1-(2-Biphenylyl)isoquinoline. The compound was prepared in the same manner as described for the *para*-isomer. The yield was 2.0 g. (14%), melting at 220–221°. The infrared spectrum showed no N—H bonding.

Anal. Calcd. for $C_{21}H_{15}N$: N, 4.98. Found: N, 4.98.

2-(p-Terphenyl-4-yl)quinoline. To a stirred solution of 1.3 g. (0.01 mole) of quinoline in 100 ml. of ether was added a solution of *p*-terphenyl-4-yllithium[7] in 100 ml. of ether. Upon completion of the addition the reaction mixture was yellow and Color Test I[5] was negative. The mixture was worked up and the intermediate oxidized as before. The product, after recrystallization from benzene, melted at 274–275°. The yield was 1.2 g. (37%). The infrared spectrum again showed the absence of N—H bonding.

Anal. Calcd. for $C_{27}H_{19}N$: N, 3.90. Found: N, 3.73.

Acknowledgments. This work was supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-59. The authors are indebted to E. Miller Layton of the Institute for Atomic Research, Ames, Iowa, for the infrared spectra, to Drs. Wright H. Langham and Donald G. Ott of the Los Alamos Scientific Laboratory for their interest and helpful suggestions and to Elizabeth Hansbury and Vernon N. Kerr also of the Los Alamos Scientific Laboratory for technical assistance.

AMES, IOWA

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(7) H. Gilman and E. A. Weipert, *J. Org. Chem.*, **22**, 446 (1957).

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Dinitriles of Acetylenedicarboxylic and Polyacetylenedicarboxylic Acids.[1] I.[2] Dicyanoacetylene and Dicyanodiacetylene

ANDREW J. SAGGIOMO

Received April 22, 1957

The synthesis of dicyanoacetylene, C_4N_2, and dicyanodiacetylene, C_6N_2, is described. The pure compound C_6N_2 is stable at room temperature in the absence of oxygen. Vapor pressure, infrared spectral data, and other physical properties are presented and discussed.

A phase of high temperature research currently under investigation in our laboratories is the production of ultrahigh temperatures by means of chemical reactions. The attainment of such temperatures depends upon the exothermicity of the reaction and the thermodynamic stability of the products of combustion. A flame temperature of slightly over 5000°K. has been reached by burning cyanogen with oxygen under pressure to CO and N_2.[3]

It was obvious that higher flame temperatures could be attained with compounds possessing a higher endothermic heat of formation than cyanogen and could also be burned to the same thermally stable products, *i.e.*, CO and N_2. A series of such compounds exists in the dinitriles of acetylenedicarboxylic and polyacetylenedicarboxylic acids or dicyanoacetylene and dicyanopolyacetylene, having the general formula

$$N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$$

where $n = 1, 2, 3 \ldots.$

The importance of these compounds in the production of high temperatures has led us to conduct a study of the preparative methods and comparative properties of the individual members in this series. This paper will present and discuss the synthesis and properties of dicyanoacetylene and dicyanodiacetylene.

Kirshenbaum and Grosse[4] found that the first member of the series ($n = 1$), carbon subnitride[5] (C_4N_2) burned with oxygen produces a temperature of 5260°K. at 1 atm. and should produce 5750°K. at 40 atm. With the substitution of ozone for molecular oxygen a temperature of 5520°K. at 1 atm. is expected. C_4N_2 was prepared by the slightly modified method of Moureu and Bongrand.[5]

$$H_3COOC{-}C{\equiv}C{-}COOCH_3 \xrightarrow{NH_4OH} H_2NOC{-}C{\equiv}C{-}CONH_2 \xrightarrow{P_2O_5} N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$$

The dinitrile, dicyanoacetylene, is a clear colorless liquid, b.p. 76.5°, which solidifies into mono-

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1475, Project No. 7-7968. Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

(2) Technical Note No. 3, Report Control No. AFOSR-TN-57-33, Contract No. AF 18(600)-1475, Project No. 7-7968, December 19, 1956, Air Force Office of Scientific Research, Air Research and Development Command, U. S. Air Force, Washington 25, D. C.

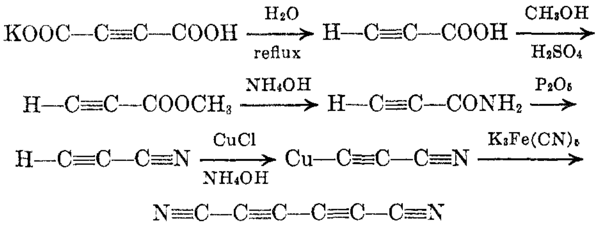
(3) J. B. Conway, W. F. R. Smith, W. J. Liddell, and A. V. Grosse, *J. Am. Chem. Soc.*, **77**, 2026 (1955).

(4) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **78**, 2020 (1956); Technical Note No. 1, Report Control No. AFOSR-TN-56-13, Contract No. AF 18(600)-1475, Project No. 7-7968, December 15, 1955.

(5) C. Moureu and J. C. Bongrand, *Bull. soc. chim.*, (V), 846 (1909); *Ann. chim.*, **14**, 5 (1920).

clinic crystals, m.p. 20.5°. Hannan and Collin[6] have reported that C_4N_2 is a symmetrical linear molecule displaying the bond lengths $C{\equiv}N$ 1.14, $C{-}C$ 1.37 and $C{\equiv}C$ 1.19 Å. The solid compound can be stored indefinitely at Dry Ice temperatures and is easily handled at room temperature. It is, of course, much more sensitive in the presence of oxygen, a polymerization or condensation reaction probably taking place. A simple vacuum sublimation or atmospheric distillation will separate pure unreacted dicyanoacetylene from the mixture of condensation and polymerization products.

In 1920 Moureu and Bongrand[7] reported trace quantities of a solid with characteristic properties from the action of aqueous potassium ferricyanide on the cuprous derivative of propiolonitrile (cyanoacetylene). Brockman[8] recently firmly established this product as dicyanodiacetylene (C_6N_2) by elementary analysis, molecular weight determinations, and by conversion on hydrogenation to hexamethylenediamine. The C_6N_2 utilized in this work was prepared according to the scheme illustrated.



$$KOOC{-}C{\equiv}C{-}COOH \xrightarrow[\text{reflux}]{H_2O} H{-}C{\equiv}C{-}COOH \xrightarrow[H_2SO_4]{CH_3OH}$$
$$H{-}C{\equiv}C{-}COOCH_3 \xrightarrow{NH_4OH} H{-}C{\equiv}C{-}CONH_2 \xrightarrow{P_2O_5}$$
$$H{-}C{\equiv}C{-}C{\equiv}N \xrightarrow[NH_4OH]{CuCl} Cu{-}C{\equiv}C{-}C{\equiv}N \xrightarrow{K_3Fe(CN)_6}$$
$$N{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$$

Dicyanodiacetylene is formed as fine white elongated needles, m.p. 64.5–65°. Brockman describes this unique compound as an *unstable* white solid which he obtained by sublimation in a stream of carbon dioxide. Pure stable crystalline dicyanodiacetylene has been successfully produced in this laboratory through the use of careful distillation and sublimation techniques under low pressures of dried prepurified nitrogen. Samples of our product were maintained *in vacuo* and under a nitrogen atmosphere at room temperature. After 3 months substantial amounts of white crystalline C_6N_2 were recovered from the samples. Only slight discoloration of the water-white liquid dinitrile occurred after several hours under nitrogen. Even at 100° only partial decomposition took place. In addition, freshly prepared dicyanodiacetylene gave an infrared spectral absorption curve identical with that of a sample which had been stored for several weeks below 0°.

It seems evident from the foregoing that dicyanodiacetylene is a relatively more stable compound than other systems of comparable multiple conjugated bonds and, hence, can be stored for long periods of time. The compound is, of course, much less stable in the presence of oxygen. Nevertheless, the pure compound can be handled for a time in an atmosphere of oxygen at room temperature although a slow polymerization or condensation reaction takes place.

Dicyanodiacetylene is unique in that it combines both a linear chain of eight atoms and a system of four conjugated triple bonds. This symmetrical molecule, $N{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$ probably displays bond lengths the same as dicyanoacetylene. Hannan and Collin[6] have found the single bond length of C_4N_2 to be virtually the same as that found in monocyanoacetylene, diacetylene, and cyanogen (Table I) indicating that the addition of the triple bond to the conjugated system has only a minor effect upon the structure. This suggests that one might expect the bond distances of dicyanodiacetylene to be in close agreement with those in Table I.

TABLE I

BOND LENGTHS (Å) OF RELATED CONJUGATED SYSTEMS[6,9]

Compound	C—C	C≡C	C≡N
$H{-}C{\equiv}C{-}C{\equiv}N$	1.382	1.203	1.157
$H{-}C{\equiv}C{-}C{\equiv}C{-}H$	1.36	1.19	. . .
$N{\equiv}C{-}C{\equiv}N$	1.37	. . .	1.16
$N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$	1.37	1.19	1.14

The physical properties of the members in the series $N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N$ where $n = 0, 1, 2, 3$, etc., conform reasonably well with the trends in vapor pressure, boiling point, density, etc., that are consistent with increasing molecular weight in a homologous series. Table II illustrates the effect of an additional $C{\equiv}C$ group upon the boiling point and melting point of adjacent members in several homologous acetylenic series. For instance, the boiling point rises with the addition of an acetylenic group. However, the difference in boiling point of two adjacent members, becomes proportionately smaller as the homologous series is ascended. The melting point also increases with the increasing molecular weight. In this case, too, the difference between the melting points of two adjacent members becomes, in general, smaller. Similar relationships are found in many other homologous series. From these regularities the boiling point estimated for C_6N_2 is in fair agreement with the extrapolated value of 154° obtained from the vapor pressure data. In this fashion properties of subsequent members (*e.g.* C_8N_2, $C_{10}N_2$) may be approximated.

The vapor pressures of dicyanodiacetylene and dicyanoacetylene were studied as a function of temperature over the ranges 21–96° and −11 to 76.5°, respectively (Table III). The method employed was an isotensimetric one with the use of a Kel-F polymer oil as the confining liquid. A semilog plot of the experimental values for P (mm.) *vs.* $1/T$°K.

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(6) R. B. Hannan and R. L. Collin, *Acta Cryst.*, **6**, 350 (1953).

(7) C. Moureu and J. Bongrand, *Ann. chim.*, **14**, 47 (1920).

(8) F. J. Brockman, *Can. J. Chem.*, **33**, 507 (1955).

(9) A. A. Westenberg and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **72**, 199 (1950).

TABLE II

Regularities in the Properties of Acetylenic Compounds

Compound	Boiling Point, °C.	Δ[a]	Melting Point, °C.	Δ[a]
$HC{\equiv}CH$	−83.6		−81.8	
		93.9		45.4
$H(C{\equiv}C)_2H$	10.3		−36.4	
		74.7		16.4
$H(C{\equiv}C)_3H$	ca. 85[b]		−20	
$H_3C{-}CH_3$	−88.3		−172	
		115.5		140
$H_3C{-}C{\equiv}C{-}CH_3$	27.2		−32.5	
		102		97
$H_3C{-}(C{\equiv}C)_2{-}CH_3$	129		64.5	
$N{\equiv}C{-}C{\equiv}N(C_2N_2)$	−20.7		−34.4	
		97.2		54.9
$N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N(C_4N_2)$	76.5		20.5	
				44.0
$N{\equiv}C{-}(C{\equiv}C)_2{-}C{\equiv}N(C_6N_2)$	ca. 155–160[c]		64.5	
$N{\equiv}C{-}(C{\equiv}C)_3{-}C{\equiv}N(C_8N_2)$	ca. 230[c]		ca. 100[c]	

[a] Δ signifies the difference in a property between adjacent members. [b] Calculated from vapor pressure data reported by W. Hunsmann, *Ber.*, **83**, 213 (1950). [c] Values are approximately those one would expect of subsequent members.

was essentially linear for the solid and liquid vapor pressure curves of C_6N_2 and C_4N_2 (Fig. 1).

TABLE III

Most Probable Values of the Vapor Pressure of Dicyanodiacetylene and Dicyanoacetylene

State	C_6N_2 Temperature °C.	C_6N_2 Temperature °K.	Experimental Vapor Pressure in Mm. Hg
Solid	21.7	294.9	15.0
	24.2	297.4	16.5
	40.3	313.5	33.5
	57.4	330.6	67.5
	62.0	335.2	80.0
Liquid	68.0	341.2	97.5
	96.2	369.4	220
	154[a]		760
	C_4N_2		
Solid	−10.6	262.6	16.1
	0.0	273.2	35.4
Liquid	22.8	296.0	140.4
	32.5	305.7	200
	76.5	349.7	760

[a] Extrapolated value of the boiling point of C_6N_2.

The vapor pressure of the crystalline solid hexacarbon dinitride can be expressed by the equation:

$$\log_{10} P_{\text{mm}} = 4.30827 + 151.654 \times \frac{1}{T} - 321{,}008 \times \frac{1}{T^2}$$

and from the experimental values there has been derived the following vapor pressure equation for the liquid:

$$\log_{10} P_{\text{mm}} = 6.6174 - 1579.2 \times \frac{1}{T}$$

where T = °K.

From the vapor pressure equations for C_6N_2 it follows that:

Heat of sublimation, ΔH_{sub} = 8590 cal./mole

Heat of vaporization, ΔH_{vap} = 7230 cal./mole

Heat of fusion, ΔH_{fus} = 1360 cal./mole

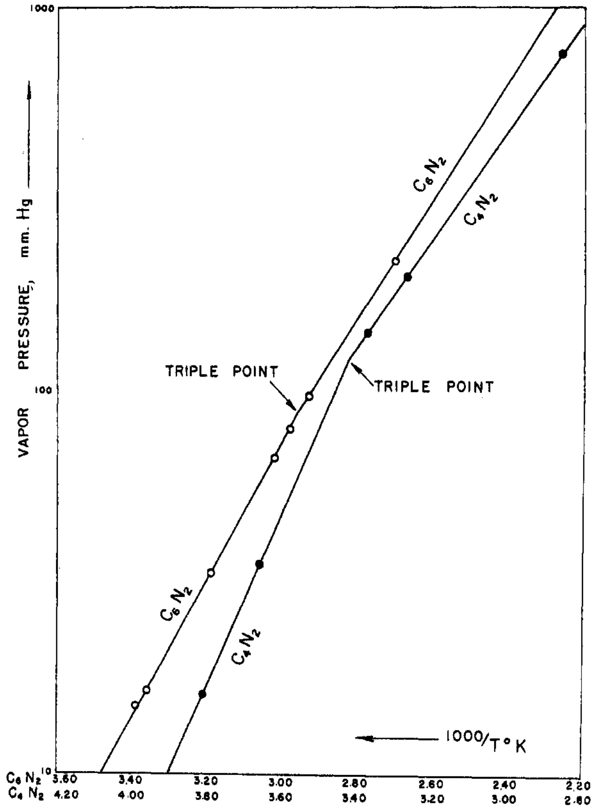

Fig. 1. Vapor Pressure of C_6N_2 and C_4N_2

From the vapor pressure equation for solid C_4N_2

$$\log_{10} P_{\text{mm}} = 10.0115 - 2312 \times \frac{1}{T}$$

and for liquid C_4N_2

$$\log_{10} P_{\text{mm}} = 6.4308 - 1093.4 \times \frac{1}{T} - 51707 \times \frac{1}{T^2}$$

the following values were obtained:

ΔH_{sub} = 10,575 cal./mole
ΔH_{vap} = 6,875 cal./mole
ΔH_{fus} = 3,700 cal./mole

In the infrared the C≡C absorption is weak and often undetectable in symmetrically disubstituted acetylenes.[10] Additional bands may arise, however, in the disubstituted alkynes as the result of overtones. The frequency of C≡C absorption is usually displaced in a conjugated system from the normal region of 4.42–4.76 microns to lower frequencies. Likewise, the position of the C≡N stretching vibration in conjugated systems (4.48–4.50 microns) has also been shown to undergo displacement from the higher frequencies found in saturated mono- and dinitriles. It is clear from the related conjugated systems in Table IV that the absorptions in the infrared by the molecules dicyanoacetylene and dicyanodiacetylene correspond well with the expected absorption regions based upon the preceding generalizations.

A Baird Associates Recording Spectrophotometer of Samuel P. Sadtler and Sons, Inc., was used to obtain the infrared spectra of monocyanoacetylene, dicyanoacetylene, and dicyanodiacetylene (Fig. 2). Attempts to prepare a KBr disk of C_6N_2 resulted in extensive decomposition of the sample. An appropriate carbon tetrachloride solution of dicyanodiacetylene was utilized with a solvent compensating cell of 0.2 mm. thickness. The spectra of liquid C_3NH and C_4N_2 were recorded at cell thicknesses of 0.2 and 0.1 mm., respectively. The absorption bands appearing at ca. 2.5–3.2 and 6.0–6.5 microns in the spectra of C_4N_2 are believed to be due to slight traces of moisture.

TABLE IV

INFRARED ABSORPTION BANDS IN RELATED CONJUGATED SYSTEMS[10]

Compound	C≡C	I^a	C≡N	I^a
$C_5H_{11}C{\equiv}C{-}C{\equiv}N$	4.71 μ	w	4.4 μ	s
$H{-}C{\equiv}C{-}C{\equiv}N$	4.88	m	4.46	s
$N{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$	4.41 (Raman)[b]	w	4.52	m
$N{\equiv}C{-}(C{\equiv}C)_2{-}C{\equiv}N$	4.84	w	4.47	m
$HC{\equiv}C{-}C{\equiv}C{-}H$	4.94			
$H_2C{=}CH{-}C{\equiv}C{-}H$	4.76			

[a] The intensities, I, of the absorptions are represented as w = weak, m = medium and s = strong.

[b] A detailed discussion of the infrared and Raman spectra of dicyanoacetylene is presented by F. A. Miller and R. B. Hannan, Jr., *J. Chem. Phys.*, **21**, 110 (1953).

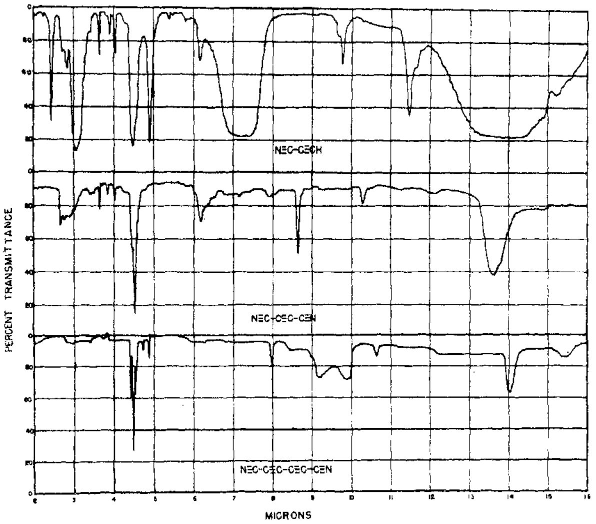

FIG. 2. INFRARED ABSORPTION SPECTRA OF MONOCYANOACETYLENE, DICYANOACETYLENE, AND DICYANODIACETYLENE.

EXPERIMENTAL[11]

Monocyanoacetylene.[7] Propiolic acid was prepared from monopotassium acetylenedicarboxylate and then esterified with methanol in the presence of sulfuric acid. Reaction with ammonium hydroxide produced propioloamide. Dehydration of the latter with phosphorus pentoxide yielded monocyanoacetylene (propiolonitrile).

Dicyanodiacetylene. Cuprous propiolonitrile, prepared by passing the nitrile in a slow stream of nitrogen through an ammoniacal cuprous chloride solution, was treated with potassium ferricyanide in water at 2–5°C. The suspension was extracted with carbon tetrachloride and the mixture centrifuged. Measures were taken to insure a temperature of <5°. The bottom carbon tetrachloride layer was withdrawn by means of a pipette. This procedure was carried out several times. The combined extracts were dried over anhydrous sodium sulfate and distilled at atmospheric pressure in helices-packed column to remove most of the solvent. The cold residue was then placed in a 10–20° bath under a 20–25 mm. pressure of dried prepurified nitrogen. The residual solvent was collected in a Dry Ice-acetone cooled trap. The light brown crystalline residue was then slowly allowed to sublime. There was obtained pure white crystalline dicyanodiacetylene, m.p. 64.5–65° in 33% yield.

Stability of C_6N_2 at room temperature. Dicyanodiacetylene was sublimed into several tubes *in vacuo.* Samples were sealed in Pyrex brand glass No. 7740 tubes in atmospheres of nitrogen, oxygen, *in vacuo,* and with a trace of organic material (benzene). The tubes were kept at room temperature (22–26°), in the absence of light for 3 months. Periodic microscopic examinations were made. After 1 month only slight discoloration of the crystalline compound under nitrogen and *in vacuo* had occurred. No crystalline material was apparent, however, in the brown oxygen tube. Crystals were apparent in the tube containing traces of benzene.

The tubes were opened *in vacuo* after three months. Considerable white crystalline dicyanodiacetylene from the nitrogen and vacuum-sealed tubes was recovered. The sample sealed under pure oxygen produced no crystalline material. Only a dark brown residue remained. The same results were obtained from the sample sealed with traces of benzene under nitrogen.

Stability of C_6N_2 above room temperature. Samples were sealed under oxygen and dried prepurified nitrogen. Upon heating for 3 hr. at 40°, only slight discoloration occurred. The oxygen tube became very dark after an additional 5 hr. at 40°. Droplets of liquid were observed. The tube was opened and no recovery was made of crystalline dicyanodiacetylene.

The nitrogen tube was only slightly discolored after 3 hr. at 60–70°. The liquid dinitrile upon cooling melted at 62–64°. The tube was then heated at 90–100° for 0.5 hr. The liquid dinitrile became very dark. However, upon cooling some crystalline dicyanodiacetylene was still present in the

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(10) For a discussion of the infrared absorption of substituted acetylenes see L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* John Wiley & Sons, Inc., New York, 1954, page 48.

(11) All melting and boiling points reported herein are uncorrected.

dark tube. After a period of time the tube was opened with recovery of trace amounts of C_6N_2.

Diamide of acetylenedicarboxylic acid. Dimethyl acetylenedicarboxylate (Madison Laboratories) (100 g., 0.705 mole) was added dropwise with stirring to 400 ml. ammonium hydroxide at −10°. After 2 hr. the precipitated diamide was filtered, washed with several portions of absolute ethanol and dried under vacuum for 2 days. There was obtained a light tan product (70 g., 89%), m.p. 190–192° (lit.[5] m.p. 290–292°). A nitrogen analysis indicated 0.5 molecule of water.

Anal. Calcd. for $C_4H_4N_2O_2 \cdot {}^1/_2H_2O$: N, 23.13. Found: N, 23.35.

Dicyanoacetylene. An intimate mixture of diamide (6 g.), fine sea sand (Calcined) (100 g.) and P_2O_5 (50 g.) was divided into four test tubes and connected to a glass apparatus. The system contained a Dry Ice–acetone-cooled receiver and was evacuated, refilled with dry nitrogen and then reevacuated. This procedure was carried out several times. The evacuated system of test tubes was then placed in a preheated bath at 215° whereupon distillation of C_4N_2 took place. After *ca.* 45 min. the cooled receiver contained 1.4 g. of fairly pure product which gave upon atmospheric distillation in a glass helices-packed column under prepurified nitrogen, pure dicyanoacetylene, m.p. 20.5–21°.[5] A discussion of the critical features of this dehydration and the system employed is found in ref. (5).

Acknowledgment. The author wishes to express his gratitude and deep appreciation to Dr. Aristid V. Grosse and E. A. Nodiff for their invaluable suggestions during the course of this work.

Philadelphia 44, Pa.

[Contribution from the Physical Research Laboratory and the Spectroscopy Laboratory, The Dow Chemical Company]

Preparation of Cyclohexanone Dimethyl Acetal[1,2]

ROBERT E. McCOY, ALVIN W. BAKER,[3] AND ROLAND S. GOHLKE

Received August 22, 1956

Cyclohexanone dimethyl acetal was identified by infrared absorption and mass spectrometry among the products of reaction of salts of *aci*-nitrocyclohexane with methanol and acid, with methyl sulfate, and with ethyl sulfate when methanol was used as solvent. Direct preparation from cyclohexanone and methanol, even without addition of a catalyst, was found feasible. The ease of obtaining this compound in contrast to ketals in general is believed explainable from steric considerations. Attempts to prepare cyclohexanone diethyl acetal directly indicate an unfavorable equilibrium, but the mass spectrometer showed an appreciable conversion.

During an investigation of conversion of nitroparaffins to oximes,[4] an unexpected by-product was discovered in several reactions of *aci*-nitrocyclohexane salts.

Acidification of methanolic solutions or suspensions of *aci*-nitrocyclohexane salts produced cyclohexanone oxime in yields of 35% or less. Infrared and mass spectra of the crude reaction mixtures showed the presence of nitrocyclohexane, cyclohexanone, and a component not immediately identified, in addition to the oxime. Reaction of methyl sulfate with salts of *aci*-nitrocyclohexane gave the same products, although the yield of oxime was higher. Substitution of ethyl sulfate for methyl sulfate gave similar results if methanol was used as solvent, but in other solvents no fourth product was found. Likewise only nitrocyclohexane, cyclohexanone, and cyclohexanone oxime were observed on acidifying salts of *aci*-nitrocyclohexane in ethanol.

When a mixture of cyclohexanone and the unknown was diluted with a large volume of water, ultraviolet and mass spectra revealed no large molecule other than cyclohexanone.

The infrared spectrum (discussed below), the mass spectrum (Table 1), and the facts presented above show clearly that the unexpected product is cyclohexanone dimethyl acetal. Preparation of this compound has been reported previously only by reaction of methyl orthosilicate[5] or methyl sulfite[6] with cyclohexanone. Direct preparation of cyclic ketals from 1,2- and 1,3-glycols is known,[7,8] but it is commonly stated that simple ketals can be prepared only by indirect methods.[9] This opinion is probably correct for most ketals, but the frequent occurrence of cyclohexanone dimethyl acetal in the above reactions suggests that its direct preparation is feasible. This was confirmed by mixing cyclohexanone and methanol, as described in the experimental section.

The successful direct preparation of cyclohexanone dimethyl acetal, contrasted to the usual ex-

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(1) Presented in part at the 129th meeting of the American Chemical Society, Dallas, Tex., April 1956.

(2) For specific compounds we have followed Chemical Abstracts' nomenclature, but generically we have used the more popular term "ketal" as a matter of convenience.

(3) Present address: The Dow Chemical Company, Pittsburg, Calif.

(4) R. E. McCoy and R. S. Gohlke, *J. Org. Chem.*, **22**, 286 (1957).

(5) B. Helferich and J. Hausen, *Ber.*, **57B**, 795 (1924).

(6) W. Voss, *Ann.*, **485**, 283 (1931).

(7) J. Boeseken and F. Tellegen, *Rec. trav. chim.*, **57**, 133 (1938).

(8) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

(9) For example: (*a*) H. W. Post, *The Chemistry of the Aliphatic Orthoesters*, ACS Monograph 92, Reinhold Publishing Corp., New York, 1943, Chapter 3. (*b*) C. A. Mackenzie and J. H. Stocker, *J. Org. Chem.*, **20**, 1695 (1955).