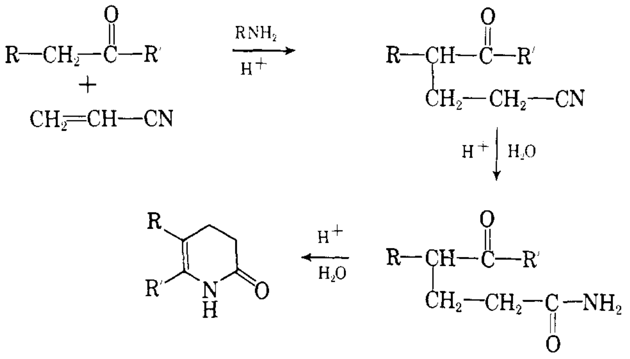
structures of all compounds were confirmed by elemental analyses and infrared and n.m.r. spectra.

The reaction path involves formation of the α-monocyanoethyl ketone, hydrolysis to the amide, and cyclodehydration to the γ,δ-unsaturated lactam.



Thus, Ia can be formed either by heating 2-(2′-cyanoethyl)cyclohexanone with a trace of 90% sulfuric acid or 50% acetic acid or by heating 2-(2′-ketocyclohexyl)propionamide with a trace of 100% sulfuric acid or glacial acetic acid.

Experimental

1,2,3,4,5,6,7,8-Octahydro-2-quinolone (Ia).—A mixture of cyclohexanone (1960 g., 20 moles), technical acrylonitrile (1060 g., 20 moles), cyclohexylamine (101 g., 1.02 moles), and glacial acetic acid (23 g., 0.34 moles) were heated with vigorous stirring. At 90°, a strongly exothermic reaction occurred; when the exotherm had subsided, heating was resumed and the mixture was maintained at 200° for 4 hr.

The product was vacuum distilled to give 2360 g. (79%) of Ia, b.p. 150–152° (1 mm.). Recrystallization from methanol–water gave white needles, m.p. 144–145° (lit.[2,3] m.p. 143–144°, 144°).

The infrared spectrum contained strong absorptions at 1680 and 1640 cm.$^{-1}$. The n.m.r. spectrum showed an NH absorption at 9.4 p.p.m., no bridgehead absorption in the 3–5-p.p.m. region, and a ratio of NH to protons of 1:12.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.48; H, 8.67; N, 9.26. Found: C, 71.48; H, 8.83; N, 9.18.

6-Methyl-1,2,3,4,5,6,7,8-octahydro-2-quinolone (Ib).—A mixture of 4-methylcyclohexanone (100 g., 0.89 mole), technical acrylonitrile (47 g., 0.89 mole), 4-methylcyclohexylamine (5 g.), and 50% acetic acid (2 ml.) was heated with vigorous stirring. After a mild exotherm at 90°, the mixture was heated to 200° for 4 hr. Upon cooling, a yellow solid mass formed. The solid was recrystallized from ethanol to give 75 g. (50%) of Ib, m.p. 138–139°. No attempt was made to obtain a second crop of product.

The infrared and n.m.r. spectra showed the same significant features as Ia and were consistent with the proposed structure.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.54; H, 9.30; N, 8.70.

6-Methyl-1,2,3,4-tetrahydro-2-pyridone (II).—A mixture of acetone (116 g., 2.0 mole), acrylonitrile (53 g., 1.0 mole), ammonium acetate (3.8 g., 0.05 mole), and 3 ml. of 29% aqueous ammonia was charged into a 300-ml. pressure vessel. The vessel was placed in an oil bath at 225°. Pressure rose rapidly to 350 p.s.i.g. and fell slowly; after 40 min., the pressure was constant at 280 p.s.i.g. The vessel was cooled to room temperature and the reaction mixture was distilled. After a forerun of acetone, a fraction was collected at 95–100° (9 mm.).

The distillate was chilled in ice and the precipitated solid was filtered. Recrystallization from ethanol gave 16.6 g., (15%) of II, m.p. 119–120°.

The infrared spectrum contained strong absorption at 1685 and 1635 cm.$^{-1}$. The n.m.r. spectrum showed olefinic absorption at 5.5 p.p.m. and was otherwise consistent with the proposed structure.

Anal. Calcd. for C_6H_8NO: C, 72.06; H, 8.06; N, 14.01. Found: C, 72.02; H, 8.14; N, 14.20.

The mother liquor was redistilled at 108–110° at 14 mm. to give 55 g. (50%) of 5-oxohexanenitrile (lit.[4] b.p. 108–112° at 14 mm.). The identity was confirmed by comparison of its infrared spectrum with that of an authentic sample.

1,2,3,4,6,7-Hexahydro-5H-1-pyrind-2-one (III).—A mixture of cyclopentanone (84 g., 1.0 mole), acrylonitrile (53 g., 1.0 mole), ammonium acetate (3.8 g., 0.05 mole), and 3 ml. of 29% aqueous ammonia were charged into a 300-ml. pressure vessel. The vessel was placed in an oil bath at 220°. Pressure rose rapidly to 125 p.s.i.g. and fell slowly; after 30 min., the pressure was constant at 100 p.s.i.g. The product was worked up in the same way as the previous run to give 23 g. (18%) of III, m.p. 103.5–105°, and 20 g. (17%) of 2-(2′-cyanoethyl)cyclopentanone, b.p. 98–100° at 1 mm. (lit.[1] b.p. 98–105° at 0.9 mm.).

The infrared spectrum contained strong absorption at 1690 and 1640 cm.$^{-1}$. The n.m.r. spectrum contained no bridgehead proton absorption in the 3–5-p.p.m. region and was consistent with the proposed structure.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.25; H, 8.12; N, 10.25.

Cyclization of 2-(2′-Cyanoethyl)cyclohexanone.—Samples (15.1 g., 0.1 mole) were heated at 200° for 4 hr. with the following catalysts: 1 ml. of glacial acetic acid, 1 ml. of concentrated sulfuric acid, 1 ml. of 50% acetic acid, and 1 ml. of 90% sulfuric acid. No change was observed with the first two, while essentially quantitative yields of Ia were obtained with the latter two.

Cyclization of 2-(2′-Ketocyclohexyl)propionamide.—Samples (16.9 g., 0.1 mole) were heated at 200° for 4 hr. with the same catalysts as the previous experiment. In all cases, essentially quantitative yields of Ia were obtained.

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An Improved Procedure for the Preparation of 2-Alkyl-5-carbethoxycyclopentanone

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2-Alkyl-5-carbethoxycyclopentanones are usually made through Dieckmann condensation of ethyl 2-alkyladipates which are prepared from 2-carbethoxycyclopentanones *via* 2-alkyl-2-carbethoxycyclopentanones.[1]

This paper describes an improved procedure for the preparation of 2-alkyl-5-carbethoxycyclopentanones from 2-alkyl-2-carbethoxycyclopentanones.

When ethyl 2-methyladipate was prepared from 2-methyl-2-carbethoxycyclopentanone[2,3] by treatment with a catalytic amount of sodium ethoxide in absolute ethanol,[3] the product, ethyl 2-methyladipate, was observed to be contaminated with 2-methyl-5-carbethoxycyclopentanone.[4] According to the present investigation, it was found that when 2-methyl-2-carbethoxycyclopentanone (I) was treated with equimolar sodium ethoxide in absolute ethanol, 2-methyl-5-carbethoxy-

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[4] For 2-methyl-2-carbethoxycyclohexanone, see D. K. Banerjee and S. N. Mahapatra, *Tetrahedron*, **11**, 234 (1960).

TABLE I

2-ALKYL-5-CARBETHOXYCYCLOPENTANONE

Alkyl	Yield, %	B.p., °C. (mm.)	$n^{20}D$	Ref.
CH_3	85	88 (6)	1.4458	3
C_2H_5	87	87 (4)	1.4505	11
$(CH_3)_2CH$	82	92 (4)	1.4520	12
$(CH_3)_2CHCH_2$	85	98–100 (4)	1.4517	a

[a] *Anal.* Calcd. for $C_{12}H_{20}O_3$: C, 67.87; H, 9.50. Found: C, 67.42, H, 9.58.

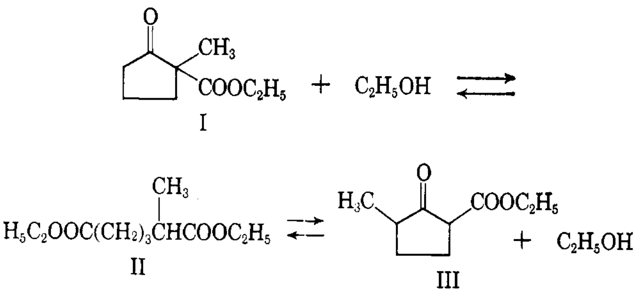
TABLE II

EQUILIBRIUM OF 2-ALKYL-2-CARBETHOXYCYCLOPENTANONES

	2-Alkyl-5-carbethoxycyclopentanone				Ethyl 2-alkyladipate			
Alkyl	Yield, %	B.p., °C. (mm.)	$n^{20}D$	Ref.	Yield, %	B.p., °C. (mm.)	$n^{20}D$	Ref.
CH_3	66	87 (6)	1.4460	3	15	102 (5)	1.4295	3
C_2H_5	66	88 (4)	1.4501	11	16	106 (4)	1.4309	11
$(CH_3)_2CH$	68	92 (4)	1.4523	12	14	107 (4)	1.4340	12
$(CH_3)_2CHCH_2$	63	98 (4)	1.4513	..	14	110 (4)	1.4372	a

[a] *Anal.* Calcd. for $C_{14}H_{26}O_4$: C, 65.08; H, 10.10. Found: C, 65.30; H, 9.92.

cyclopentanone (III) and ethyl 2-methyladipate (II) were obtained in 66% and 15% yield, respectively. When ethyl 2-methyladipate (II) or 2-methyl-5-carbethoxycyclopentanone (III) was treated in the same way the results were essentially the same as in the case of 2-methyl-2-carbethoxycyclopentanone (I)—namely, 2-methyl-5-carbethoxycyclopentanone (III) and ethyl-2-methyladipate (II) were observed to exist in yields of 65% and 18%, or 71% and 22%, respectively.



As to this type of equilibrium in alicyclic system ethyl 3-(1-carbethoxy-2-oxocyclopentyl)propionate[5] and other cyclic compounds[6–10] have been studied.

Removing ethanol by azeotropic distillation with toluene shifted the equilibrium to the right. The yield of 2-methyl-5-carbethoxycyclopentanone (III) was increased to 85% with no appreciable amount of ethyl 2-methyladipate (II) being formed.

Other homologs were treated similarly. From 2-ethyl-,[11] 2-isopropyl-,[12] and 2-isobutyl-2-carbethoxycyclopentanone[13] there were obtained 2-ethyl-,[11] 2-isopropyl-,[12] and 2-isobutyl-5-carbethoxycyclopentanone, respectively, in good yields. These results are shown in Table I.

When alkyl halide was added to this reaction mixture, 2-alkyl-5-alkyl-5-carbethoxycyclopentanone was obtained in good yield.[14]

Experimental

Preparation of 2-Alkyl-5-carbethoxycyclopentanone.—To a sodium ethoxide solution, prepared from 510 ml. of absolute ethanol and 34.5 g. (1.5 g.-atom) of sodium were added 1.5 moles of 2-alkyl-2-carbethoxycyclopentanone.[2,3,11–14] The solution was heated under reflux for 8 hr., and about a half of the ethanol was removed by distillation. On addition of 500 ml. of toluene the remainder of ethanol was distilled off azeotropically. The residue was poured into 1.5 l. of 10% acetic acid under ice cooling. The aqueous layer was extracted three times with a 300-ml. portion of benzene. The organic layer and the benzene extract were combined and washed with 7% sodium carbonate solution and water. The mixture of benzene and toluene was removed and the residue was fractionated with a Podbielniak-type column of 50-cm. long. Results are shown in Table I.

When toluene was not added, that is, after treatment with sodium ethoxide in absolute ethanol the reaction mixture was poured into 1.5 l. of 10% acetic acid and treated as above, 2-alkyl-5-carbethoxycyclopentanone and ethyl 2-alkyladipate were obtained. Results are shown in Table II.

Reaction of 2-Methyl-5-carbethoxycyclopentanone (III) with Sodium Ethoxide.—To a solution of 40 ml. of absolute ethanol and 2.5 g. of sodium, 17.0 g. of 2-methyl-5-carbethoxycyclopentanone (III) was added and the mixture was heated under reflux for 8 hr. Working up the reaction mixture analogously gave 10.9 g. (65%) of 2-methyl-5-carbethoxycyclopentanone (III) and 3.9 g. (18%) of ethyl 2-methyladipate (III).

Dieckmann Condensation of Ethyl 2-Methyladipate (II) in Absolute Ethanol.—To a solution of 30 ml. of absolute ethanol and 2.3 g. of sodium, 18.0 g. of ethyl 2-methyladipate[3] (II) was added and refluxed for 8 hr. After cooling, the reaction mixture was poured into 100 ml. of 10% acetic acid and extracted with benzene. The benzene solution was washed with water, 7% sodium carbonate solution, and water. After removal of benzene the residue was fractionated to afford 10.1 g. (71%) of 2-methyl-5-carbethoxycyclopentanone (III), b.p. 89–92° (5 mm.), and 4.0 g. (22%) of ethyl 2-methyladipate (II), b.p. 105–115° (5 mm.).

Dieckmann Condensation of Ethyl 2-Methyladipate (II) in Toluene.—To a solution of 35 ml. of absolute ethanol and 2.5 g. of sodium, 20.0 g. of ethyl 2-methyladipate was added. After 8 hr. of refluxing 15 ml. of ethanol was removed from the reaction mixture and on addition of 150 ml. of toluene ethanol was removed completely as an azeotropic mixture with toluene until the boiling point of the distilate became 110°. The reaction mixture was poured into 120 ml. of 10% acetic acid and the toluene layer was washed with water, 7% sodium carbonate solution, and water. After removal of toluene, the product was distilled to afford 12.6 g. (80%) of 2-methyl-5-carbethoxycyclopentanone (III), b.p. 87–92° (5 mm.).

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