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Decarboxylation Reactions. II.[1] Reaction of Conjugated Unsaturated Ketones and Nitriles with Carboxylic Acids

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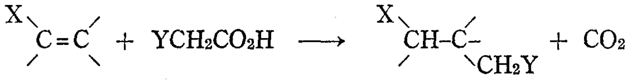
The present paper discloses a decarboxylation reaction of several conjugated unsaturated ketones and nitriles with carboxylic acids such as acetoacetic acid, malonic acid and cyanoacetic acid. In the reaction these carboxylic acids are decarboxylated and introduced at β-carbon of the conjugated unsaturated compounds. Thus there have been provided a effective means of introducing acetonyl, carboxymethyl and cyanomethyl at that position.

α,β-Double bond of conjugated unsaturated ketones or nitriles has been known to suffer the reaction with nucleophiles. The present paper describes our finding that such conjugated unsaturated compounds react with acetoacetic acid, malonic acid and cyanoacetic acid usually in the presence of base as in the following scheme.



$$\mathrm{X{>}C{=}C{<}} + \mathrm{YCH_2CO_2H} \longrightarrow \mathrm{X{>}CH{-}C{<}_{CH_2Y}} + \mathrm{CO_2}$$

X=-CO-, -CN Y=$\mathrm{CH_3CO}$-, NC-, $\mathrm{HO_2C}$-

The reaction proceeded with decarboxylation, where α-carbon of the carboxylic acids used attacked at β-carbon of the conjugated unsaturated compounds. Normally the reaction was carried out in pyridine or in dioxane in the presence or the absence of pyridine at the temperature causing considerable evolution of carbon dioxide. Results of the experiments carried out with acetoacetic acid, malonic acid and cyanoacetic acid are summerized in Table I, II and III, respectively. The substrates used were five benzylidene compounds such as benzylidenemalononitrile (I), 2-benzylidene-1,3-indanedione (II), 5-benzylidene-1,3-dimethylbarbituric acid (III), 5-benzylidenebarbituric acid (IV) and α-benzoylcinnamonitrile (V). In most runs shown in the Tables the reactions smoothly proceeded in the presence of pyridine, in some runs even if in the absence, according to the above reaction scheme to give the corresponding products. Therefore the reaction provides a new effective means of introducing acetonyl, carboxymethyl and cyanomethyl directly at β-carbon of conjugated unsaturated compounds.

This decarboxylation reaction with carboxylic acid resembles that with formic acid reported[3] previously in the reaction pattern. However, it is obscure in this reaction whether before decarboxylation the carbanion of α-carbon or the carboxylate anion attacks at β-carbon of the conjugated unsaturated compounds. Carboxylic acids not having active methylene, such as trichloroacetic acid and phenylpropiolic acid, were innert to this reaction suffering self-decarboxylation. From this fact the attack of anion of α-carbon appeared to be prefarable.

In some runs hydrolysis and cyclization of the normal products succeeded in the reactions. These are shown in the reaction of V with acetoacetic acid, I and V with malonic acid and V with cyanoacetic acid, giving those presented by X, XI, XV and XIX in the Tables.

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1) Part I: N. Kumagaya, K. Suzuki, and M. Sekiya, *Chem. Pharm. Bull.* (Tokyo), **21**, 1601 (1973).

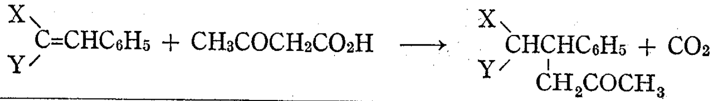
2) Location: *2-2-1, Oshika, Shizuoka.*

3) *a)* M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 747 (1969); *b)* M. Sekiya and K. Suzuki, *ibid.*, **18**, 1530 (1970); *c)* T. Okugawa, K. Suzuki, and M. Sekiya, *ibid.*, **22**, 448 (1974).

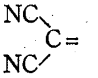
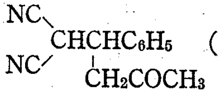
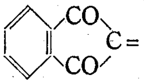
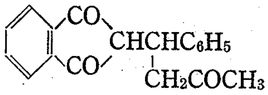
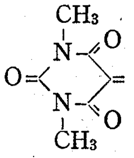
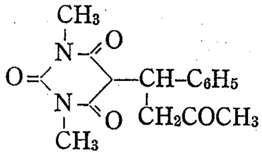
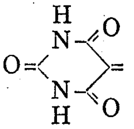
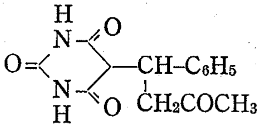
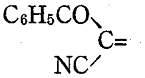
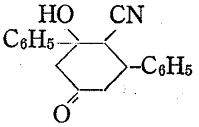
The structures of the reaction products presented in Table I, II and III except X, XI and XIX were proved by their infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra, and from elementary analyses. The UV spectra of the products showed no absorption band at 300—340 nm resion observed in the substrates, indicating disappearance of the conjugated α,β-double bonds. The IR and NMR spectra of the products are interpreted to fit their structures. While the NMR proton signals of $-CH_2-\dot{C}H-CH<$ of the product VI appeared in a simple pattern; a doublet at τ 6.7 (2H, J=6.6 Hz), two overlapping triplets at τ 6.2 (1H, J=6.6, J=4.8 Hz) and a doublet at τ 5.5 (1H, J=4.8 Hz), those of the other products exhibited further splitting owing to non equivalence of the methylene protons. Therefore some of them are complicated. A clear example is that of the product VII; a doublet of doublets at τ 6.9 (1H, J=16.8, J=12.0 Hz), a doublet at τ 6.5 (1H, J=3.6 Hz), a doublet of doublets at τ 6.4 (1H, J=16.8, J=9.6 Hz) and a doublet of doublets of doublets at τ 5.9 (1H, J=12.0, J=9.6, J=3.6 Hz).

The compounds XI and XIX were analysed as the corresponding formula, while the compound X as $C_{19}H_{17}O_2N \cdot 1/2C_4H_8O_2$ (crystals recrystallized from dioxane) and as $C_{19}H_{17}O_2N \cdot C_2H_5O$ (crystals recrystallized from EtOH). IR, NMR and UV spectral data obtained from these products are well interpreted to fit their structures.

TABLE I. Reaction[a] with Acetoacetic Acid



$$\begin{matrix}X\\Y\end{matrix}\!\!>C{=}CHC_6H_5 + CH_3COCH_2CO_2H \longrightarrow \begin{matrix}X\\Y\end{matrix}\!\!>\underset{|}{CH}\underset{CH_2COCH_3}{CHC_6H_5} + CO_2$$

Substrate $\left(\begin{matrix}X\\Y\end{matrix}\!\!>C{=}\right)$		Product		Yield (%)
	(I)		(IV)	45
	(II)		(VII)	93 (79)[b]
	(III)		(VIII)	90 (83)[b]
	(IV)		(IX)	18
	(V)		(X)	9

a) normal condition: benzylidene compound: acetoacetic acid: pyridine=2:3:1 in molar proportion, solvent: dioxane, reaction temp.: 65—75°
b) This run was carried out in the absence of pyridine.

Experimental[4)]

Experiments are constituted of the reactions of α,β-unsaturated ketones and nitriles with acetoacetic acid,[1)] malonic acid and cyanoacetic acid. As the conjugated ketones and nitriles the following compounds

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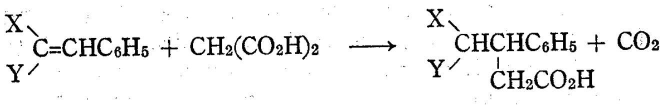
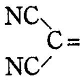
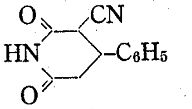
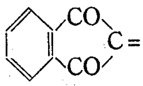
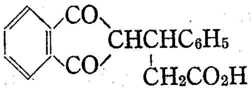
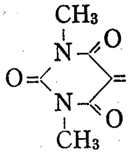
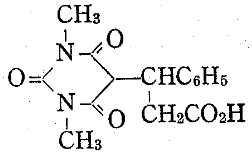
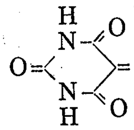
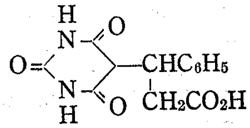
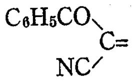
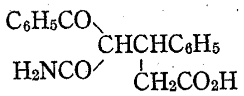
4) All melting points were uncorrected. IR and UV spectra were recorded on a Hitachi EPI-G2 spctrophotometer and a Hitachi EPS-3T spectrophotometer, respectively. NMR spectra were taken at 60 MHz with a JEOL-JNM-C-60H spectrometer using tetramethylsilane as an internal standard. The following abbreviations are used; s=singlet, d=doublet, t=triplet, m=multiplet.

TABLE II. Reaction[a] with Malonic Acid



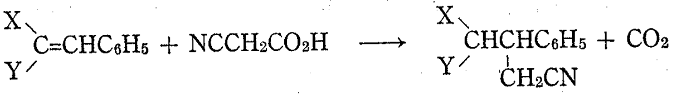
$$\begin{matrix}X\diagdown\\ \quad C{=}CHC_6H_5\\ Y\diagup\end{matrix} + CH_2(CO_2H)_2 \longrightarrow \begin{matrix}X\diagdown\\ \quad CHCHC_6H_5\\ Y\diagup\ \ |\quad\ \\ \quad CH_2CO_2H\end{matrix} + CO_2$$

Substrate $\left(\begin{matrix}X\diagdown\\ \quad C=\\ Y\diagup\end{matrix}\right)$	Product	Yield (%)
 $\begin{matrix}NC\diagdown\\ \quad C=\\ NC\diagup\end{matrix}$ (I)	 (XI)	49
 (II)	 (XII)	30
 (III)	 (XIII)	90 (53)[b]
 (IV)	 (XIV)	71
 $\begin{matrix}C_6H_5CO\diagdown\\ \quad C=\\ NC\diagup\end{matrix}$ (V)	 $\begin{matrix}C_6H_5CO\diagdown\\ \quad CHCHC_6H_5\\ H_2NCO\diagup\ \ |\quad\\ \quad CH_2CO_2H\end{matrix}$ (XV)	13

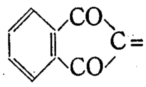
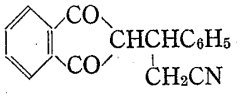
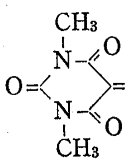
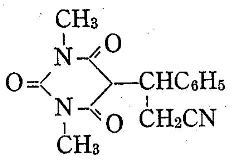
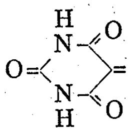
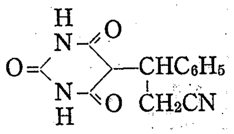
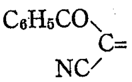
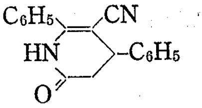
[a] normal condition: benzylidene compound:malonic acid=2:3 in molar proportion, solvent: pyridine, reaction temp.: 90—100°

[b] This run was carried out in dioxane in the presence of pyridine (1/2 molar proportion to the substrate).

TABLE III. Reaction[a] with Cyanoacetic Acid



$$\begin{matrix}X\diagdown\\ \quad C{=}CHC_6H_5\\ Y\diagup\end{matrix} + NCCH_2CO_2H \longrightarrow \begin{matrix}X\diagdown\\ \quad CHCHC_6H_5\\ Y\diagup\ \ |\quad\ \\ \quad CH_2CN\end{matrix} + CO_2$$

Substrate $\left(\begin{matrix}X\diagdown\\ \quad C=\\ Y\diagup\end{matrix}\right)$	Product	Yield (%)
 (II)	 (XVI)	29
 (III)	 (XVII)	66 (66)[b]
 (IV)	 (XVIII)	62
 $\begin{matrix}C_6H_5CO\diagdown\\ \quad C=\\ NC\diagup\end{matrix}$ (V)	 (XIX)	22

[a] normal condition: benzylidene compound:cyanoacetic acid=2:3 in molar proportion, solvent: pyridine, reaction temp.: 100—115°

[b] This run was carried out in dioxane in the presence of pyridine (1/2 molar proportion to the sbustrate).

shown with their melting points were used, which were prepared by the previously reported methods. benzylidenemalononitrile[5] (I), mp 82—83°; 2-benzylidene-1,3-indanedione[3b] (II), mp 154°; 5-benzylidene-1,3-dimethylbarbituric acid[3a] (III), mp 157—158°; 5-benzylidenebarbituric acid[3a] (IV), mp 254—256°; α-benzoylcinnamonitrile (V), mp 82—84°, which was prepared by condensation of benzoylacetonitrile with benzaldehyde using B_2O_3 as dehydrating agent, referring to the previous paper.[3b]

General Procedure——Normally each 0.01—0.02 mole of the conjugated unsaturated compounds (I, II, III, IV and V) and the carboxylic acid were used in 2 : 3 molar proportion. However, when self-decarboxylation of the carboxylic acid was occurred to a considerable extent (in the runs of I and V with acetoacetic acid, II and IV with malonic acid and V with cyanoacetic acid), additional amount of the carboxylic acid was used. For carrying out the reaction they are dissolved in dioxane (prefarable in the presence of pyridine) or in pyridine, and heated with stirring at the temperature causing considerable evolution of carbon dioxide. After subsidence of the evolution of carbon dioxide the reaction mixture was, in most runs, subjected to evaporation under reduced pressure and the residue was treated as described in the following. The reaction and yield of the product are listed in Table I, II and III.

Reactions with Acetoacetic Acid——1) Reaction of Benzylidenemalononitrile (I): Distillation of the oily residue under reduced pressure gave α-acetonylbenzylmalononitrile (VI). Redistillation gave pure material which boiled at 157° (0.5 mmHg) and solidified to crystals, mp 50—51°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2254 (CN), 1715 (CO). NMR ($CDCl_3$) τ: 7.80 (3H, s, $COCH_3$), 6.9 (2H, d, J=6.6 Hz, –CH_2–), 6.2 (1H, d.t, J=6.6 Hz, J=4.8 Hz, $>\mathrm{CH{-}\dot{C}\underline{H}{-}CH_2{-}}$), 5.5 (1H, d, J=4.8 Hz, $>\mathrm{C\underline{H}{-}\dot{C}H{-}CH_2{-}}$), 2.60 (5H, s, C_6H_5). *Anal.* Calcd. for $C_{13}H_{12}ON_2$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.31; H, 5.80; N, 12.91.

2) Reaction of 2-Benzylidene-1,3-indanedione (II): The residue was solidified by trituration with small amount of ethanol. Recrystallization from ethanol gave pure 2-(α-acetonylbenzyl)-1,3-indanedione (VII), prisms, mp 113—114° (lit.,[6] mp 113—114°). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1740, 1701 (CO). NMR ($CDCl_3$) τ: 7.82 (3H, s, $COCH_3$), 6.9 (1H, d.d, J=16.8 Hz, J=12.0 Hz, $-\mathrm{C\underline{H}_AH_B}-$), 6.5 (1H, d, J=3.6 Hz, $>\mathrm{C\underline{H}{-}\dot{C}H{-}CH_2{-}}$), 6.4 (1H, d.d, J=16.8 Hz, J=9.6 Hz, $-\mathrm{CH_A\underline{H}_B}-$), 5.9 (1H, d.d.d, J=12.0 Hz, J=9.6 Hz, J=3.6 Hz, $>\mathrm{CH{-}\dot{C}\underline{H}{-}CH_2{-}}$), 3.1—2.6 (5H, m, C_6H_5), 2.5—1.9 (4H, m, C_6H_5). *Anal.* Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.15; H, 5.68.

This reaction also proceeded in the absence of pyridine.

3) Reaction of 5-Benzylidene-1,3-dimethylbarbituric Acid (III): Dry ether was added to the residue and insoluble material was removed by filtration. After evaporation of the filtrate the residue was solidified by trituration with ethanol. Recrystallization from ethanol to give 5-(α-acetonylbenzyl)-1,3-dimethylbarbituric acid (VIII), prisms, mp 82°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1742, 1673 (CO), NMR ($CDCl_3$) τ: 7.77 (3H, s, $COCH_3$), 7.1 (1H, d.d, J=18.0 Hz, J=6.0 Hz, $-\mathrm{C\underline{H}_AH_B}-$), 6.98, 6.88 (6H, 2s, N–CH_3), 6.5 (1H, d.d, J=18.0 Hz, J=9.0 Hz, $-\mathrm{CH_A\underline{H}_B}-$), 6.1 (1H, d, J=4.2 Hz, $>\mathrm{C\underline{H}{-}\dot{C}HCH_2{-}}$), 5.9 (1H, d.d.d, J=9.0 Hz, J=6.0 Hz, J=4.2 Hz, $>\mathrm{CH{-}\dot{C}\underline{H}{-}CH_2{-}}$), 3.2—2.4 (5H, m, C_6H_5). *Anal.* Calcd. for $C_{16}H_{18}O_4N_2$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.57; H, 5.90; N, 9.31.

This reaction also proceeded in the absence of pyridine.

4) Reaction of 5-Benzylidenebarbituric Acid (IV): The residue obtained by evaporation was extracted with dry ether. After concentration of the ethereal solution crystals were deposited on cool. Recrystallization from ethanol gave 5-(α-acetonylbenzyl)barbituric acid (IX), prisms, mp 157—158°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3174, 3056 (NH), 1723, 1701 (CO). NMR [$(CD_3)_2SO$] τ: 7.87 (3H, s, $COCH_3$), 7.2—5.7 (4H, m, $>\mathrm{CH\dot{C}HCH_2{-}}$), 3.1—2.5 (5H, m, C_6H_5), *ca.* −1.0 (2H, broad s, NH). *Anal.* Calcd. for $C_{14}H_{14}O_4N_2$: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.35, H, 5.32; N, 10.35.

5) Reaction of β-Benzoylcinnamonitrile (V): The residue was dissolved in hot ethanol and in the solution crystals were deposited on cool. Recrystallization from ethanol gave needles of 3-hydroxy-1-oxo-3,5-diphenyl-4-cyclohexanecarbonitrile (X), mp 241—243°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3325 (OH), 2242 (CN), 1724 (CO). *Anal.* Calcd. for $C_{19}H_{17}O_2N \cdot C_2H_6O$: C, 74.75; H, 6.87; N, 4.15. Found: C, 75.03; H, 6.89; N, 4.24.

Recrystallization from dioxane gave needles, mp 240—241°. *Anal.* Calcd. for $C_{19}H_{17}O_2N \cdot 1/2C_4H_8O_2$: C, 75.20; H, 6.31; N, 4.18; Found: C, 75.20; H, 6.08; N, 4.31.

Reaction with Malonic Acid——1) Reaction of Benzylidenemalononitrile (I): A small amount of ethanol was added to the residue. The crystals deposited were collected by filtration and washed with ethanol. Recrystallization from ethanol gave 2-cyano-3-phenylglutarimide (XI), prisms, mp 218° (lit.,[7] mp 224—225°). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3198, 3094 (NH), 2255 (CN), 1724, 1682 (CO). NMR [$(CD_3)_2SO$] τ: 7.4 (1H, d.d, J=16.8 Hz, J=6.0 Hz, $-\mathrm{C\underline{H}_AH_B}-$), 7.0 (1H, d.d, J=16.8 Hz, J=10.8 Hz, $-\mathrm{CH_A\underline{H}_B}-$), 6.2 (1H, d.d.d, J=12.0 Hz, J=10.8 Hz, J=6.0 Hz, $>\mathrm{CH{-}\dot{C}\underline{H}{-}CH_2{-}}$), 5.1 (1H, d, J=12.0 Hz, $>\mathrm{C\underline{H}{-}\dot{C}HCH_2{-}}$), 2.62 (5H, s, C_6H_5), *ca.* −0.5 (1H, broad s, NH). *Anal.* Calcd. for $C_{12}H_{10}O_2N_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.35; H, 4.61; N, 13.50.

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[5] B.B. Corson and K.W. Stoughton, *J. Am. Chem. Soc.*, **50**, 2828 (1928).

[6] L. Zalukajevs, *Z. Obshch. Khim.*, **26**, 3125 (1956).

[7] C. Barat, *J. Indian Chem. Soc.*, **8**, 37 (1931).

2) Reaction of 2-Benzylidene-1,3-indanedione (II): The residue was washed with ethanol and crystals deposited were collected by filtration. Recrystallization from ethanol gave prisms of 1,3-dioxo-β-phenyl-2-indanpropionic acid (XII), mp 171—172° (lit.,[8] mp 173°). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3000—2500 (OH), 1739, 1701 (CO). NMR [$(\mathrm{CD_3})_2\mathrm{SO}$] τ: 7.1 (1H, d.d, $J=16.8$ Hz, $J=8.4$ Hz. $-\mathrm{C\underline{H}_AH_B}-$), 6.7 (1H, d.d, $J=16.8$ Hz, $J=7.2$ Hz, $-\mathrm{CH_A\underline{H}_B}-$), 6.3 (1H, d, $J=3.6$ Hz, $>\mathrm{C\underline{H}}-\dot{\mathrm{C}}\mathrm{HCH_2}-$), 6.0 (1H, d.d.d, $J=8.4$ Hz, $J=7.2$ Hz, $J=3.6$ Hz, $>\mathrm{CH}-\dot{\mathrm{C}}\mathrm{\underline{H}}-\mathrm{CH_2}-$), 2.95 (5H, s, $\mathrm{C_6H_5}$), 2.21 (4H, s, $\mathrm{C_6H_4}$). *Anal.* Calcd. for $\mathrm{C_{18}H_{14}O_4}$: C, 73.46; H, 4.80. Found: C, 73.46; H, 4.79.

3) Reaction of 5-Benzylidene-1,3-dimethylbarbituric Acid (III): The residue was washed with ethanol to give crystals. Recrystallization from ethanol gave pure hexahydro-1,3-dimethyl-2,4,6-trioxo-β-phenyl-5-pyridinepropionic acid (XIII), needles, mp 201—203°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3000—2500 (OH), 1720, 1659 (CO). NMR [$(\mathrm{CD_3})_2\mathrm{SO}$] τ: 7.7—5.8 (4H, m, $>\mathrm{CH}\dot{\mathrm{C}}\mathrm{HCH_2}-$), 7.12, 7.07 (6H, 2s, $\mathrm{N-CH_3}$), 3.2—2.5 (5H, m, $\mathrm{C_6H_5}$). *Anal.* Calcd. for $\mathrm{C_{15}H_{16}O_5N_2}$: C, 59.20; H, 5.30; N, 9.21. Found: C, 59.22; H, 5.38; N, 9.31.

This reaction also proceeded in the presence of pyridine in dioxane to give the same product as above.

4) Reaction of 5-Benzylidenebarbituric Acid (IV): The residue was washed with ethanol to give the pyridine salt as a crystalline solid. This solid was dissolved in 5% hydrochloric acid and crystals deposited on standing were filtered, washed with water and dried. The resulting crystals were pure hexahydro-2,4,6-trioxo-β-phenyl-5-pyrimidinepropionic acid (XIV), prisms, mp 187—189°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3217, 3098 (NH), 3000—2500 (OH), 1756, 1710 (CO). NMR [$(\mathrm{CD_3})_2\mathrm{SO}$] τ: 7.5—5.8 (4H, m, $>\mathrm{CH}\dot{\mathrm{C}}\mathrm{HCH_2}-$), 3.1—2.6 (5H, m, $\mathrm{C_6H_5}$), *ca.* -1.1 (2H, broad s, NH). *Anal.* Calcd. for $\mathrm{C_{13}H_{12}O_5N_2}$: C, 56.52; H, 4.38; N, 10.14. Found: C, 56.32; H, 4.29; N, 10.02.

5) Reaction of β-Benzoylcinnamonitrile (V): The residue was solidified by washing with hot petr. ether. Recrystallization from ethanol gave 4-benzoyl-3-phenylglutaramic acid (XV), needles, mp 200°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3441, 3305 (NH), 3000—2500 (OH), 1714, 1670, 1624 (CO). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 246 (4.12). NMR [$(\mathrm{CD_3})_2\mathrm{SO}$] τ: 7.5—4.8 (4H, m, $>\mathrm{CH}\dot{\mathrm{C}}\mathrm{HCH_2}-$), 3.1—1.6 (12H, m, $\mathrm{C_6H_5}$, NH). *Anal.* Calcd. for $\mathrm{C_{18}H_{17}O_4N}$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.30; H, 5.49; N, 4.60.

Reaction with Cyanoacetic Acid——1) Reaction of 2-Benzylidene-1,3-indanedione (II): The residue was dissolved in ethanol and a small amount of insoluble material was removed by filtration. After evaporation of ethanol the residue was extracted with ether under refluxing. The ethereal layer was concentrated to dryness. The solid residue was recrystallized from ethanol to give 1,3-dioxo-β-phenyl-2-indanpropionitrile (XVI), needles, mp 122°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2243 (CN), 1747, 1708 (CO). NMR ($\mathrm{CDCl_3}$) τ: 6.9 (1H, d.d, $J=16.2$ Hz, $J=7.2$ Hz, $-\mathrm{C\underline{H}_AH_B}-$), 6.55 (1H, d.d, $J=16.2$ Hz, $J=9.0$ Hz, $-\mathrm{CH_A\underline{H}_B}-$), 6.5 (1H, d, $J=3.6$ Hz, $>\mathrm{C\underline{H}}-\mathrm{CHCH_2}-$), 6.0 (1H, d.d.d, $J=9.0$ Hz, $J=7.2$ Hz, $J=3.6$ Hz, $>\mathrm{CH}-\dot{\mathrm{C}}\mathrm{\underline{H}}-\mathrm{CH_2}-$), 2.85 (5H, s, $\mathrm{C_6H_5}$), 2.5—1.9 (4H, m, $\mathrm{C_6H_4}$). *Anal.* Calcd. for $\mathrm{C_{18}H_{13}O_2N}$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.44; H, 4.70; N, 4.80.

2) Reaction of 5-Benzylidene-1,3-dimethylbarbituric Acid (III): The residue was washed with ethanol to give a crystalline solid. Recrystallization from ethanol gave hexahydro-1,3-dimethyl-2,4,6-trioxo-β-phenyl-5-pyrimidinepropionitrile (XVII), prisms, mp 125—126°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 2245 (CN), 1750, 1671 (CO). NMR ($\mathrm{CDCl_3}$) τ: 7.0 (1H, d.d, $J=16.8$ Hz, $J=7.8$ Hz, $-\mathrm{C\underline{H}_AH_B}-$), 6.92, 6.90 (6H, 2s, $\mathrm{N-CH_3}$), 6.6 (1H, d.d, $J=16.8$ Hz, $J=9.0$ Hz, $-\mathrm{CH_A\underline{H}_B}-$), 6.2 (1H, d, $J=3.6$ Hz, $>\mathrm{C\underline{H}}-\dot{\mathrm{C}}\mathrm{HCH_2}-$), 5.9 (1H, d.d.d, $J=9.0$ Hz, $J=7.8$ Hz, $J=3.6$ Hz, $>\mathrm{CH}-\dot{\mathrm{C}}\mathrm{\underline{H}}-\mathrm{CH_2}-$), 3.2—2.3 (5H, m, $\mathrm{C_6H_5}$). *Anal.* Calcd. for $\mathrm{C_{15}H_{15}O_3N_3}$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.02; H, 5.23; N, 14.98.

This reaction also proceeded in the presence of pyridine in dioxane to give the same product as above.

3) Reaction of 5-Benzylidenebarbituric Acid (IV): In this run, on cool the pyridinium salt of the product was precipitated in the reaction solution. To the aqueous solution of this salt addition of hydrochloric acid gave hexahydro-2,4,6-trioxo-β-phenyl-5-pyrimidinepropionitrile (XVIII) as almost pure crystals, needles, mp 197—199°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3234, 3123 (NH), 2246 (CN), 1755, 1708 (CO). NMR [$(\mathrm{CD_3})_2\mathrm{SO}$] τ: 7.7—5.6 (4H, m, $>\mathrm{CH}\dot{\mathrm{C}}\mathrm{HCH_2}-$), 3.3—2.5 (5H, m, $\mathrm{C_6H_5}$), *ca.* -1.2 (2H, broad s, NH). *Anal.* Calcd. for $\mathrm{C_{13}H_{11}O_3N_3}$: C, 60.69; H, 4.31; N, 16.34. Found: C, 60.36; H, 4.41; N, 16.23.

4) Reaction of β-Benzoylcinnamonitrile (V): After topping a distillable by-product off under high reduced pressure the residue was dissolved in hot ethanol, whereupon a small amount of insolved material was removed by filtration. On cool the crystals of 1,2,3,4-tetrahydro-2-oxo-4,6-diphenyl-5-pyridinecarbonitrile (XIXI) were deposited. Recrystallization from ethanol gave prisms, mp 197°. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3188, 3123 (NH), 2200 (CN), 1683, 1620 (CO). UV $\nu_{\max}^{\mathrm{EtOH}}$ nm (log ε): 292 (4.01). NMR [$(\mathrm{CD_3})_2\mathrm{SO}$] τ: 7.3 (1H, d.d, $J=16.2$ Hz, $J=5.4$ Hz, $-\mathrm{C\underline{H}_AH_B}-$), 6.9 (1H, d.d, $J=16.2$ Hz, $J=6.6$ Hz, $-\mathrm{CH_A\underline{H}_B}-$), 5.9 (1H, d.d, $J=6.6$ Hz, $J=5.4$ Hz, $>\mathrm{CH}-$), 2.6 (5H, s, $\mathrm{C_6H_5}$), 2.9—2.1 (5H, m, $\mathrm{C_6H_5}$), *ca.* -0.6 (1H, broad s, NH). *Anal.* Calcd. for $\mathrm{C_{18}H_{14}ON_2}$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.29; H, 5.27; N, 10.02.

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[8] M. Ionescu, *Bull. Soc. Chim.*, 37, 913 (1925).