bubbled through a concentrated chloroform solution of III. After recrystallization from 95% ethanol to which a few drops of concentrated hydrochloric acid had been added, the compound melted at 295–298° dec., softening at 266°.

Anal. Calcd. for $C_{13}H_9N_2SCl$: C, 59.88; H, 3.48; N, 10.75. Found: C, 59.56; H, 3.32; N, 10.57.

The hydriodide was formed when a warm solution of III in 1:1 absolute ethanol–methyl iodide was allowed to stand in a stoppered flask for 9 days. After concentration of the solution, the salt precipitated as golden yellow needles. An analytical sample was prepared by treatment with Darco, followed by two recrystallizations from methanol; m.p. 254–257° dec.

Anal. Calcd. for $C_{13}H_9N_2SI$: C, 44.33; H, 2.58; N, 7.96. Found: C, 43.94; H, 2.31; N, 7.82.

The identity of the compound was further substantiated by treatment with aqueous sodium hydroxide to give III, which was identified by its infrared spectrum and melting point.

1-Acetylpyrrolo[3,2-b]thieno[3,2-b]quinoline (IV).—A solution of 0.20 g. (0.9 millimole) of III in 10 ml. of acetic anhydride was refluxed for 6 hours, and *ca.* 7 ml. of solvent was removed by distillation. Upon cooling, the product crystallized as long, white, cotton-like needles. The yield was 0.22 g. or over 90%. After treatment with Darco and two recrystallizations from benzene, an analytical sample melted at 168–169°.

Anal. Calcd. for $C_{15}H_{10}N_2OS$: C, 67.65; H, 3.78; N, 10.52. Found: C, 67.84; H, 3.79; N, 10.64.

4-Acetyl-2-(*o*-diacetylimidobenzylidene)-2*H*,3*H*-thieno-[3,2-b]pyrrol-3-one (V).—A suspension of 0.470 g. (1.94 millimoles) of IIc in 15 ml. of acetic anhydride was heated under reflux for 5 hours with the exclusion of moisture. After about 10 minutes, the solution had changed in color from red to yellow. About 10 ml. of solvent was distilled, and the red sirupy residue was allowed to cool in an ice–water-bath; 10 ml. of cold water was added in one portion, the mixture was refrigerated for 4 hours, and the resulting yellow solid was filtered and washed thoroughly with water. After drying *in vacuo* overnight, the product, m.p. 174–176°, weighed 0.689 g. (96.5%). An analytical sample was prepared by suspending a small amount of the compound in water, filtering, and washing again with water to free the sample from all traces of acid. After two recrystallizations from 95% ethanol the product melted at 173–174°.

Anal. Calcd. for $C_{19}H_{16}N_2O_4S$: C, 61.94; H, 4.38; N, 7.61. Found: C, 61.86; H, 4.13; N, 7.58.

2-(*o*-Acetamidobenzylidene)-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (VI).—A solution of 0.336 g. (1.19 millimoles) of V in 25 ml. of 10% aqueous acetic acid and 10 ml. of methanol was refluxed for 12 hours, during which time there appeared a beautiful orange crystalline precipitate. The material was filtered and washed thoroughly with water affording a nearly quantitative yield of VI, m.p. 280–281° dec. The highly insoluble product was suitable as an analytical sample after drying.

Anal. Calcd. for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.26; N, 9.85. Found: C, 63.64; H, 4.17; N, 9.91.

Reacetylation of VI.—A suspension of 0.251 g. (0.885 millimole) of VI in 10 ml. of acetic anhydride was heated under reflux for 4 hours. About one-half of the solvent was removed by distillation, the residue cooled, and 10 ml. of water added in one portion. After standing 2 hours, the product was filtered and washed thoroughly with water affording 0.301 g. (92.3%) of V, m.p. 175–176°.

Basic Hydrolysis of V.—To a warm solution of 1.00 g. of potassium hydroxide in 9 ml. of 95% ethanol was added 0.176 g. (0.479 millimole) of V. The resulting rose-colored solution was refluxed for 2 hours, 15 ml. of hot water was added, and the solution allowed to cool. The resulting orange precipitate was washed with water, and dried. The yield of IIc was 0.078 g. (74%). The identity of the product was verified by its melting point (258–260°), infrared spectrum and by microanalysis.

Anal. Calcd. for $C_{13}H_{10}N_2OS$: C, 64.44; H, 4.16; N, 11.56. Found: C, 64.07; H, 4.35; N, 10.95.

N,N-Diacetyl-*o*-toluidine (IX).—The procedure followed in the preparation of VIII was essentially that of Sudborough,[20] b.p. 105–105.5° (1.2 mm.), n^{26}_{D} 1.5270.

4-Acetyl-2-benzylidene-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (X).—A suspension of 0.250 g. of IIa in 10 ml. of acetic anhydride was refluxed for 5 hours, and *ca.* 7 ml. of solvent was distilled. The solution was allowed to cool, and the resulting precipitate was washed with water and dried. The yield of crude product was 0.264 g. (89.2%). An analytical sample, m.p. 147–148.5°, was prepared by treatment with Darco, followed by recrystallization from a large volume of methylcyclohexane.

Anal. Calcd. for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20. Found: C, 66.87; H, 4.17; N, 5.16.

2-Benzyl-2*H*,3*H*-thieno[3,2-b]pyrrol-3-one (XI).—Lithium aluminum hydride (0.50 g.) was added cautiously to an ice-cooled solution of 0.203 g. (0.894 millimole) of IIa in 15 ml. of tetrahydrofuran. The reaction mixture was allowed to stand overnight at room temperature in a loosely stoppered flask. The excess lithium aluminum hydride was hydrolyzed by the dropwise addition of water to the cold solution. The resulting mixture was diluted with 50 ml. of ether and filtered. The precipitate was suspended in ether and again filtered. The combined filtrates were dried over magnesium sulfate, and the ether was distilled. The yellow crystalline residue was washed with pentane and sublimed at 130° (0.1 mm.) to give a slightly oily substance. Two additional sublimations were required to purify the product. The yield of analytically pure X, m.p. 160–161°, was 0.028 g. (13.8%).

Anal. Calcd. for $C_{13}H_{11}NOS$: C, 68.09; H, 4.84; N, 6.11. Found: C, 68.17; H, 4.89; N, 5.88.

URBANA, ILL.

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(20) J. J. Sudborough, *J. Chem. Soc.*, **79**, 533 (1901).

[CONTRIBUTION NO. 590 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. XV.[1] A New Synthesis of 3,4-Dicyano-2(1H)-pyridones

BY C. L. DICKINSON

RECEIVED JANUARY 28, 1960

A convenient new route to 3,4-dicyano-2(1H)-pyridones has been discovered. They are formed when $\beta,\beta,\gamma,\gamma$-tetracyanoketones, obtained by adding ketones to tetracyanoethylene, are heated in ethanol. In several cases, intermediate ethoxy dihydropyridones have been isolated.

We have found that the reaction of $\beta,\beta,\gamma,\gamma$-tetracyanoketones with ethanol provides a facile route to a variety of substituted 3,4-dicyano-2-(1H)-pyridones. The reaction is general and the only limitation appears to be that the carbon atom between the carbonyl and the dicyanomethylene group must possess a hydrogen. The ready availability of the $\beta,\beta,\gamma,\gamma$-tetracyanoketones from the addition of tetracyanoethylene (TCNE)[2] and

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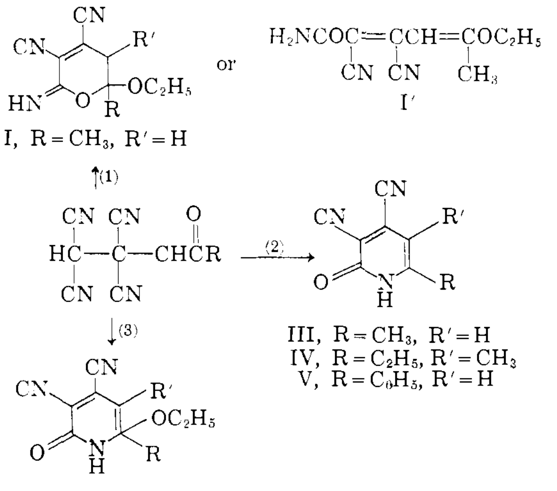
(1) See J. K. Williams, THIS JOURNAL, **81**, 4013 (1959), for paper XIV.

(2) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

the appropriate ketones makes this a convenient synthesis.

In several cases it is possible to isolate intermediates that give a clue to the general mechanism of the reaction.


I, $R = CH_3$, $R' = H$

I′

III, $R = CH_3$, $R' = H$
IV, $R = C_2H_5$, $R' = CH_3$
V, $R = C_6H_5$, $R' = H$

II, $R = C_2H_5$, $R' = CH_3$

In reaction 1, which was observed only with the TCNE–acetone adduct, the product I was a bright yellow solid that was unstable to base. An alternative structure for this compound is the linear isomer I′. It seems more probable that compound I would have λ_{max} at 358 mμ, and an effort was made to distinguish between these two isomers by microhydrogenation, but a hydrogen uptake of 1.3 moles was inconclusive.

This compound was converted to the pyridone III by boiling in water or acetic anhydride. The melting point was identical with that reported in the literature[3] for 3,4-dicyano-6-methyl-2(1H)-pyridone. The two adjacent cyano groups were established by careful hydrolysis with sodium hydroxide to form the bright yellow imide VI. The infrared and ultraviolet spectra of subsequent pyridones were consistent with III.

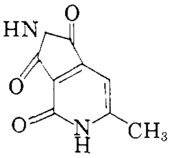
The tetracyano ketones derived from diethyl ketone and cyclohexanone appeared to follow reaction 3, and the products obtained were colorless with λ_{max} 330 mμ for the former. The infrared spectrum showed a strong band at 6.05 μ as would be expected of a cyclic lactam. The diethyl ketone product II could be smoothly converted into the pyridone IV by boiling it with water. The cyclohexanone adduct did not respond to this treatment, but ethanol was successfully eliminated by dissolving the ethoxy compound in concentrated hydrochloric acid and collecting the tetrahydroquinolone that separated. The yield in this case was low; it may be that a mixture of stereoisomers was obtained in the initial reaction, and the *trans* form was the one that gave the pyridone.

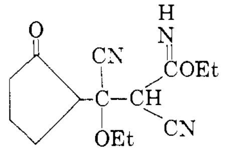
The aromatic ketone adducts from acetophenone, *p*-methoxy-acetophenone and desoxybenzoin were converted directly to the 2-pyridones by boiling them in ethanol. The preparation of the 5,6-diphenyl-2(1H)-pyridone illustrates the broad scope of this reaction. The pinacolone adduct was also converted directly to the pyridone, an exception for the aliphatic substituents.

One possible mechanism for the reaction would involve the formation of a hemiketal, followed by addition of the resulting hydroxyl to one of the γ-nitriles. Hydrogen cyanide could be eliminated at either step. This would give the compound corresponding to I, and this might readily rearrange to type II and the elimination of ethanol would give the pyridone.

An unusual property of the pyridones is their intense fluorescence, which ranges from blue to blue-green. The 3,4-dicyano-6-methyl-2-pyridone exhibits a blue fluorescence that is visible at concentrations as low as 0.001% in water.

The diisopropyl ketone adduct with tetracyanoethylene failed to give a characterizable product and this would be expected since it does not have the required hydrogen, while reaction of the cyclopentanone adduct with ethanol took a different course. The product obtained from the latter had lost one mole of hydrogen cyanide and picked up two moles of ethanol. The compound retained the carbonyl as evidenced by a band at 5.7 μ in the infrared spectrum. A possible structure is one with an imino-ether group present (VII).


VI


VII

If the mechanism of the reaction is such that the alcohol first adds to the carbonyl of the ketone and the hemiketal formed then cyclizes, the difference between the cyclopentanone and cyclohexanone adducts is quite reasonable. Cyclopentanone is known to be far less reactive in addition reactions than cyclohexanone.

Experimental

I. **Preparation of TCNE/Ketone Adducts.**—Tetracyanoethylene–ketone adducts were prepared by the standard procedures.[2]

A. **4,4,5,5-Tetracyano-*p*-methoxybutyrophenone.**—A solution of 12.8 g. (0.01 mole) of TCNE and 30.0 g. (0.02 mole) of *p*-methoxyacetophenone in 50 ml. of tetrahydrofuran was allowed to stand over 1.0 g. of "molecular" silver for 2 days. The solution was filtered to remove the silver, and diluted with petroleum ether. An orange oil that separated solidified upon standing. The solid was collected and recrystallized from a mixture of ethyl acetate and hexane; yield 18.0 g. (65%), m.p. 104–106° dec. The white product obtained after several recrystallizations turned orange on short exposure to air and melted at 135–140° dec.

Anal. Calcd. for $C_{15}H_{10}O_2N_4$: C, 64.8; H, 3.6. Found: C, 65.0; H, 3.8.

B. **3-Phenyl-4,4,5,5-tetracyanobutyrophenone.**—A solution of 6.4 g. (0.05 mole) of TCNE and 11.0 g. (0.056 mole) of desoxybenzoin in 25 ml. of tetrahydrofuran was allowed to stand over 1 g. of "molecular" silver for 1 week. The solution was filtered to remove the silver and diluted with petroleum ether. The orange oil that separated soon solidified and was collected; yield 14.0 g. (85%), m.p. 128–130° dec. After several recrystallizations from benzene, the melting point was 141–142° dec.

Anal. Calcd. for $C_{20}H_{12}ON_4$: C, 74.1; H, 3.70; N, 17.3. Found: C, 74.1; H, 3.81; N, 17.2.

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[3] J. F. Mowat, F. J. Pilgrim and G. H. Carlson, This Journal, **65**, 954 (1943).

C. 2,2-Dimethyl-5,5,6,6-tetracyano-3-hexanone.—A solution of 12.8 g. (0.10 mole) of tetracyanoethylene, 30 g. of pinacolone and 1 ml. of boron trifluoride etherate in 40 ml. of tetrahydrofuran was allowed to stand for 18 days. The resulting mixture was drowned with petroleum ether and the solid that formed was collected; yield 16.5 g., m.p. 150–152° dec.

Anal. Calcd. for $C_{12}H_{12}N_4O$: C, 63.2; H, 5.3; N, 24.6. Found: C, 63.0; H, 5.2; N, 24.5.

II. **Reaction of Aliphatic Ketone Adducts with Ethanol.**[4] **A. 3,4 - Dicyano - 6 - ethoxy - 5,6 - dihydro - 2 - imino - 6-methyl - 2H - pyran** (I).—A solution of 9.4 g. (0.05 mole) of 4,4,5,5-tetracyano-2-pentanone in 150 ml. of ethanol was heated under reflux on a steam-bath for 40 minutes. The resultant dark solution was concentrated to about 30 ml. at room temperature under reduced pressure and the yellow solid that separated was collected and washed with ethanol. There was obtained 6.57 g. (64%) of bright yellow solid, m.p. 150–160° dec. The compound was recrystallized from ethyl acetate, λ_{max} 358 mμ, ϵ 15,100.

Anal. Calcd. for $C_{10}H_{11}N_3O_2$: C, 58.5; H, 5.4; N, 20.5. Found: C, 58.7; H, 5.5; N, 20.5.

B. 3,4-Dicyano-5,6-dihydro-6-ethoxy-ethyl-5-methyl-2(1H)-pyridone (II).—A solution of 14.0 g. (0.065 mole) of 4-methyl-5,5,6,6-tetracyano-3-hexanone in 150 ml. of ethanol was heated under reflux for 1 hour and poured into 500 ml. of ice-water. A gray precipitate was collected; yield 11.6 g. (75%). After recrystallization from ethyl acetate, the tetrahydropyridine melted at 139.5–140.5° with evolution of a gas. Presumably the gas is ethanol, λ_{max} 330 mμ, ϵ 6,600, 229 mμ, ϵ 12,300.

Anal. Calcd. for $C_{12}H_{14}O_2N_3$: C, 61.8; H, 6.4; N, 18.0. Found: C, 62.0; H, 6.4; N, 17.7.

C. 3,4-Dicyano-8a-ethoxy-4a,5,6,7,8,8a-hexahydro-2(1H)-quinolone.—A solution of 11.3 g. (0.05 mole) of 2-(1,1,2,2-tetracyanoethyl)-cyclohexanone in 100 ml. of ethanol was heated under reflux for 30 minutes and then poured into 500 ml. of ice-water. The solid that separated was collected; yield 10.0 g. (82%), m.p. 160–161°. A gas, presumably ethanol, was evolved when the compound melted. After recrystallization from ethanol, the pale yellow octahydroquinoline melted at 161–162° dec.

Anal. Calcd. for $C_{13}H_{15}O_2N_3$: C, 63.7; H, 6.1; N, 17.3. Found: C, 63.9; H, 6.1; N, 17.4.

III. **Preparation of 3,4-Dicyano-2(1H)-pyridones. A. 3,4-Dicyano-6-methyl-2(1H)-pyridone** (III).—A mixture of 2.40 g. (0.012 mole) of 3,4-dicyano-6-ethoxy-5,6-dihydro-2-imino-6-methyl-2H-pyran and 50 ml. of water was heated at the boiling point until solution resulted. This solution was treated with decolorizing charcoal and filtered hot. Upon cooling there was obtained 1.30 g. (70%) of the pyridone in the form of pale yellow crystals that sublimed at 210° and melted at 241–242° dec. λ_{max} 373 mμ, ϵ 9,100, 229 mμ, ϵ 18,300.

Anal. Calcd. for $C_8H_5ON_3$: C, 60.4; H, 3.2; N, 26.4. Found: C, 60.1; H, 3.3; N, 26.0.

B. 3,4-Dicyano-6-ethyl-5-methyl-2(1H)-pyridone (IV).—3,4 - Dicyano - 5,6 - dihydro - 6 - ethoxy - 6-ethyl - 5 - methyl - 2(1H) - pyridone (3.00 g., 0.013 mole) was placed in 60 ml. of water. The mixture was heated to boiling until a solution resulted, and this solution was treated with decolorizing charcoal and filtered while hot. The pale yellow crystals that separated upon cooling were collected; yield 1.50 g. (62%), m.p. 226–230° dec. An aqueous solution of this compound exhibited a blue fluorescence, λ_{max} 340 mμ, ϵ 8,600, 233 mμ, ϵ 17,200.

Anal. Calcd. for $C_{10}H_9ON_3$: C, 64.2; H, 4.8; N, 22.5. Found: C, 64.2; H, 4.6; N, 22.6.

C. 3,4-Dicyano-5,6,7,8-tetrahydro-2(1H)-quinolone.—A solution of 3.50 g. (0.014 mole) of 3,4-dicyano-8a-ethoxy-4a,5,6,7,8,8a-hexahydro-2(1H)-quinolone in 10 ml. of concentrated HCl was allowed to stand at room temperature. After 5 minutes crystals began to separate. These were collected and recrystallized from ethanol; yield 0.72 g. (26%), m.p. 259–261° dec.

Anal. Calcd. for $C_{11}H_9ON_3$: C, 66.4; H, 4.5; N, 21.2. Found: C, 66.4; H, 4.6; N, 20.9.

D. 3,4-Dicyano-6-phenyl-2(1H)-pyridone (V).—A solution of 15.0 g. (0.065 mole) of 4,4,5,5-tetracyanobutyrophenone in 250 ml. of ethanol was heated under reflux for 3.5 hr. and then concentrated to 50 ml. The solid was collected and washed with ethanol; weight 7.9 g. (59%). Recrystallization from dioxane gave 5.0 g. of the pyridone as a pale yellow solid that melted above 300°.

Anal. Calcd. for $C_{13}H_7ON_4$: C, 70.6; H, 3.2; N, 19.0. Found: C, 70.7; H, 3.2; N, 18.5.

E. 3,4-Dicyano-6-*p*-methoxyphenyl-2(1H)-pyridone.—A solution of 5.0 g. (0.018 mole) of 4,4,5,5-tetracyano-*p*-methoxybutyrophenone in 50 ml. of ethanol was heated under reflux for 3 hours. During this time a solid was formed. This solid was collected (3.40 g.) and recrystallized from dioxane to give the pyridone as yellow needles; weight 1.20 g. (27%), m.p. >300°. A dilute solution of this compound in acetone exhibited an intense blue-green fluorescence.

Anal. Calcd. for $C_{14}H_9O_2N_3$: C, 66.9; H, 3.6; N, 16.7. Found: C, 66.9; H, 3.8; N, 16.9.

F. 3,4-Dicyano-5,6-diphenyl-2(1H)-pyridone.—A solution of 2.00 g. (0.0062 mole) of 3-phenyl-4,4,5,5-butyrophenone in 30 ml. of ethanol was heated under reflux for 5 hours, and then concentrated to 10 ml. A deep red solid separated upon standing, and this was collected to give 0.73 g., m.p. 223–228°. After numerous recrystallizations from ethanol, 0.13 g. (7%) of bright yellow crystals was obtained, m.p. 266–268°.

Anal. Calcd. for $C_{19}H_{11}ON_3$: C, 76.2; H, 3.7; N, 14.1. Found: C, 76.5; H, 3.7; N, 13.9.

G. 3,4-Dicyano-6-*t*-butyl-2(1H)-pyridone.—A solution of 10.5 g. (0.046 mole) of the pinacolone–TCNE adduct in 75 ml. of ethanol was heated under reflux for 30 minutes. The solution was then cooled and a precipitate was collected; yield 1.5 g. The filtrate was concentrated to about 15 ml. and an additional 2.75 g. of solid was obtained. The combined precipitates were recrystallized from ethanol (decolorizing charcoal), to give 3.00 g. (32%) of the pyridone, m.p. 226–228°.

Anal. Calcd. for $C_{11}H_{11}N_3O$: C, 65.7; H, 5.5; N, 20.9. Found: C, 65.7; H, 5.4; N, 20.6.

H. The Imide of 3,4-Dicarboxy-6-methyl-2(1H)-pyridone (**VI**).—A mixture of 25 ml. of 4% sodium hydroxide solution and 0.75 g. (4.7 mmoles) of 3,4-dicyano-6-methyl-2-(1H)-pyridone was warmed on a steam-bath until a yellow solution resulted. The solution was cooled and acidified with hydrochloric acid to give 0.81 g. (93%) of the imide with a melting point >300°. Recrystallization from water gave bright yellow needles. The infrared spectrum of this compound had a doublet at 5.61 and 5.74 μ characteristic of imides.

Anal. Calcd. for $C_8H_6O_3N_2$: C, 53.9; H, 3.4; N, 15.7. Found: C, 54.3; H, 3.6; N, 15.7.

I. **Reaction of 2-(1,1,2,2-Tetracyanoethyl)-cyclopentanone with Ethanol** (**VII**).—A solution of 10.0 g. (0.0475 mole) of 2-(1,1,2,2-tetracyanoethyl)-cyclopentanone in 100 ml. of ethanol was heated under reflux for 50 minutes, and then concentrated under reduced pressure The yellow solid that formed was collected and washed with a small amount of ethanol; yield 3.30 g. After several recrystallizations from ethyl acetate, there was obtained a white solid, m.p. 139–140° dec.

Anal. Calcd. for $C_{14}H_{19}O_3N_3$: C, 60.9; H, 6.5; N, 15.2. Found: C, 60.8; H, 6.9; N, 15.1.

WILMINGTON, DEL.

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(4) C. L. Dickinson, U.S. Patent 2,925,422 (1960).