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N-Cyanoacetyl pyrrolidine, piperidine and morpholine reacted with ethyl phenylpropiolate to give the rearranged Michael addition products III. Some interesting results obtained from the bromination, hydrolysis and reduction of III are reported. 2-Thiophene and 2-furaneacetonitriles reacted with ethyl phenylpropiolate to give the Claisen addition products XVIII. Reaction of either III or XVIII with hydrazine hydrate, phenylhydrazine and hydroxylamine hydrochloride afforded 3-phenylpyrazol-5-one, 1,3-diphenylpyrazol-5-one and 3-phenylisoxazol-5-one together with the appropriate starting cyanoacetyl or cyanomethylene compounds, respectively. The mechanism for the formation of the various reaction products beside the ir and nmr spectral results are discussed.

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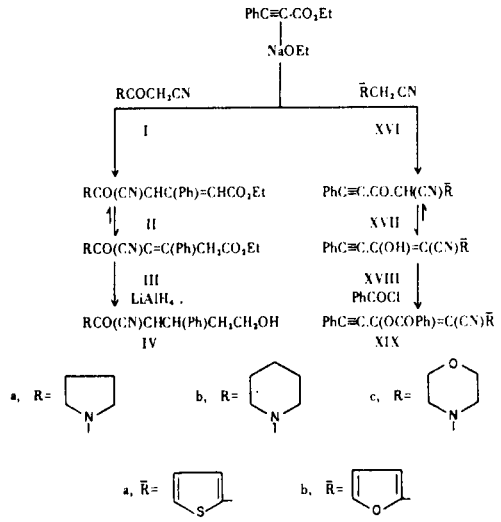
In a previous paper (2) we reported the condensation between the acetylenic ester and some arylacetonitriles where the corresponding acetylenic β-keto cyanides were obtained as a Claisen addition products and were subjected to biological screening tests. This paper describes the results obtained from the condensation of ethyl phenylpropiolate with each of 1-cyanoacetyl-pyrrolidine, 1-cyanoacetylpiperidine, 4-cyanoacetylmorpholine, 2-thiophene and 2-furaneacetonitriles (I and XVI).

In general, the condensation between the acetylenic ester and 1-cyanoacetyl heterocycles (I) in the presence of sodium ethoxide afforded the Michael addition products IIa-c. The ir spectra of the products showed a carbonyl stretching band between 1732-1742 cm^{-1}, due to saturated ester, and lack the absorption due to the acetylenic group near 2200 cm^{-1}. The nmr spectra showed a methylene singlet between 3.45-3.8 δ and lack the signals due to the ethylenic protons expected to be present in compounds IIa-c. Moreover the nmr spectra showed other absorptions due to the ethyl and ring proton signals. These spectral informations supported the existance of the reaction products in their rearrangement forms IIIa-c.

Reduction of compounds IIIa-c with excess of lithium aluminium hydride in ether afforded products in which their ir and nmr spectra indicated that both the ethylenic and ester groups were attacked by the reagent. The above nmr spectra showed four protons in excess compared with the starting materials IIIa-c and therefore the products were identified as saturated alcohols (IVa-c). The OH signal which was overlaped with other methylene and methine protons was detected by running the nmr spectra at higher temperatures where upon the OH proton was shielded and absorbed as a sharp signal (3). Bromination of compounds IIIa-c under anhydrous conditions with excess bromine afforded products in which their elementary analysis showed no bromine. The nmr spectra of the bromination products lack the absorption due to the methylene signals present in compounds IIIa-c. Moreover, the ir spectra showed absorptions due to the cyano,

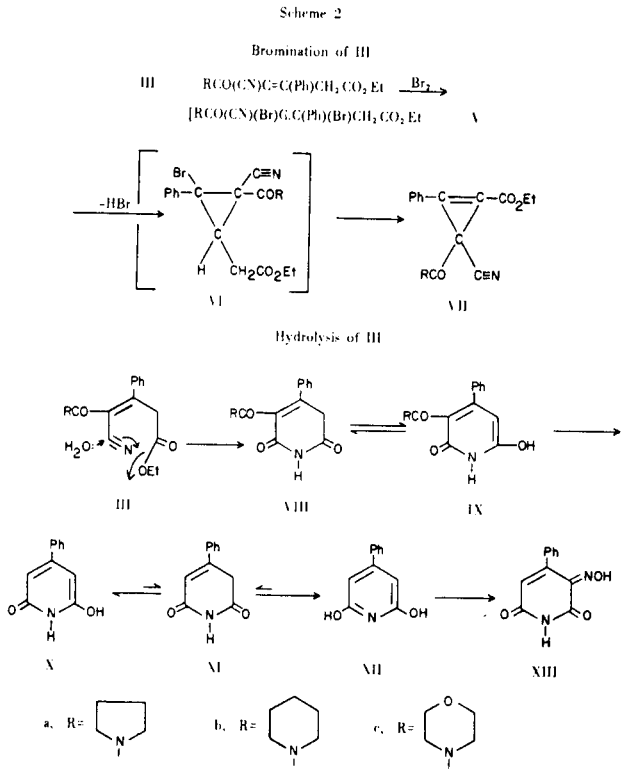
Scheme 1

Reaction of Ethyl Phenylpropiolate with I and XVI



amido and ester groups (see Experimental). The absorption of the latter carbonyl ester group at 1700, rather than 1732-1742 cm^{-1} present in compounds IIIa-c, reveals to be of a conjugated type (4). According to the above information, the structure of the bromination products could be formulated as tetrasubstitutedcyclopropenes (VIIa-c) as illustrated in Scheme 2. The formation of compounds VIIa-c could be explained by the addition of one molecule of bromine to the ethylenic double bonds of IIIa-c to form the intermediates Va-c. Cyclisation of the latter, through the loss of a molecule of HBr to form the substituted bromocyclopropane intermediates (VIa-c), followed by spontaneous loss of another molecule of HBr gave the products VIIa-c.

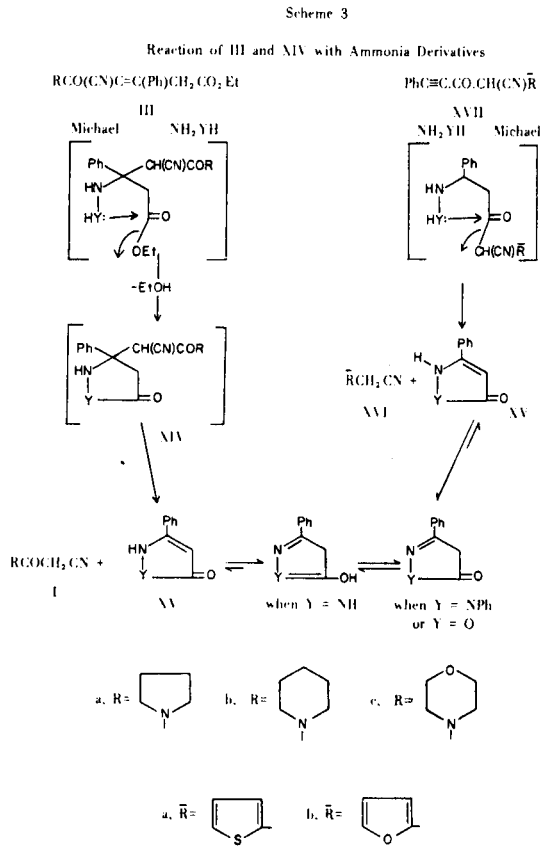
Both the acid and alkaline hydrolysis of compounds IIIa-c gave a rather interesting results. The hydrolysis products obtained from compounds IIIa and IIIc were identical and have the following properties: (a) relatively high melting point (255°), (b) insoluble in most organic



Scheme 2

Bromination of III

Hydrolysis of III



Scheme 3

Reaction of III and XIV with Ammonia Derivatives

solvents, while slightly soluble in methanol and ethanol, (c) formation of deep-violet coloration with ferric chloride solution. These chemical properties were identical with those reported earlier for the hydrolysis products of cyanoglutaconic esters in which 2,6-pyridinediols were identified (5,6). The nmr spectrum of our hydrolysed product showed a sharp singlet at 6.02 δ integrated for two protons and were exchangeable with deuterium oxide. The latter absorption is attributed to the two OH protons and therefore the product is identified as 4-phenyl-2,6-dihydroxypyridine (XII). The above hydrolysed product is most likely obtained by cyclisation of compound III followed by hydrolysis and decarboxylation of the intermediate VIII (Scheme 2). On the other hand, the presence of an ir carbonyl stetching band at 1650 beside a broad absorption between 2200-3500 cm^{-1} in the solid phase spectrum of the hydrolysed product indicated that the 2-oxo-6-hydroxy tautomeric form (X) is predominant. According to the above ir and nmr results, the hydrolysis product is present in an equilibrium between the tautomeric forms X and XII. The presence of such equilibrium beside the form XI has been reported earlier for analogous dihydroxypyridine compounds (7). Nitrosation of the above hydrolysis product with sodium nitrite in acetic acid and according to the procedure given by Gibson and Simonsen (5) afforded 3-hydroxyimino-glutaconimide derivative (XIII). The ir and nmr spectra of the latter is relatively similar to those reported for the nitrosation product of the unsubstituted glutaconimide (8) and therefore the nitrosation product is identified as 1,2,3,6-tetrahydro-3-hydroxyimino-2,6-dioxypyridine (XIII) (see Experimental).

Moreover the hydrolysis of compound IIIb under the above conditions mentioned for compounds IIIa,c afforded a product whose ir and nmr spectral data beside elemental analysis indicated that the *N*-carbonylpiperidine group is retained in the hydrolysed product. The presence of one exchangeable proton at 5.75 δ in the nmr spectrum of the latter hydrolysis product could be attributed to the OH proton by analogy to the nmr spectrum of compound XII. Furthermore, there is another exchangeable proton absorbed in the region of the aromatic protons which could be attributed to the NH proton. Therefore, the hydrolysed product is most likely present in the 2-oxo-6-hydroxy tautomeric form (IX). On the other hand the ir spectrum of the solid phase of IX showed a carbonyl stretchings at 1725 and 1660 cm^{-1} which could be attributed to the absorption of the 2,6-dioxo form (VIII) (9). From the above spectral data, the hydrolysis product is present in an equilibrium between the two tautomeric forms VIII and IX. In this regards, the formation of compound VIIIb or IXb is considered as the intermediate product in the formation of compounds X-XII. Several attempts to isolate analogous intermediates from the hydrolysis of compounds IIIa,c were failed even when more drastic conditions were used. Further attempts to hydrolyse the intermediate compound VIIIb, obtained from IIIb, to

X-XII were failed also. Similar example has been reported earlier in which 3-alkyl-3-carbethoxyglutaconimide was considered as an intermediate step in the formation of 2,6-pyridinediol from 2-cyanoglutaconate (8).

Furthermore, the reaction of compound III with excess of hydrazine hydrate, phenylhydrazine and hydroxylamine hydrochloride gave 3-phenylpyrazol-5-one (XV, Y = NH), 1,3-diphenylpyrazol-5-one (XV, Y = NPh) and 3-phenylisoxazole-5-one (XV, Y = O), respectively, together with the appropriate starting cyanoacetyl compounds I (Scheme 3). The isolation of the above products could be explained by initial Michael addition of the ammonia derivatives (NH_2YH) to the conjugated nitrile group of III followed by cyclisation and loss of ethanol to give the intermediate pyrazolidones XIV. Spontaneous cleavage of XIV afforded the pyrazolones or isoxazolone (XV) and the cyanoacetyl compounds I. Analogous 5-pyrazolone formation through the cleavage of the intermediate pyrazolidone, obtained from α-benzylglutaconic esters, were recently reported (10). Moreover, the above cleavage products were also isolated from the reactions involving acetylenic β-keto cyanides which will be discussed latter.

In addition, the reaction of ethyl phenylpropiolate with each of 2-thiophene and 2-furaneacetonitriles (XVIa,b) were also carried out and afforded the corresponding acetylenic β-keto cyanides as Claisen addition products XVIIa,b (Scheme 1). The formation of XVIIa,b were similar to those reported earlier for the corresponding aryl-analogues (2). These compounds XVIIa,b are present mainly in their enol forms XVIIIa,b as shown from the ir and nmr spectra (see Experimental). Benzoylation of XVIIIa gave the corresponding *O*-benzoyl derivative XIXa as shown from the ir carbonyl absorption at 1748 cm^{-1} attributed to the vinyl ester (11). Reactions of XVIIIa,b with each of hydrazine hydrate, phenylhydrazine and hydroxylamine hydrochloride afforded the same heterocyclic products (XV), obtained above from compounds IIIa-c, beside the starting cyanomethylene compounds (XVIa,b) (Scheme 3). We have reported similar observations using aryl substituted acetylenic β-keto cyanides and esters (12).

In conclusion, it can be generalised that as Michael addition is involved in the reaction of cyanoacetyl heterocycles with the acetylenic ester, Claisen addition is observed when cyanomethylene heterocycles are used.

EXPERIMENTAL

Infrared spectra were recorded with Beckman Ir 10 spectrophotometer and nmr spectra on a Varian T-60A spectrometer using tetramethylsilane as internal standard. Microanalytical samples were analysed using 185B HP CHN analyzer. Melting points were determined with a Kofler hotstage apparatus and were uncorrected. The purity of the various reaction products were checked by thin layer chromatography done on glass slides coated with silica gel.

Ethyl 4-(*N*-Carbonylpyrrolidine)-4-cyano-3-phenylbut-3-enoate (IIIa).

1-Cyanoacetylpyrrolidine (3.9 g.) dissolved in benzene (50 ml.) and ethyl phenylpropiolate (5.0 g.) were added successively with stirring to a benzene solution (100 ml.) of sodium ethoxide [prepared from sodium (0.66 g.) and absolute ethanol (1.6 ml.)]. The reaction mixture was left for three days at room temperature and then poured onto water. The alkaline solution was acidified with dilute sulfuric acid and then poured onto water. The combined benzene and chloroform extracts were dried over magnesium sulfate and evaporated *in vacuo* to give 8.0 g. (81.62% yield) of compound IIIa, m.p. 78-80° (from ether); ir (Nujol): 2220 (C≡N), 1742 (C=O ester), 1635 (C=O amide) cm^{-1}; nmr (deuteriochloroform): δ 1.17 (t, 3H, CH_3), 1.8-2.2 (m, 4H, $2CH_2$), 3.5-3.9 (m, 4H, CH_2NCH_2), 3.72 (s, 2H, CH_2), 4.05 (q, 2H, CH_2), 7.38 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{18}H_{20}N_2O_3$: C, 69.23; H, 6.41; N, 8.97. Found: C, 69.52; H, 6.62; N, 9.00.

Ethyl 4-(*N*-Carbonylpiperidine)-4-cyano-3-phenylbut-3-enoate (IIIb).

1-Cyanoacetylpiperidine (4.37 g.), ethyl phenylpropiolate (5.0 g.) and sodium ethoxide [from sodium (0.66 g.) and absolute ethanol (1.6 ml.) in benzene (100 ml.)] were condensed under similar conditions used for compound IIIa to give 7.0 g. (67.83% yield) of compound IIIb, m.p. 96-98° (from ether); ir (Nujol): 2220 (C≡N), 1740 (C=O ester), 1642 (C=O amide) cm^{-1}; nmr (deuteriochloroform): δ 1.25 (t, 3H, CH_3), 1.0-1.7 (m, 6H, $3CH_2$), 3.2-3.5 (t, 4H, CH_2NCH_2), 3.8 (s, 2H, CH_2), 4.2 (q, 2H, CH_2), 7.35 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{19}H_{22}N_2O_3$: C, 69.94; H, 6.75; N, 8.60. Found: C, 70.17; H, 6.91; N, 8.59.

Ethyl 4-(*N*-Carbonylmorpholine)-4-cyano-3-phenylbut-3-enoate (IIIc).

4-Cyanoacetylmorpholine (4.43 g.), ethyl phenylpropiolate (5.0 g.) and sodium ethoxide [from sodium (0.66 g.) and absolute ethanol (1.6 ml.) in benzene (100 ml.)] were condensed under similar conditions used for compound IIIa to give 6.4 g. (67.86% yield) of compound IIIc, m.p. 120-122° (from ether); ir (Nujol): 1732 (C=O ester), 1645 (C=O amide), 2198 (C≡N); nmr (deuteriochloroform): δ 1.2 (t, 3H, CH_3), 3.45 (s, 2H, CH_2), 3.6-4.0 (m, 8H, $4CH_2$), 4.1 (q, 2H, CH_2), 7.4 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: C, 65.90; H, 6.10; N, 8.55. Found: C, 65.81; H, 6.18; N, 8.55.

4-(*N*-Carbonylpyrrolidine)-4-cyano-3-phenylbutan-1-ol (IVa).

A solution of compound IIIa (0.5 g.) in dry ether (50 ml.) was added dropwise with stirring to a suspension of lithium aluminium hydride (0.5 g.) in dry ether (20 ml.). The reaction mixture was refluxed for five hours and worked up in the usual manner to give 0.4 g (93.1% yield) of compound IVa, m.p. 106-108° (from ether); ir (chloroform): 3450 (OH), 2222 (C≡N), 1650 (C=O amide) cm^{-1}; nmr (deuteriochloroform): δ 1.6-4.0 (m, 15H, OH and aliphatic protons), 7.32 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{16}H_{20}N_2O_2$: C, 70.59; H, 7.35; N, 10.29. Found: C, 70.98; H, 7.51; N, 10.4.

4-(*N*-Carbonylpiperidine)-4-cyano-3-phenylbutan-1-ol (IVb).

A solution of compound IIIb (0.5 g.) in dry ether (50 ml.) was added dropwise with stirring to a suspension of lithium aluminiumhydride (0.5 g.) in dry ether (20 ml.). The reaction mixture was refluxed for thirty hours and worked out to give

0.35 g. (80% yield) of compound IVb, m.p. 110-112° (from ether); ir (chloroform): 3400 (OH), 2220 (C≡N), 1645 (C=O amide) cm^{-1}; nmr (deuteriochloroform): δ 1.0-4.0 (m, 17H, OH and aliphatic protons), 7.33 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{17}H_{22}N_2O_2$: C, 71.32; H, 7.69; N, 9.97. Found: C, 71.4; H, 7.73; N, 9.83.

4-(*N*-Carbonylmorpholine)-4-cyano-3-phenylbutan-1-ol (IVc).

A solution of compound IIIc (0.5 g.) in dry ether (50 ml.) was added dropwise with stirring to a suspension of lithium aluminium-hydride (0.5 g.) in dry ether (20 ml.). The reaction mixture was refluxed for 1.5 hours to give 0.35 g. (79.54% yield) of compound IVc, m.p. 101-103° (from ether); ir (chloroform): 3470 (OH), 2226 (C≡N), 1655 (C=O amide) cm^{-1}; nmr (deuteriochloroform): δ 1.4-4.0 (m, 15H, OH and aliphatic protons), 7.32 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{16}H_{20}N_2O_3$: C, 66.66; H, 6.94; N, 9.72. Found: C, 66.54; H, 6.99; N, 9.58.

Ethyl 3-(*N*-Carbonylpyrrolidine)-3-cyano-2-phenylcyclopropene-1-carboxylate (VIIz).

Bromine (0.6 ml.) was added dropwise with stirring to a solution of compound IIIa (0.2 g.) in carbon tetrachloride (20 ml.). The reaction mixture was left overnight at room temperature. Evaporation of the solvent afforded 0.15 g. (78.94% yield) of compound VIIa, m.p. 145° (from methanol); ir (Nujol): 2183 (C≡N), 1700 (C=O ester), 1630 (C=O amide) cm^{-1}; nmr (deuteriochloroform): δ 1.15 (t, 3H, CH_3), 2.0 (m, 4H, $2CH_2$), 3.75 (m, 4H, CH_2NCH_2), 4.15 (q, 2H, CH_2), 7.4 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.67; H, 5.8; N, 9.03. Found: C, 69.86; H, 6.1; N, 9.05.

Ethyl 3-(*N*-Carbonylpiperidine)-3-cyano-2-phenylcyclopropene-1-carboxylate (VIIb).

Compound IIIb (0.3 g.) was similarly treated with bromine (0.6 ml.) as mentioned above for VIIa to give 0.1 g. (36.0% yield) of compound VIIb, m.p. 124-126° (from methanol); ir (chloroform): 2200 (C≡N), 1700 (C=O conjugated ester), 1600 cm^{-1}; nmr (deuteriochloroform): δ 1.15 (t, 3H, CH_3), 1.75 (m, 6H, $3CH_2$), 3.75 (m, 4H, CH_2NCH_2), 4.2 (q, 2H, CH_2), 7.5 (m, 5H, C_6H_5).

Ethyl 3-(*N*-Carbonylmorpholine)-3-cyano-2-phenylcyclopropene-1-carboxylate (VIIc).

Compound IIIc (0.3 g.) was treated with bromine (0.6 ml.) as for compound VIIa to give 0.25 g. (83.34% yield) of VIIc, m.p. 155-157° (from methanol); ir (Nujol): 2190 (C≡N), 1700 (C=O ester), 1630 (C=O amide) cm^{-1}; nmr (deuteriochloroform): δ 1.1 (t, 3H, CH_3), 2.0 (m, 4H, CH_2CH_2), 3.72 (m, 4H, CH_2NCH_2), 4.2 (q, 2H, CH_2), 7.45 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{18}H_{18}N_2O_4$: C, 66.30; H, 5.52; N, 8.58. Found: C, 66.48; H, 5.83; N, 8.43.

4-Phenyl-2,6-dihydroxypyridine (XII).

Compound IIIa (0.5 g.) was added to 70% sulfuric acid (8 ml.) and the mixture was heated on a steam bath for two hours. The reaction mixture was cooled and poured onto ice and then filtered to give 0.22 g. (78.57% yield) of compound XII. Similarly 0.25 g. (89.28% yield) of compound XII was obtained upon hydrolysis of compound IIIc, m.p. 255-256° (from ethanol), lit. (6), m.p. 256-257°, ir (Nujol): 3500-2200 (OH and NH), 1650, 1640, 1600 (C=O, C=N and C=C) cm^{-1}; nmr (deuteriodimethylsulfoxide): δ 7.3-8.0 (m, 7H, aromatic protons), 6.02 (s, 2H, 2 OH, exchangeable with deuterium oxide).

Anal. Calcd. for $C_{10}H_9NO_2$: C, 70.59; H, 4.81; N, 7.49. Found: C, 70.39; H, 4.92; N, 7.34.

1,2,3,6-Tetrahydro-4-phenyl-3-hydroxyimino-2,6-dioxypyridine (XIII).

A solution of compound XII (0.5 g.) in 10% sodium hydroxide (10 ml.) was saturated with sodium nitrite, cooled and acidified with acetic acid where upon yellow solid compound separated. Recrystallisation of the latter from methanol afforded 0.25 g. (41.1% yield) of compound XIII, m.p. 215-217°; ir (Nujol): 3180 (OH), 1690 (C=O imide), 1650 (C=N) cm^{-1}; nmr (deuteriodimethylsulfoxide): δ 7.8-11.3 (very broad, 2H, NH and OH, exchangeable with deuterium oxide), 7.45 (s, 5H, C_6H_5), 6.26 (s, 1H, =CH).

Anal. Calcd. for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.70; N, 12.96. Found: C, 61.01; H, 3.78; N, 12.64.

5-(*N*-Carbonylpiperidine)-6-hydroxy-4-phenyl-2-pyridone (IXb).

A mixture of compound IIIb (0.5 g.) and 70% sulfuric acid (8 ml.) was heated on a steam bath for thirty minutes. The reaction mixture was worked out as mentioned for XII to give 0.8 g. (87.91% yield) of compound IXb, m.p. 194-195° (from acetone); ir (Nujol): 3400-2400, 1725 and 1660 (C=O imide); nmr (deuteriodimethylsulfoxide): δ 1.3 (m, 6H, $3CH_2$), 3.3 (m, 4H, CH_2NCH_2), 5.75 (s, 1H, OH, exchangeable with deuterium oxide), 7.0-8.0 (s, 7H, C_6H_5 and C=CH protons plus one exchangeable NH proton).

Anal. Calcd. for $C_{17}H_{18}N_2O_3$: C, 68.45; H, 6.04; N, 9.39. Found: C, 68.29; H, 6.33; N, 9.10.

Several attempts to get compound XII by further hydrolysis of IXb, obtained from IIIb, or increase of the above hydrolysis time and up to eight hours were failed. Further increase of the hydrolysis time resulted in the formation of black tarry material.

Reaction of Hydrazine Hydrate with III.

A mixture of compound III (5.0 g.) and hydrazine hydrate (99%, 3 ml.) in ethanol (10 ml.) was refluxed for three hours. Evaporation of the solvent followed by cooling and filtration resulted in a white precipitate which was recrystallized from methanol to give 3-phenylpyrazol-5-one (XV, Y = NH), m.p. and mixed m.p. with authentic sample 240-242° lit. (12), m.p. 242°. The mother liquor was purified and identified as the appropriate starting cyanoacetyl compounds (I) based on comparison of the ir spectra and tlc results with the starting cyanoacetyl compounds.

Reaction of Phenylhydrazine with III.

A mixture of compound III (0.5 g.) and phenylhydrazine (0.3 g.) in ethanol (20 ml.) was refluxed for twelve hours and worked out as mentioned above for the reaction of hydrazine hydrate to give 1,3-diphenylpyrazol-5-one (XV, Y = NPh), m.p. 136-137° (from methanol) lit. (12), m.p. 137°. The mother liquor was identified as the appropriate starting cyanoacetyl compounds (I) and as mentioned above.

Reaction of Hydroxylamine Hydrochloride with III.

A mixture of anhydrous sodium acetate (0.5 g.) and hydroxylamine hydrochloride (0.5 g.) in water (6 ml.) was added to a solution of compound III in ethanol (50 ml.). The reaction mixture was kept under reflux for 4 hours and then cooled. The solid obtained was identified as 3-phenylisoxazol-5-one (XV, Y = O), m.p. 150-151° Ifrom carbon tetrachloride) lit. (12), m.p. 152°. The mother liquor was similarly identified to be the starting cyanoacetyl compound as mentioned above.

3-Hydroxy-2-(2-thienyl)-5-phenylpent-2-en-4-ynentrile (XVIIIa).

2-Thiopheneacetonitrile (3.54 g.) and ethyl phenylpropiolate (5.0 g.) were added successively and dropwise to an ethereal solution (150 ml.) of sodium ethoxide [from sodium (0.66 g.) and ethanol (1.6 ml.)]. The deep red reaction mixture was left at 0°

for three hours and then poured onto water. The alkaline aqueous layer was acidified with dilute sulfuric acid and then extracted with ether. The ethereal solution was woeked out to give 4.6 g. (62.7% yield) of compound XVIIIa, m.p. 172° (from carbon tetrachloride); ir (Nujol): 3300-2700 (OH), 2220 (C≡N and C≡C), 1620 (C=C-OH) cm^{-1}; nmr (deuteriochloroform): δ 6.6-8.2 (m, 9H, all protons, one proton was exchangeable with deuterium oxide).

Anal. Calcd. for $C_{15}H_9NOS$: C, 71.75; H, 3.84; N, 5.41. Found: C, 71.71; H, 3.59; N, 5.58.

3-Benzoyloxy-2-(2-thienyl)-5-phenylpent-2-en-4-ynenitrile (XIXa).

To compound XVIIIa (0.2 g.) in 1% sodium hydroxide solution (150 ml.) was added benzoyl chloride (1 ml.). The mixture was shaken for one hour and then cooled to give 0.2 g. (74% yield) of compound XIXa, m.p. 144° (from methanol); ir (chloroform): 2218, 2175 (C≡N and C≡C), 1748 (C=O vinyl ester) cm^{-1}.

Anal. Calcd. for $C_{21}H_{13}NO_2S$: C, 74.37; H, 3.66; N, 3.94. Found: C, 74.18; H, 3.80; N, 3.84.

3-Hydroxy-2-(2-furanyl)-5-phenylpent-2-en-4-ynenitrile (XVIIIb).

2-Furaneacetonitrile (3.1 g.) and ethyl phenylpropiolate (5.0 g.) were condensed similarly as mentioned for compound XVIIIa to give 2.0 g. (20.8% yield) of compound XVIIIb, m.p. 138° dec. (from carbon tetrachloride); ir (Nujol): 3400-2500 (OH), 2180 (C≡N and C≡C), 1640 (C=C-OH) cm^{-1}; nmr (deuteriochloroform): δ 6.55 (m, 2H, =CHOCH=), 7.3-8.2 (m, 7H, C_6H_5 and one ethylenic protons plus one exchangeable proton).

Anal. Calcd. for $C_{15}H_9NO_2$: C, 76.61; H, 3.83; N, 5.96. Found: C, 76.51; H, 3.79; N, 5.90.

Reactions of XVIIIa,b with Hydrazine Hydrate, Phenylhydrazine and Hydroxylamine Hydrochloride.

These reactions were carried out as mentioned above for compounds IIIa-c to give XV and the appropriate cyanomethylene starting materials XVIa,b.

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