippincott, and J. M. Stutman, *Z. Naturforsch.*, **20a**, 786 (1965); (n) F. A. Miller, D. H. Lemon, and R. E. Witkowski, *Spectrochim. Acta*, **21**, 1709 (1965); (o) A. E. Potter and B. DelDuca, *Icarus*, **3**, 103 (1964).

[4] The following reactions of dicyanoacetylene have been reported: halogenation and hydrohalogenation;[1] addition of alcohols,[1,5a] amines,[1,5a,b] and mercaptans;[3k] reaction with phosphines,[5c] mercuric chloride,[5b] and pentacyanocobaltate ion;[5d] cycloadditions;[5b,e–j,m] and polymerization.[5k,l]

[5] (a) E. Winterfeldt, W. Krohn, and H. Preuss, *Chem. Ber.*, **99**, 2572 (1966); (b) C. D. Weis, *J. Org. Chem.*, **28**, 74 (1963); (c) G. S. Reddy and C. D. Weis, *ibid.*, **28**, 1822 (1963); *cf.*, however, G. Märkl, *Angew. Chem.*, **77**, 1109 (1965); (d) M. E. Kimball, J. P. Martella, and W. C. Kaska, *Inorg. Chem.*, **6**, 414 (1967); (e) A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945); (f) R. C. Cookson and J. Dance, *Tetrahedron Letters*, 879 (1962); (g) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **86**, 1434 (1964); (h) P. G. Gassman and K. Mansfield, *Chem. Commun.*, 391 (1965); (i) C. Dufraisse, J. Rigaudy, and M. Ricard, *Tetrahedron Suppl.*, **8**, Part II, 491 (1966); (j) E. Ciganek, *Tetrahedron Letters*, 3321 (1967); (k) M. Beneš, J. Peška, and O. Wichterle, *Chem. Ind.* (London), 562 (1962); *J. Polymer Sci.*, Part C, No. 4, 1377 (1964); (l) N. R. Byrd, NASA Accession No. N64-20601, Report No. NASA-CR-56035; Report 166-F, 1964; *Chem. Abstracts*, **62**, 2831 (1965); (m) C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

[6] E. L. Martin, U. S. Patent 3,070,622 (1962); *Chem. Abstr.*, **59**, 454 (1963).

[7] C. D. Weis, *J. Org. Chem.*, **27**, 3520 (1962).

[8] P. D. Zavitzanos, French Patent 1,460,282 (1966); *Chem. Abstr.*, **67**, 63861 (1967).

[9] The synthesis of dicyanoacetylene from **5** and **6** is subject of a patent: E. Ciganek and J. R. Roland, U. S. Patent 3,322,816 (1967); *Chem. Abstr.*, **67**, 90414 (1967).

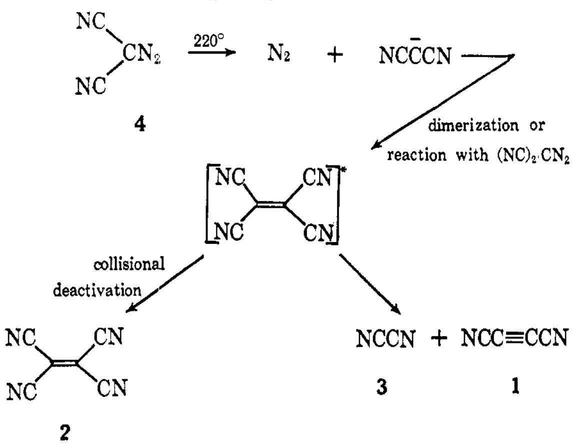
[10] E. Ciganek, *J. Am. Chem. Soc.*, **88**, 1979 (1966).

[11] E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

[12] Thermal decomposition of **4** occurs at *ca.* 70°; the higher pyrolysis temperature was used to ensure vaporization of the products.

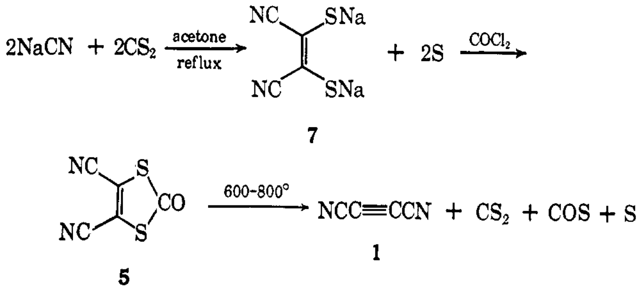
mined amounts. A control experiment showed that tetracyanoethylene was stable under the conditions of this pyrolysis. To explain the formation of cyanogen and dicyanoacetylene, we suggest the following reaction path (Scheme I): decomposition of dicyanodiazomethane affords dicyanocarbene, which dimerizes, or reacts with undecomposed diazo compound, to give tetracyanoethylene. Either of the latter two processes should be highly exothermic and the tetracyanoethylene, at the moment of its formation, may be expected to be vibrationally excited or, in other words, at a higher temperature than its surroundings.[13] Deactivation by collision with the walls of the reaction vessel or with carrier gas molecules does not seem to be efficient, since part of the "hot" tetracyanoethylene decomposes into cyanogen and dicyanoacetylene. Evidence in favor of this hypothesis was obtained by pyrolyzing tetracyanoethylene (**2**) at higher temperatures. This experiment was carried out by passing tetracyanoethylene vapors, entrained in helium, into a hot tube filled with quartz chips and analyzing the products by gas chromatography. The contact time was *ca.* 5 sec. The starting material remained undecomposed at tube temperatures of up to 600°. At 700°, partial decomposition to dicyanoacetylene (**1**) and cyanogen (**3**) occurred; it was almost complete at 800°. At 980°, only cyanogen was observed, the dicyanoacetylene apparently having been destroyed during the pyrolysis. This result explains why previous workers[14] had obtained only cyanogen in the pyrolysis of tetracyanoethylene at 1000°. The formation of dicyanoacetylene and cyanogen from tetracyanoethylene is endothermic by 32.8 kcal/mole as calculated from the published[3b,15,16] heats of formation in the gas phase (tetracyanoethylene, 168.5 kcal/mole; cyanogen, 73.8 kcal/mole; and dicyanoacetylene, 127.5 kcal/mole).

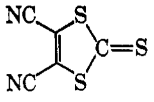
Scheme I



On a preparative scale, dicyanoacetylene could be obtained in this manner in up to 72% yield. However, the output per time unit proved to be small and the reaction could not be accelerated by increasing the tube temperature or the contact time, since the decomposition temperature of tetracyanoethylene was not much lower than that of dicyanoacetylene. On the assumption that other compounds containing the maleonitrile unit might yield dicyanoacetylene at elevated temperatures, the pyrolytic behavior of a number of such derivatives was investigated. The compound that proved to be best suited was 4,5-dicyano-1,3-dithiol-2-one (**5**), since it was readily accessible, had low sublimation and decomposition temperatures, and gave dicyanoacetylene in good yields.[17] Its previously described synthesis[18] is shown in Scheme II. Reaction between sodium cyanide and carbon disulfide in refluxing acetone gives a mixture of sulfur and the disodium salt of dimercaptomaleonitrile (**7**); passing phosgene into the filtered aqueous solution of **7** affords a precipitate of 4,5-dicyano-1,3-dithiol-2-one (**5**). The yield, based on sodium cyanide, is 53–57%. Gas phase pyrolysis of **5** under reduced pressure at 600°, and more rapidly at 800°, gave dicyanoacetylene in 59–76% yield in addiction to carbon disulfide, carbonyl sulfide, and sulfur. The over-all yield, based on sodium cyanide, was thus up to 43% and neither of the intermediates **7** and **5** needed to be purified for use in the next step. The mechanism of the formation of dicyanoacetylene from 4,5-dicyano-1,3-dithiol-2-one is unknown; it must involve at least two steps, since it was found that at a pyrolysis temperature of 500° the yield of dicyanoacetylene dropped to almost zero even though the starting material (**5**) was completely consumed. The thio analog of **5**, 4,5-dicyano-1,3-dithiol-2-thione (**6**)[18c,d] also gave dicyanoacetylene on gas phase pyrolysis, but the yield was low (19%).

Scheme II





6

Dicyanoacetylene is a hazardous material. Because of its toxicity[31] and high vapor pressure at room temperature, it should be handled only in a hood. It is potentially explosive, both in the pure state and in concentrated solutions,[19] but its thermal stability in dilute solutions in inert solvents is greater than previously re-

---

[13] For a review of chemical activation, see B. S. Rabinovitch and M. C. Flowers, *Quart. Rev.* (London), **18**, 122 (1964).

[14] T. L. Cairns, *et al., J. Am. Chem. Soc.*, **80**, 2775 (1958).

[15] R. H. Boyd, *J. Chem. Phys.*, **38**, 2529 (1963).

[16] J. W. Knowlton and E. J. Prosen, *J. Res. Natl. Bur. Std.*, **46**, 489 (1951).

[17] A preliminary experiment on the pyrolysis of 4,5-dicyano-1,3-dithiol-2-one (**5**) was carried out by Dr. J. R. Roland.

[18] (a) G. Bähr and G. Schleitzer, *Chem. Ber.*, **88**, 1771 (1955); (b) H. Hahn, G. Mohn, and A. V. Schoor, German Patent 1,158,056 (1963); *Chem. Abstr.*, **60**, 5341 (1964); (c) Farbenfabriken Bayer A.G., British Patent 829,529 (1960); *Chem. Abstr.*, **54**, 19498 (1960); (d) C. G. Krespan, U. S. Patent 3,140,295 (1964); *Chem. Abstr.*, **61**, 8239 (1964).

[19] The only explosion in our work occurred when an equimolar mixture of dicyanoacetylene and tropone was allowed to stand at room temperature in a sealed tube; in dilute solution, the reaction between these two substances required prolonged heating at elevated temperatures.

ported.[20] Pure dicyanoacetylene turns dark slowly at room temperature, but it can be kept almost indefinitely at Dry Ice temperature.

Experimental Section

Pyrolysis of Dicyanodiazomethane.—The pyrolysis was carried out in the preheater of a gas chromatography column, the outlet of which was connected to a time-of-flight mass spectrometer. The temperature of the preheater was 210–220°, that of the column (2 m, packed with 30% Dow-Corning FS 1265 silicone oil on 60–80 mesh Chromosorb P), 150°. Samples (4–9 mg) of solid dicyanodiazomethane[11] were injected and the products were identified by their mass spectra. The yields of tetracyanoethylene (TCNE) were determined by comparing the areas under the TCNE peaks with the areas of standard samples. In all runs, considerable but undetermined amounts of cyanogen and dicyanoacetylene were also formed. The following yields of TCNE were obtained: 30% (from 4.01 mg of dicyanodiazomethane), 25% (from 8.05 mg), and 39% (from 9.04 mg).

Pyrolysis of Tetracyanoethylene. A. Microscale Pyrolysis in a Stream of Helium.—The experiment was carried out in an 11 × 0.5 in. tube, filled with 20-mesh quartz chips, connected to a gas chromatographic column (same packing and temperature as above; flow rate of helium 50 ml/min). The contract time was *ca.* 5 sec. With the temperature of the tube varying from 400 to 980°, samples of solid TCNE (*ca.* 15 mg) were injected; the products were collected and identified by infrared and mass spectroscopy. TCNE was recovered unchanged at temperatures up to 600°. At 700°, cyanogen and dicyanoacetylene were observed in addition to unchanged TCNE; at 800°, the TCNE was converted completely into cyanogen and dicyanoacetylene. At 980° the peak corresponding to the latter disappeared but cyanogen was still being formed.

B. Pyrolysis under Vacuum.—The pyrolysis was carried out in a 25 × 2 cm vertical quartz tube packed with (a) quartz tubes of 5-mm diameter, cut into pieces 5 mm long, or (b) 8–14 mesh Amersil fused silica, or (c) 20–35 mesh quartz chips. The tetracyanoethylene was sublimed into the tube from a flask heated with an air bath (120–140°). The products were collected in two traps in series, the first cooled with Dry Ice–acetone, the second with liquid nitrogen. Unreacted TCNE collected at the upper end of the pyrolysis tube. The dicyanoacetylene was identified by comparison of its infrared spectrum with that of an authentic sample.[1] The following results were obtained (tube packing, tube temperature, pressure (mm), yield, and conversion given in this order): a, 800, 2.2, 0, 0; a, 900, 3.8–4.1, 0, 0; a, 970, 6.2, 72, 18; b, 970, 3.5, 60, 32; c, 970, 2.6, 51, 50; c, 970, 1.2, 61, 48.

Disodium dimercaptomaleonitrile (7) was prepared by a modification of the procedure given in ref 18b. In a 5-l. three-necked flask, equipped with a thermometer, a mechanical stirrer with a water-cooled jacket, and two efficient reflux condensers stacked one on top of the other, was placed a mixture of 2400 ml of reagent grade acetone, 100 ml of water, and 300 ml (*ca.* 380 g, 5.0 moles) of carbon disulfide. The stirrer was started and 200 g (4.1 moles) of sodium cyanide was added all at once. The flask was immersed in a water bath and the mixture was stirred at 50–55° inside temperature for 7 hr. The dark solution was decanted while hot and the solids were washed with two 100-ml portions of hot methanol. The combined solutions were concentrated, using a rotary evaporator equipped with a rotating trap immersed in a Dry Ice–acetone bath. Most of the solvents were removed under aspirator vacuum at a temperature not exceeding 45°. The flask containing the residue was then connected, through a trap cooled with Dry Ice–acetone, to an oil pump and evacuated until all the remaining organic solvents had collected in the trap. The residue weighed *ca.* 520 g and still contained most of the water. The amount of disodium dimercaptomaleonitrile present in this product was determined from the ultraviolet spectrum of a representative sample in methanol solution by measuring the extinction coefficient of the maximum at *ca.* 375 mμ. Pure disodium dimercaptomaleonitrile (7) has $\lambda_{\max}^{\mathrm{MeOH}}$ 372 (ϵ 12,000).[21] The yield thus calculated was 250–275 g (66–72%). The crude product was used in the next step without further purification.

4,5-Dicyano-1,3-dithiol-2-one (5).—The following is a modification of the procedure described in ref 18c. The crude disodium dimercaptomaleonitrile was stirred at room temperature with 1200 ml of water for 15 min, the solution was filtered, and the solids (sulfur) were washed once with 200 ml of water. To the combined filtrates was added 100 g of borax (sodium tetraborate) and the mixture was placed in a 5-l. three-necked flask fitted with a pressure-equalizing, 500-ml addition funnel connected to a nitrogen bubbler, a mechanical stirrer, a gas inlet tube reaching below the level of the liquid, and a low-temperature thermometer. In the addition funnel was placed 500 ml of 10% sodium hydroxide solution and the whole apparatus was blanketed with nitrogen. The mixture was cooled to 0° with a Dry Ice–acetone bath. Phosgene was condensed in a 250-ml graduated trap containing a few boiling chips and cooled to −40°; the amount of phosgene needed (in milliliters at −40°) was determined by multiplying the weight of disodium dimercaptomaleonitrile in the product by a factor of 0.4. The phosgene was allowed to vaporize and pass into the stirred solution, which was kept at 0–2°. The pH of the solution was checked at intervals and kept slightly basic (pH 7–8) by addition of the 10% sodium hydroxide solution. About 250 ml of the solution was needed. When the addition of phosgene was complete (2–3 hr), the cooling bath was removed and the mixture was stirred until it reached room temperature. It was filtered and the solid was washed with four 500-ml portions of water. It was sucked dry for about 1 hr and then transferred into a 2-l. three-necked flask equipped with a mechanical stirrer (water-cooled sleeve) and a Dean–Stark water separator. Benzene (700 ml) was added and the mixture was stirred and heated under reflux until no more water distilled azeotropically. The benzene was removed, using a rotary evaporator with a rotating trap cooled in Dry Ice–acetone, and the residual dark solid was dried to constant weight under oil pump vacuum.[22] The yield of crude 4,5-dicyano-1,3-thiol-2-one (5) was 185–200 g (53–57% based on sodium cyanide).

Dicyanoacetylene (1).—The pyrolysis of 4,5-dicyano-1,3-dithiol-2-one (5) was carried out in a vertical quartz tube, 2 cm in diameter and 25 cm in length, and packed with quartz tubes of 0.5 cm diameter, cut into pieces 0.5 cm long. The tube temperature was controlled by a thermocouple contained in a well in the center of the tube and connected to a "Pyro Vane" temperature control unit. The lower end of the tube was connected to a 200-ml round-bottomed flask containing a mixture of 75 g of 4,5-dicyano-1,3-dithiol-2-one (5) and 75 g of sand (Fisher Scientific Co. silica, SiO_2). The upper end of the pyrolysis tube was connected to two inverted traps in series, the first (1) containing a magnetic stirring bar and cooled with Dry Ice–acetone, the second (2) cooled with liquid nitrogen. The whole apparatus was shielded. With the tube temperature at 800°, the whole system was evacuated to *ca.* 0.2 mm, using an oil pump. The outlet of the pump vented into a hood. The flask was then immersed in an air bath, the temperature of which was raised to *ca.* 135° during 1–2 hr. During this time, the pressure increased to *ca.* 3–5 mm. When the pressure had decreased again to *ca.* 2 mm, the bath temperature was raised slowly to 160° and kept there until the pressure decreased to below 1 mm. The whole pyrolysis took about 6–8 hr. Nitrogen was admitted to the system and the stirred contents of trap 1 were flash-distilled under vacuum into another trap, cooled with Dry Ice–acetone. During this operation, trap 1 was immersed in hot water and the pressure was regulated to prevent excessively fast distillation which resulted in freezing of the dicyanoacetylene in trap 1. The yield of dicyanoacetylene was 20–26 g (59–76%). The product so obtained usually contained less than 0.1% of carbon disulfide and if the precursor was dried azeotropically, *ca.* 0.5–1% of benzene. The carbon disulfide can be removed by distillation through an efficient column; dicyanoacetylene boils at 76° (atmospheric pressure).[1] Dicyanoacetylene was analyzed by gas chromatography, using a Dow-Corning 550 silicone oil column

---

[20] Cookson and Dance[5f] report that dicyanoacetylene begins to decompose at 150°; we have heated benzene solutions of dicyanoacetylene at 180° for 2 days and recovered a large amount of the unreacted acetylene.[5j]

[21] H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962).

[22] Azeotropic drying was found to be much faster than drying in air or in a desiccator. However, the last traces of benzene are difficult to remove and the dicyanoacetylene prepared from this product may contain small amounts (<1%) of benzene, which cannot be removed by distillation. If benzene-free dicyanoacetylene is required, the product should be dried in a desiccator.

for the separation of dicyanoacetylene and benzene and a Dow-Corning XF-1150 silicone oil column for detection of carbon disulfide. The contents of trap 2 were allowed to evaporate in the hood. Before reuse, the sulfur and dark deposits were removed by passing air through the shielded pyrolysis tube at 600–800°; the sulfur ignited. Pure oxygen had been used in place of air for a number of times, but an explosion occurred in one instance.

Pyrolysis of 4,5-Dicyano-1,3-dithiol-2-thione (6).—The apparatus was the same as that used for the pyrolysis of 4,5-dicyano-1,3-dithiol-2-one. The flask was charged with 5.400 g of 4,5-dicyano-1,3-dithiol-2-thione.[18c,d] The pyrolysis was carried out at 650° tube temperature; the bath temperature was 100–160°, the pressure 0.2 mm. Only part of the thione (1.625 g) sublimed into the pyrolysis tube during 5 hr. The contents of both traps, on flash distillation, gave 310 mg of a mixture of dicyanoacetylene (42%; 19% yield) and carbon disulfide (54%) as determined by gas chromatography (conditions as above).

Registry No.—1, 1071-98-3.

Synthetic Reactions by Complex Catalysts. VIII. Copper-Catalyzed Reactions of Thiol and Alcohol with Diazoacetate

TAKEO SAEGUSA, YOSHIHIKO ITO, SHIRO KOBAYASHI, KIWAMI HIROTA, AND TOYOJI SHIMIZU

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

Received July 11, 1967

The reactions of thiols and alcohols with diazoacetate by copper compound catalysts were examined, in which R of RSH (thiol) and ROH (alcohol) were n-C_4H_9, $C_6H_5CH_2$, and $CH_2{=}CHCH_2$. All the products were isolated and identified, the total yields of the products based on diazoacetate being almost quantitative. In the reaction with thiols, the carbene from ethyl diazoacetate was inserted into the sulfur–hydrogen linkage to produce ethyl alkylthioacetate (IV) in a high yield and a high selectivity. In addition, diethyl alkylthiosuccinate (V) and diethyl thiodiglycolate (VI) were isolated as the by-products. On the other hand, the reaction of alcohol with ethyl diazoacetate afforded the insertion reaction products in low selectivity. The O analogs corresponding to V and VI as well as triethyl 1-alkoxypropane-1,2,3-tricarboxylate (X), triethyl propene-1,2,3-tricarboxylate (XIII), diethyl fumarate, and diethyl maleate (XII) were formed. In the allyl alcohol–diazoacetate reaction, the cyclopropane derivatives were also formed.

We have reported a series of reactions of isocyanide with amines,[1] alcohols,[2,3] and thiols[4] to produce formamidine (I), formimidate (II), and thioformimidate (III), respectively (see eq 1–3). These reactions are all

$$\mathrm{RN{\equiv}C\colon + NHR'R'' \longrightarrow \underset{I}{RN{=}CHNR'R''}} \qquad (1)$$

$$\mathrm{RN{\equiv}C\colon + HOR' \longrightarrow \underset{II}{RN{=}CHOR'}} \qquad (2)$$

$$\mathrm{RN{\equiv}C\colon + HSR' \longrightarrow \underset{III}{RN{=}CHSR'}} \qquad (3)$$

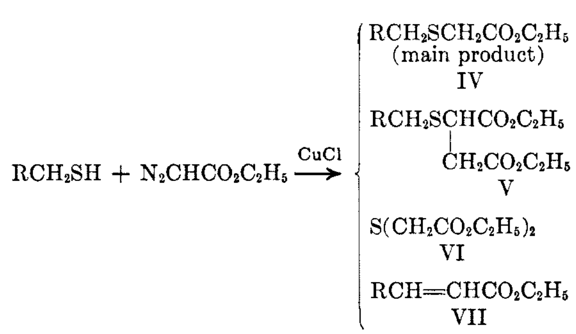
catalyzed by copper compounds and are characterized by the common feature that the isocyanide carbon atom having lone-pair electrons is inserted into N–H, O–H, and S–H linkages.

The carbene produced by the decomposition of diazoalkane is another species having the lone-pair electrons of carbon, which resembles isocyanide also in the property of coordinating with copper compounds.[5] These facts prompted us to explore the copper-catalyzed reactions of diazoacetate. We have hitherto found that the carbene carbon is inserted quite selectively into N–H linkage in the copper-catalyzed reactions of ethyl diazoacetate with amines.[6]

$$\mathrm{RR'N{-}H + N_2CHCOOC_2H_5 \xrightarrow{\text{Cu compounds}} RR'NCH_2COOC_2H_5} \qquad (4)$$

The present paper describes the reactions of thiols and alcohols with ethyl diazoacetate in the presence of copper compounds as catalysts.

The reaction of thiols with ethyl diazoacetate without a catalyst was once studied by Müller and Freytag,[7] and it was reported that benzenethiol reacted with ethyl diazoacetate to form ethyl phenylthioacetate, whereas aliphatic thiols did not react even at 80°. It has now been found that, in the presence of cuprous chloride as catalyst, aliphatic thiols (alkane and aralkane thiols) react satisfactorily with ethyl diazoacetate at 80–90° to produce the corresponding thioacetate (IV) as the main product along with three by-products (V, VI, and VII).



$$\mathrm{RCH_2SH + N_2CHCO_2C_2H_5 \xrightarrow{CuCl}} \left\{ \begin{array}{l} \mathrm{RCH_2SCH_2CO_2C_2H_5} \\ \quad\text{(main product)} \\ \qquad \mathrm{IV} \\ \mathrm{RCH_2S\underset{|}{C}HCO_2C_2H_5} \\ \qquad \mathrm{CH_2CO_2C_2H_5} \\ \qquad \mathrm{V} \\ \mathrm{S(CH_2CO_2C_2H_5)_2} \\ \qquad \mathrm{VI} \\ \mathrm{RCH{=}CHCO_2C_2H_5} \\ \qquad \mathrm{VII} \end{array} \right.$$

Each product was isolated by means of preparative glpc and was identified by elemental analysis and infrared and nmr spectra. Typical results are shown in Table I. Both diethyl maleate and fumarate were formed only in quite small yields in these reactions.

It is clearly indicated that the carbon having lone-pair electrons of the carbene from diazoacetate is inserted between sulfur and hydrogen of thiol to form the main product (IV). The insertion of carbene into the S–H linkage may be compared with the corresponding

---

[1] T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Letters*, 6121 (1966).

[2] T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *ibid.*, 521 (1967).

[3] T. Saegusa, Y. Ito, S. Kobayashi, N. Takeda, and K. Hirota, *ibid.*, 1273 (1967).

[4] T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and Y. Okumura, Abstracts, Annual Meeting of Chemical Society of Japan, Tokyo, April 1967.

[5] H. Nozaki, S. Moriuchi, H. Tanaka, and R. Noyori, *Tetrahedron Letters*, 5239 (1966).

[6] T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and T. Shimizu, *ibid.*, 6131 (1967).

[7] E. Müller and A. Freytag, *J. Prakt. Chem.*, **146**, 56 (1931).