Preparation of Diurethan of Pyrazine-2,5-dicarboxylic Acid.—Seventy-seven hundredths gram of the dried azide was suspended in 200 cc. of absolute ethanol and warmed gradually in a water-bath to boiling. It was then refluxed for one hour during which time the azide dissolved. The mixture was evaporated *in vacuo* to a small volume, cooled, filtered, and dried *in vacuo*; yield 0.70 g.; m. p. above 270°. The crude product was purified by digesting in a large volume of absolute ethanol, filtering, washing with ether and drying *in vacuo*.

Anal. Calcd. for $C_{10}H_{14}O_4N_4$: C, 47.24; H, 5.51; N, 22.05. Found: C, 47.20, 47.37; H, 5.80, 5.89; N, 22.29, 22.76.

A series of experiments attempting to hydrolyze the urethan included the following methods

(1) Urethan + fuming hydrochloric acid in bomb tube at 110° for four hours
(2) Urethan + fuming hydrochloric acid in bomb tube at 150° for fifteen hours
(3) Urethan + fuming hydrochloric acid in bomb tube at 210° for fifteen hours
(4) Urethan + alcoholic potassium hydroxide, refluxed on water-bath for two hours
(5) Urethan + concd. sulfuric acid
(6) Urethan + solid potassium hydroxide, fused and steam distilled

Preparation of Diisocyanate of Pyrazine-2,5-dicarboxylic Acid.—Seven-tenths gram of dried azide was suspended in 250 cc. of dry benzene and warmed on a water-bath to boiling. After refluxing for two hours, the mixture was concentrated *in vacuo*, cooled and filtered. The yellow amorphous isocyanate was washed with ether and dried *in vacuo*; yield 0.48 g.; m. p. 250°. A sample for analysis was digested in a large volume of dry benzene, filtered, washed twice with ether and dried *in vacuo*.

Anal. Calcd. for $C_6H_2O_2N_2$: C, 44.44; H, 1.24. Found: C, 44.15, 44.06; H, 1.89, 1.70.

Preparation of Diamide of Pyrazine-2,5-dicarboxylic Acid.—One gram of dimethyl ester was dissolved in 50 cc. of hot absolute methanol and refluxed for one-half hour while passing through a stream of ammonia. The reaction mixture was chilled in an ice-bath, saturated with ammonia, and allowed to stand overnight. The mixture was concentrated *in vacuo* on a water-bath, chilled, and the white amorphous amide filtered off and dried *in vacuo*; yield 0.75 g.; m. p. above 270°.

Anal. Calcd. for $C_6H_6O_2N_4$: C, 43.37; H, 3.61 Found: C, 43.75, 44.00; H, 3.95, 3.73.

Summary

In an attempt to apply the Curtius and Hofmann rearrangements to the pyrazine series, the intermediate products characteristic of these series of reactions have been isolated in pure form.

Starting with the known pyrazine-2,5-dicarboxylic acid, the following new derivatives have been prepared and described: (1) dimethyl ester, (2) dihydrazide, (3) diazide, (4) diurethan, (5) diisocyanate, (6) diamide, (7) diacid chloride.

BROOKLYN, N. Y. RECEIVED DECEMBER 4, 1937

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

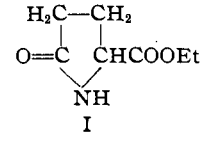
The Selective Hydrogenation of Substituted Amides

BY JOHN C. SAUER AND HOMER ADKINS

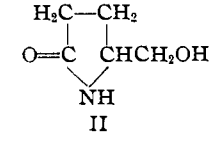
Hydrogen under 100 to 300 atm. reacts with amides in dioxane at 200–260° under the influence of copper–chromium oxide to give amines.[1] Alkenes, ketones, aldehydes, cyanides, oximes, furanoid and pyridinoid nuclei react with hydrogen under much less drastic conditions so that among the unsaturated groups probably only benzenoid and pyrroloid nuclei and perhaps carbalkoxy groups will remain unchanged during the hydrogenation of an amide. The study reported herewith is primarily concerned with the behavior toward hydrogen of several compounds which are amido or carbethoxy pyrrolidones, piperidones, or quinolones. The objective of the investigation has been to ascertain the relationship of structure to the relative reactivity with hydrogen of the amide and ester groups concerned. The results are summarized in Table I.

(1) Wojcik and Adkins, THIS JOURNAL, **56**, 2419 (1934); Paden and Adkins, *ibid.*, **58**, 2487 (1936).

Pyrrolidones.—5-Carbethoxypyrrolidone-2, I, was hydrogenated rapidly, the ester group being converted in 93% yield to a carbinol group, II, without any reaction occurring at the amide group.

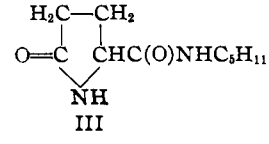


I

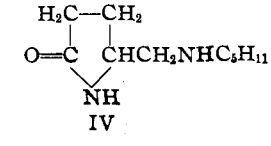


II

In a similar fashion the side chain amide group in 5-amylcarbamylpyrrolidone-2, III, was hydrogenated in preference to the lactam group in the ring, the chief product in 68% yield being 5-amylaminomethylenepyrrolidone-2, IV. The minor



III



IV

TABLE I

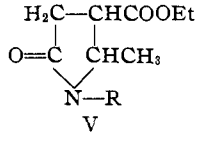
HYDROGENATION OF AMIDES AND ESTERS OVER COPPER–CHROMIUM OXIDE

Hydrogen acceptor	Moles Comp.	H_2	Temp., °C.	Time, min.	%	Yield of products
5-Carbethoxypyrrolidone-2	0.24	0.47	210–220	30	93	5-Hydroxymethylpyrrolidone-2
5-*n*-Amylcarbamylpyrrolidone-2	.15	.36	210	35	68	5-*n*-Amylaminomethylpyrrolidone-2
1-*n*-Amyl-4-carbethoxy-5-methyl-2,3-dihydropyrrolone-2	.08	.35	220–230	40	60	1-*n*-Amyl-5-methyl-4-hydroxymethylpyrrolidone-2
					15	1-*n*-Amyl-2-methyl-3-carbethoxypyrrolidone-5
					15	1-*n*-Amyl-2-methyl-3-hydroxymethylpyrrolidine
1-Phenethyl-4-carbethoxy-5-methylpyrrolidone-2	.15 (.04)[a]	.30	235–240	35	55	1-Phenethyl-4-hydroxymethyl-5-methylpyrrolidone-2
					13	1-Phenethyl-2,3-dimethylpyrrolidine
1-*n*-Amyl-5-carbethoxy-6-methylpiperidone-2	.19 (.04)	.41	240–250	20	49	1-*n*-Amyl-5-hydroxymethyl-6-methylpiperidone-2
					30	1-*n*-Amyl-2,3-dimethylpiperidine
1-*n*-Amyl-5-*n*-amylcarbamylpiperidone-2	.12 (.04)	.22	235–240	60	60	1-*n*-Amyl-3-*n*-amylcarbamylpiperidine
					31	1-*n*-Amyl-3-hydroxymethylpiperidine
					6	1-*n*-Amyl-3-*n*-amylaminomethylpiperidine
4-Carbethoxyquinolone-2	.08	.25	215–220	15	29	4-Hydroxymethyldihydroquinolone-2
					9	4-Carbethoxydihydroquinolone-2[4]
					24	4-Methyl-1,2,3,4-tetrahydroquinoline
4-Carbethoxyquinolone-2	.12	.71	210–215	20	82	1,2,3,4-Tetrahydro-4-methylquinoline
3-Carbethoxydihydroquinolone-2	.13 (.04)	.30	220–225	30	66	1,2,3,4-Tetrahydroquinoline[2,3]
β-Carbethoxypropionylpiperidine	.23 (.12)	.46	230	35	57	4-Piperidinobutanol-1
					20	Butanediol-1,4
β-Carbethoxypropionylpiperidine	.10	.40	240	90	62	4-Piperidinobutanol-1[5]
					28	Butanediol-1,4[6]
Δ-Carbethoxyvalerylpiperidine	.17 (.05)	.40	235–240	60	35	6-Piperidinohexanol-1
					33	Hexanediol-1,6[7]

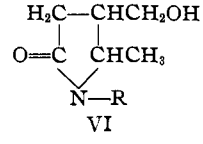
[a] The figures in parentheses represent the moles of original compound recovered. Yields are based upon amide not recovered.

products apparently included 5-hydroxymethylpyrrolidine and 2-amylaminomethylenepyrrolidine in yields totaling 25%, but these further hydrogenation products could not be separated or characterized with certainty.

Two β-carbethoxypyrrolidones, V, where R is *n*-amyl or phenethyl, were submitted to the action of hydrogen. The compound placed in the reaction vessel in one case was a dihydropyrrolone (Table I) but this was converted to a pyrrolidone by hydrogenation during the interval of heating the reactants to 200°.



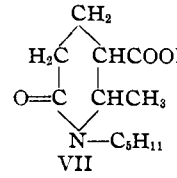
V



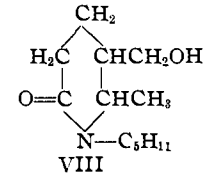
VI

The carbethoxy group in these pyrrolidones was preferentially hydrogenated to a carbinol group, the yield of the amido alcohol, VI, bring 50 to 60% upon the basis of the material reacting with hydrogen. However, if reaction was allowed to proceed the carbonyl of the lactam was converted to a methylene group. The reaction may go even further with the reduction of the carbinol group and the formation of a pyrrolidine.

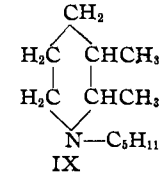
Piperidones.—The β-carbethoxypiperidone, VII, reacted with hydrogen first at the carbethoxy rather than at the carbonyl in the cyclic amide. The carbinol, VIII, was the chief product, but



VII



VIII



IX

even when less than 75% of the original ester had reacted, there had already been formed a 24% yield of the piperidine IX. There were thus three competing reactions, *i. e.*, conversion of carbethoxy to carbinol, of carbonyl of the amide to methylene, and of carbinol to methyl. The two latter reactions took place almost as readily as the first, so that only about half of the ester reacting was separated as the alcohol.

(2) M. p. hydrochloride, 180–180°; Friedlaender and Ostermaier, *Ber.*, **15**, 335 (1882).

(3) M. P. hydrobromide, 167°; v. Braun, *ibid.*, **42**, 2223 (1909).

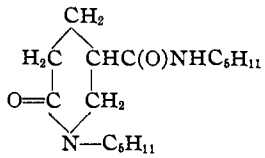
(4) M. p. 155°; Hill, Schultz and Lindwall, THIS JOURNAL, **52**, 773 (1930).

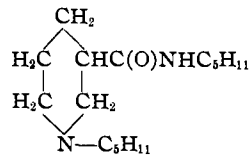
(5) M. p. hydrochloride, 160–161°; v. Braun, *Ber.*, **49**, 973 (1916).

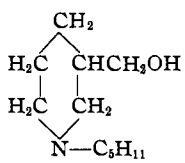
(6) M. p. phenylurethan, 183°; Müller, *Monatsh.*, **49**, 27–30 (1928).

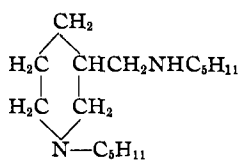
(7) M. p. dibenzoate, 56°; Hamonet, *Bull. soc. chim.*, [3] **33**, 539 (1905).

In contrast with all the cases noted above the initial point of reaction in the diamide, X, was at the carbonyl in the ring, the chief product being the piperidine, XI. The secondary product involved a hydrogenolysis of a carbon to nitrogen bond with the formation of the carbinol XII, accompanied by a few per cent. of the diamine XIII resulting from hydrogenation of both amide groups.

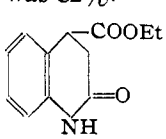

X

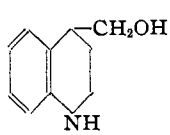

XI

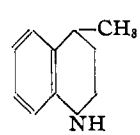

XII


XIII

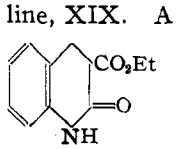
Quinolones.—In the case of the quinolones the first reaction is the addition of two hydrogens to the pyridinoid nucleus, a reaction which takes place under relatively mild conditions. The 4-carbethoxy-dihydroquinolone-2 thus formed from 4-carbethoxy-quinolone-2, XIV, undergoes reaction at the amide and carbethoxy groups with the formation of the carbinol, XV, which is then converted in part to a methyl group as in XVI. The yields of these two compounds (24 to 29%) were similar when the reaction was interrupted after the absorption of about three moles of hydrogen per mole of quinolone. However, if the reaction was allowed to go to completion the yield of the 4-methyltetrahydroquinoline, XVI, was 82%.

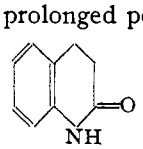

XIV

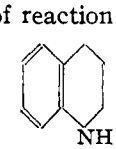

XV


XVI

When the carbethoxy group was in the 3-position in a dihydroquinolone-2, XVII, the carbethoxy group was first eliminated by hydrogenolysis. The resulting dihydroquinolone-2, XVIII, was then in part converted to tetrahydroquinoline, XIX. A more prolonged period of reaction resulted in an 85% yield of XIX as the only reaction product.


XVII


XVIII


XIX

Open Chain Amido Esters.—Two pentamethylene amido esters of the type $C_5H_{10}NC(O)(CH_2)_nCO_2Et$ were allowed to absorb from 2 to 2.5 moles of hydrogen per mole of compound in an attempt to determine whether the amide or the carbethoxy group would be hydrogenated first. It was found that even when 30 to 50% of the original compound remained in the reaction mixture there was no evidence of a hydroxy amide or an amino ester of the types $C_5H_{10}NC(O)(CH_2)_nCH_2OH$ or $C_5H_{11}NCH_2(CH_2)_nCOOEt$. The products found were the amino alcohol (35–57%) or glycol (20–33%), resulting from reduction of both the esters and amide groups. The absorption of four moles of hydrogen per mole of $C_5H_{10}NC(O)(CH_2)_2COOEt$ resulted in a 62% yield of 1-piperidinobutanol-4.

The results given above may be summarized as follows:

1. There appears to be no difference between the relative ease of hydrogenation of a carbethoxy group and an amide group when both are similarly placed in the same molecule.

2. A carbethoxy or amido group in the 5-position in a pyrrolidone-2 is more reactive toward hydrogen than is the lactam group of the ring. In the case of the ester the reaction may be readily stopped at the alcohol stage. The alcohol may also be obtained from the 4-carbethoxypyrrolidone-2, but further reaction occurs more readily than in the case of the compound substituted in the 5-position.

3. A carbethoxy group in the 5-position of a piperidone-2 was hydrogenated more readily than the lactam group but the difference between the readiness of hydrogenation of the ester and amide groups was much less in the piperidones than in the pyrrolidones. Subsequent reactions involving both the carbinol and amide groups took place readily under the same conditions.

4. A carbethoxy group in the 4-position of a tetrahydroquinolone-2 reacted before the lactam group and gave an alcohol.

5. A carbethoxy group in the 3-position of a dihydroquinolone-2, since it is a derivative of a malonic ester, was removed by hydrogenolysis.[8]

6. An amide group in a chain was less reactive toward hydrogen than the amide group in a piperidone.

(8) Connor and Adkins, THIS JOURNAL, 54, 4678 (1932).

TABLE II

ANALYTICAL DATA FOR UNREPORTED COMPOUNDS

Compound	Formula	B. p. or m. p. °C.	Mm.	$n^{25}D$	Nitrogen, % Calcd.	Found	Name	Derivative m. p.	Calcd.	Found
β-Carbethoxy-propionyl-piperidine	$C_{11}H_{19}O_3N$	B. 108	1	1.4769	6.57	6.64				
Δ-Carbethoxyvaleryl-piperidine	$C_{13}H_{23}O_3N$	B. 134–136	1	1.4762	5.81	5.80				
1-Amyl-4-carbethoxy-5-methylpyrrolidone-2	$C_{13}H_{23}O_3N$	B. 153	3	1.4630	5.81	5.79				
1-β-Phenethyl-4-carbethoxy-5-methylpyrrolidone-2	$C_{16}H_{21}O_3N$	B. 167	1		5.09	5.16				
1-β-Phenethyl-2,3-dihydro-4-carbethoxy-5-methyl-pyrrolone-2	$C_{16}H_{19}O_3N$	M. 67 B. 170 M. 77	1		5.13	5.26				
1-Amyl-5-carbethoxy-6-methylpiperidone-2	$C_{14}H_{25}O_3N$	B. 127	1	1.4692	5.49	5.42				
1-Amyl-1,2,3,4-dihydro-5-carbethoxy-6-methyl-pyridone-2	$C_{14}H_{23}O_3N$	B. 130	1	1.4857	5.54	5.55				
1-Amyl-5-amylcarbamyl-piperidone-2	$C_{16}H_{30}O_2N_2$	B. 200 M. 102	1		10.02	10.35				
5-Amylcarbamyl-pyrrolidone-2	$C_{10}H_{18}O_2N_2$	M. 110–111			14.14	14.15				
5-Hydroxymethyl-pyrrolidone-2	$C_5H_9O_2N$	B. 185–187 M. 87	4		12.17	12.21	3,5-Dinitrobenzoate	109–110	13.59	13.64 (N)
1-Amyl-4-hydroxymethyl-5-methylpyrrolidone-2	$C_{11}H_{21}O_2N$	B. 176	2	1.4778	7.03	7.28	Phenylurethan	73	8.80	8.73 (N)
1,2,3,4-Tetrahydro-4-hydroxymethylquinolone-2	$C_{10}H_{11}O_2N$	B. 172–175	8	1.5650	7.91	7.66	3,5-Dinitrobenzoate	134–136	11.32	11.51 (N)
1-β-Phenethyl-4-hydroxy-methyl-5-methyl-pyrroli-done-2	$C_{14}H_{19}O_2N$	B. 180–183	1	1.5343	6.01	5.92	3,5-Dinitrobenzoate	141–142	9.88	9.98 (N)
1-Amyl-5-hydroxymethyl-6-methylpiperidone-2	$C_{12}H_{23}O_2N$	B. 156	1	1.4851	6.57	6.80	Phenylurethan	103	8.44	8.63 (N)
5-Amylaminomethyl-pyrrolidone-2	$C_{10}H_{20}ON_2$	B. 156–158	1	1.4758	15.21	15.43	Hydrochloride	181–185	12.73	13.03 (N)
1-Amyl-3-amylcarbamyl-piperidine	$C_{16}H_{32}ON_2$	B. 141–144	1		10.41	9.91	*p*-Methyl toluene-sulfonate	147–148	6.17	6.12 (N)
1,2,3,4-Tetrahydro-4-methylquinoline	$C_{10}H_{13}N$	B. 143–144 110	26 8	1.5771	9.53	9.65	Benzoyl	138	5.58	5.69 (N)
6-Piperidinohexanol-1	$C_{11}H_{23}ON$	127–128 B. 96	8 1	1.4730	7.56	7.45	3,5-Dinitrobenzoate	171–172	11.08	11.10 (N)
1-Amyl-2,3-dimethyl-piperidine	$C_{12}H_{25}N$	B. 93–95	9	1.4523	7.65	7.56	Hydrochloride	148–151	16.17	16.28 (Cl)
1-β-Phenethyl-2,3-dimethyl-pyrrolidine	$C_{14}H_{21}N$	B. 73–75	2	1.5042	6.89	7.04	Hydrochloride	190–192	14.88	14.78 (Cl)
1-Amyl-3-amylaminomethyl-piperidine	$C_{16}H_{34}N_2$	B. 67	8	1.4383	11.10	11.14	Hydrochloride	184–186	21.68	21.38 (Cl)
1-Amyl-3-hydroxymethyl-piperidine	$C_{11}H_{23}ON$	B. 89–90	1	1.4671	7.57	7.62	Hydrochloride	188–191	16.03	16.16 (Cl)
1-Amyl-2-methyl-3-hydroxy-methylpyrrolidine	$C_{11}H_{23}ON$	B. 76–78	12	1.4390	7.58	7.65				

Experimental Part

The hydrogenations were carried out in a steel reaction vessel under 200 to 300 atm. of hydrogen at the temperatures and for the length of time given in Table I. Approximately 60 ml. of dioxane and 4 g. of copper–chromium oxide were used per 0.1 mole of compound to be hydrogenated. The preparation of the catalyst and the apparatus have been described.[1,9] In most of the experiments the reaction was stopped after the amount of hydrogen indicated in Table I was taken up.

The catalyst was centrifuged out of the reaction mixtures and the latter carefully fractionated through a Widmer or modified Widmer column as described elsewhere.[10] Amines which distilled over in the dioxane–water fraction were separated as hydrochlorides.

The products were characterized by comparison with previous preparations, by neutral equivalents, by analysis, and by the preparation and analysis of derivatives. These data are given in Table II. The alcohols, 5-hydroxymethylpyrrolidone-2, 1-amyl-4-hydroxymethyl-5-methylpyrrolidone-2, 1-phenethyl-4-hydroxymethyl-5-methylpyrrolidone-2, 1-*n*-amyl-5-hydroxymethyl-6-methylpiperidone-2, and 6-piperidinohexanol-1 were characterized further by determination of the moles of methane evolved with methylmagnesium iodide in a Grignard machine. In these determinations pyridine was used as a solvent, a correction being made for moisture in the solvent.

The amino-amide, IV, from the hydrogenation of 5-*n*-amylcarbamylpyrrolidone-2 was shown to have the structure given and not that of the isomeric *n*-amylcarbamylpyrrolidine by the facts that acid hydrolysis gave no amylamine, and that the other product of hydrolysis

(9) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937.

(10) The method and apparatus for fractionation are to be described in a paper by Martha E. Smith and Homer Adkins entitled "The Relative Reactivity of Amines in the Aminolysis of Amides" to be published in THIS JOURNAL.

readily was reconverted to the original compound, IV.

The amino-amide, XI, from the hydrogenation of X was shown to have the structure given and not that of the isomeric piperidone by an acid hydrolysis to 1-*n*-amyl-3-carboxypiperidine with the elimination of *n*-amylamine. The piperidine showed the correct analysis for nitrogen (found, 7.02; calcd., 7.04) and gave a hydrochloride having the correct analysis (found, 15.02; calcd., 15.00) for chlorine.

The 5-carbethoxypyrrolidone-2, b. p. 157° (4 mm.), was obtained (97 g.) from technical glutamic acid (150 g.).[11] The 5-*n*-amylcarbamylpyrrolidone-2, m. p. 110–111° (from ethyl acetate), was obtained in 74% yield by heating 48 g. of the 5-carbethoxypyrrolidone-2 with 53 g. of *n*-amylamine for three hours at 150° under hydrogen in a steel reaction vessel.

The 1-*n*-amyl-2,3-dihydro-4-carbethoxy-5-methylpyrrolone-2, b. p. 138–140 (1 mm.), m. p. 60–61°, was obtained (84 g.) by allowing 36.5 g. of amylamine and 91 g. of ethyl acetosuccinate with 5 ml. of ethanol to stand at room temperature for three days.[12] The corresponding phenethyl compound, b. p. 169–171 (0.5 mm.), was obtained similarly using phenethylamine. This pyrrolone (0.2 mole) was converted to the pyrrolidone over Raney nickel in four and one-half hours at 110–115°.

The 1-*n*-amyl-1,2,3,4-dihydro-5-carbethoxy-6-methylpyridone-2, b. p. 129–130 (0.5 mm.), was prepared similarly by substituting α-acetoglutarate for the α-acetosuccinate in the preparation above. The dihydropyridone (0.3 mole) was converted quantitatively to the piperidone over Raney nickel at 120–125° in twelve hours.

1-*n*-Amyl-5-*n*-amylcarbamylpiperidone-2, b. p. 200–210° (0.5 mm.), m. p. 102°, was prepared by converting malic acid into coumalic acid,[13] then into the ethyl ester, and then to the lactone of ethyl α-hydroxymethylglutarate and that into the desired compound. Two hundred and fifty grams of ethyl coumalate, b. p. 108–110° (2 mm.), was obtained from 900 g. of malic acid. The ester in two portions was hydrogenated quantitatively over Raney nickel at 100–300 atm. within four hours. The lactone, b. p. 103–104° (1 mm.) (29 g.), was converted to the desired amide in 55% yield by heating with 58 g. of amylamine at 250° for five hours. After the removal of the alcohol and excess amine at 20–30 mm., the diamide solidified. It was distilled and crystallized from ethyl acetate.

(11) Fischer and Boehner, *Ber.*, **44**, 1333 (1911).

(12) Emery, *Ann.*, **260**, 137–150 (1890); *Org. Syntheses*, **15**, 38 (1932), John Wiley and Sons, New York City.

(13) Pechmann and Welsh, *J. Chem. Soc.*, **47**, 146 (1885).

4-Carbethoxyquinolone-2 (40 g.), m. p. 202–203°, was obtained by the esterification of the corresponding acid which was made from isatin (80 g.) and malonic acid (64 g.).[14]

3-Carbethoxy-1,2,3,4-tetrahydroquinolone-2 (110 g.), m. p. 134–135°, was prepared from ethyl *o*-nitrobenzalmalonate by hydrogenation over Raney nickel in dioxane at 95–105° in 90–95% yield. Reissert[15] has prepared the compound in 60% yield using zinc and acid. The *o*-nitrobenzalmalonate was prepared as by Meyer.[16]

β-Carbethoxypropionylpiperidine, b. p. 105–108 (1 mm.) (160 g.), was prepared by treating β-carbethoxypropionyl chloride with piperidine (204 g.) in 400 ml. of dry ether in an ice-bath. The acid chloride was made by treating 165 g. of the corresponding acid with 142 g. of pure thionyl chloride. After the vigorous reaction had ceased the mixture was heated on a steam-bath for an hour and the excess thionyl chloride removed at 15–20 mm.

The β-carbethoxypropionic acid was made from 150 g. of succinic anhydride and 71 g. of dry ethanol under a reflux in six to eight hours. The product was fractionated, the desired product having a boiling range of 109–112° (2 mm.).

Δ-Carbethoxyvalerylpiperidine (250 g.), b. p. 134–136° (1 mm.), was prepared as in the case of the propionyl compound described above. Δ-Carbethoxyvaleric acid (196 g.), b. p. 142–146° (5 mm.), was made from diethyl adipate (516 g.).[17] The acid chloride was made from the acid and thionyl chloride (144 g.). The crude acid chloride was treated with piperidine (236 g.).

Summary

Several amido esters and amido- or carbethoxypyrrolidones, piperidones or quinolones have been submitted to partial or complete hydrogenation over copper–chromium oxide at 200–250°. The relation of the structure in these compounds to the point and extent of hydrogenation has been summarized in the numbered paragraphs preceding the "Experimental Part."

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(14) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York City, 1932, p. 321; Hill, Schultz and Lindwall, THIS JOURNAL, **52**, 772 (1930).

(15) Reissert, *Ber.*, **29**, 665 (1896).

(16) Meyer, *Monatsh.*, **28**, 53 (1907).

(17) Grün and Wirth, *Ber.*, **55**, 2215 (1922).