UDC 542.91:547.391.1'491:547.821.2

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The action of pyridine on α -cyanoacrylic acid leads to the rapid and quantitative formation of 2,4-dicyano-4-pentenoic acid. In the presence of excess p-nitrobenzaldehyde, 1-hydroxy-1-p-nitrophenyl-2-cyano-2-butene is formed in this reaction in addition to 2,4-dicyano-4-pentenoic acid.

The reaction of activated olefins $CH_2=CHX$ (X = CO_2R , COR, and CN) with aldehydes [1] in the presence of tertiary amines has attracted recent interest as a powerful synthetic tool [2]. One of the interesting variants of this reaction is the dimerization catalyzed by tertiary amines or phosphines [3, 4]. The mechanism of this reaction [2] probably entails the addition of a nucleophile to the olefin with the formation of zwitterion (A), which, in turn, attacks a second olefin molecule:

$$\begin{array}{c} \mathrm{CH}_{2} = \mathrm{CHX} + \mathrm{Nu} : \rightarrow \overset{+}{\mathrm{Nu}} - \mathrm{CH}_{2} \overline{\mathrm{C}} \mathrm{HX} \xrightarrow{\mathrm{CH}_{2} = \mathrm{CHX}} \mathrm{Nu} - \mathrm{CH}_{2} - \mathrm{CHX} - \mathrm{CH}_{2} - \overline{\mathrm{C}} \mathrm{HX} \rightarrow \\ & \stackrel{+}{\mathrm{Nu}} - \overline{\mathrm{C}} \mathrm{H}_{2} - \overline{\mathrm{C}} \mathrm{X} - \mathrm{CH}_{2} - \mathrm{CH}_{2} \mathrm{X} \xrightarrow{\mathrm{CH}_{2}} \mathrm{CH}_{2} = \mathrm{CX} - \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{X} \\ & \stackrel{+}{\to} \overset{+}{\mathrm{Nu}} - \overline{\mathrm{C}} \mathrm{H}_{2} - \overline{\mathrm{C}} \mathrm{X} - \mathrm{CH}_{2} - \mathrm{CH}_{2} \mathrm{X} \xrightarrow{\mathrm{CH}_{2}} \mathrm{CH}_{2} = \mathrm{CX} - \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{X} \end{array}$$

It would appear that an increase in the electrophilicity of the double bond should lead to an increase in the rate of both the first and second reaction steps and this is supported by data on the effect of substituent X on the rate of such reactions [3]. Disubstituted olefins, $CH_2=CXY$, should be even more active in these reactions. However, as seen in the scheme presented, the formation of dimer (I) is possible only in the case of monosubstituted olefins since loss of the catalyst in the last step requires displacement of the anionic site to the β -position. Otherwise, only polymerization can occur as seen, for example, for α -cyanoacrylates [5].

In the present work, we report a reaction of α -cyanoacrylic acid (II) catalyzed by tertiary amines. The addition of 0.15-0.20 equivalent pyridine to a solution of (II) in acetone leads immediately to a precipitate (apparently, a pyridine salt), which dissolves over 2-3 min with the concurrent release of CO₂. This results in the quantitative formation of 2,4-dicyano-4-pentenoic acid (III)

$$\begin{array}{c} 2\text{CH}_2 = \text{C(CN)COOH} \xrightarrow{P_Y} \text{CH}_2 = \text{C(CN)} - \text{CH}_2 - \text{CH}(\text{CN}) - \text{COOH} \\ (\text{III}) \end{array}$$

The structure of (III) was indicated by PMR, 13 C NMR, and IR spectroscopy and conversion to ester (IV). This reaction apparently may entail the formation of zwitterion (A) (X = CN) as a result of the decarboxylation of the initial intermediate (A')

$$(II) + C_{5}H_{5}N \rightleftharpoons CH_{2} = C(CN)COO^{-}C_{5}H_{5}NH \rightleftharpoons C_{5}H_{5}N - CH_{2} - \check{\mathbf{C}}(CN)COOH \rightarrow C_{5}H_{5}N^{\bullet} - CH_{2} - CH_{2} - CH(CN)COO^{-} \xrightarrow[(A')]{} - CH_{2} - CH_$$

In this case, (II) may be seen as an activated acrylonitrile. The dimerization of (II) by the action of tertiary amines proceeds more slowly by a factor of -10^3 [3].*

*The use of a pressure of 2000-5000 atm has recently been proposed to achieve a sharp increase in the rate of the such reactions [6].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2644-2646, November, 1989. Original article submitted April 17, 1989. We should note that, to our knowledge, pyridine has not been used previously as a catalyst for such reactions. Usually, 1,4-diazabicyclo[2.2.2]octane (DABCO) has been used for this purpose [2]. In some cases, NEt₃ has also been used although its relatively low activity has been noted [6]. We have found that DABCO is less efficient in the reaction with (II) than pyridine. The reaction is slower when DABCO is used and the yield of (III) does not exceed 60-70%. In this case, NEt₃ is completely unsuitable since its leads to the polymerization of (II) (CO₂ is virtually not released).

The high electrophilicity of the double bond in (II) does not permit the use of benzaldehyde as a trap for zwitterion (A). Adduct (V) is not formed even in the presence of a three-fold excess of benzaldehyde. Small amounts of (V) are formed only when p-nitrobenzaldehyde is used



The structure of (V) was indicated by PMR and IR spectroscopy and mass spectrometry.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were taken on a Bruker WH-200-SY spectrometer in deuteroacetone with TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer. The mass spectra were taken on a DS-60 mass spectrometer. α -Cyanoacrylic acid was prepared according to Schlueter and Marten [7].

Reaction of α -Cyanoacrylic Acid Catalyzed by Tertiary Amines. a. Pyridine as Catalyst. A solution of 1.8 g (0.02 mole) pyridine in 5 ml acetone was added to a solution of 10 g (0.1 mole) α -cyanoacrylic acid in 25 ml acetone and stirred until the precipitate formed was completely dissolved and there was no longer gas evolution. After the removal of acetone in vacuum, the residue was dissolved in 12 ml 2 N hydrochloric acid, extracted with ether, and dried over MgSO₄. Ether was removed to give 7.3 g (94%) 2,4-dicyano-4-pentenoic acid (III) as an oil which readily crystallizes, mp 7.4°C* (from toluene). Found: C, 56.20; H, 4.24; N, 19.07%. Calculated for $C_{7H_6}N_2O_2$: C, 56.00; H, 4.03; N, 18.65%. PMR spectrum (δ , ppm): 2.9-3.1 m (2H), 4.2-4.3 m (1H), 6.19 t (1H), 6.21 t (1H), 10.26 br. s (1H). ¹³C NMR spectrum (δ , ppm): 34.0 (CH₂), 37.3 (<u>C</u>H-CN), 117.3 and 118.6 (CN), 117.8 (=<u>C</u>-CN), 134.8 (CH₂=), 167.7 (CO₂H). IR spectrum (ν , cm⁻¹): 1632 (C=C), 1750 (C=O), 2250 and 2275 (C=N), 2400-3500 (CO₂H).

b. DABCO as Catalyst. The reaction was carried out by analogy to the above procedure. Complete dissolution of the precipitate and the end of gas evolution were noted 1 h after mixing of the reagents. Work-up of the reaction mixture gave 4.8 g (62%) (III).

c. NEt₃ as Catalyst. The addition of 1 g (0.01 mole) NEt₃ to a solution of 5 g (0.05 mole) (II) in acetone gave a white precipitate. The evolution of CO_2 was not noted. This precipitate, which is insoluble even in ethanol and benzene, dissolves readily in water. The PMR spectrum of this product in D_2O is a group of poorly resolved signals at 2-3 ppm and narrow signals for the triethylammonium ethyl protons at 1.08 (t, CH_3) and 3.05 ppm (q, CH_2).

Esterification of 2,4-dicyano-4-pentenoic Acid (III). A sample of 6.5 g (0.055 mole) SOCl₂ was added dropwise with stirring to a solution of 7.3 g (0.05 mole) (III) in 40 ml. abs. ethanol and left overnight at ~20°C. After removal of excess ethanol, the residue was poured into ice water and extracted with ether. The extract was washed with aq. sodium carbonate and water and dried over MgSO₄. After removal of ether, the residue was subjected to chromatography on a silica gel column using chloroform as the eluent to give 4.5 g (52%) ethyl 2,4-dicyano-4-pentenoate (IV), bp 112-113°C (1 mm). Found: C, 60.60; H, 5.96; N, 15.74%. Calculated for $C_{9H_{10}N_2O_2}$: C, 60.67; H, 5.66; N, 15.72%. PMR spectrum (δ , ppm): 1.30 t (3H), 2.96-3.01 m (2H), 4.15-4.33 m (3H), 6.15 t (1H), 6.19 t (1H). PMR spectrum of H_xH_zC=C(CN)CH_AH_BCH_M(CN)CO₂CH₂CH₃ (IV) (δ , ppm): 2.98 (H_A), 3.00 (H_B), 4.19 (H_M), 6.15 (H_x), 6.19 (H_z); J_{AB} = -14, J_{AM} = 8.0, J_{BM} = 5.5, J_{AX} = J_{BX} = 0.6, J_{AZ} = J_{BZ} = 1.2 Hz. In addition, we isolated 1 g (9%) of the diethyl ester of 2-cyano-4-pentenedicarboxylic acid (VI), bp 115-116°C (1 mm). Found: C, 58.43; H, 6.49; N, 6.77%. Calculated for C₁₁H₁₅NO₄: C, 58.66; H, 6.71; N, 6.22%. PMR spectrum of H_xH_zC=C(CN)CH₂^ACH^M(CO₂CH₂CH₃)₂ (VI) (δ , ppm): 1.25 t (6H), 2.86 m (2H), 3.70 t (1H), 4.20 q (2H), 6.00 t (1H), 6.10 t (1H); J_{AM} = 7.5, J_{AX} = 1.6, J_{AZ} = 0.9 Hz.

*As in Russian original - Editor.

of 9 g (0.06 mole) p-nitrobenzaldehyde in 50 ml benzene containing 0.32 g (0.004 mole) pyridine. After 20 min, the reaction mixture was evaporated to dryness and 30 ml acetone was added to the residue. The mixture was thoroughly stirred and most of the unreacted p-nitrobenzaldehyde was filtered off. The filtrate was evaporated and the residue, containing a 6:4.5:1 mixture of p-nitrobenzaldehyde, (III), and (IV), was subjected to chromatography on a silica gel column using 9:1 hexane-ethanol as the eluent to give 0.6 g (10%) 1-hydroxy-1-pnitrophenyl-2-cyano-2-butene (IV), mp 70-71°C (from 1:1 hexane-benzene). Found: C, 58.82; H, 4.15; N, 13.80%. Calculated for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.95; N, 13.72%. PMR spectrum (δ , ppm): 5.66 s (1H), 6.16 s (1H), 6.34 s (1H), 7.77 d (2H), 8.29 d (2H). Mass spectrum (m/z): 204 (M^+ , 43%), 152 ($M^+ - CH_2$ =CH(CN), 100%). IR spectrum (ν , cm⁻¹): 1360, 1520 (arom. NO₂), 2250 (C=N), 3300-3600 (OH). Product (IV) was obtained in the same yield upon the addition of pyridine to a solution containing (II) and p-nitrobenzaldehyde.

LITERATURE CITED

- A. B. Baylis and M. E. D. Hillman, German Patent No. 2,155,113; Chem. Abstr., <u>77</u>, 34174 (1972).
- 2. S. E. Drewes and G. H. P. Roos, Tetrahedron, <u>44</u>, No. 15, 4653 (1988).
- D. Basavaiah, V. V. L. Gowriswari, and T. K. Bharati, Tetrahedron Lett., <u>28</u>, No. 39, 4591 (1987).
- 4. M. Takeda and M. Kaito, J. Synth. Org. Chem. Jpn., <u>39</u>, 813 (1981).
- 5. H. Lee (ed.), Cyanoacrylate Resins The Instant Adhesives, Pasadena Technology Press, Pasadena (1981).
- 6. J. S. Hill and N. S. Isaacs, Tetrahedron Lett., <u>27</u>, No. 41, 5007 (1986).
- K. Schlueter and K. Marten, Ger. Offen. DE 3,415,181; Chem. Abstr., <u>104</u>, 148334 (1986).