pheric pressure, and the residue was poured into 250 ml. of ice-water. The mixture was extracted with two 75-ml. portions of ether, and the ether extracts were combined and dried. The ether was removed and the residue was fractionally distilled in vacuum, b. p. 61–63° (0.5 mm.); yield 48 g. (74%); $n^{20}D$ 1.4455 (Kirrmann and Rambaud reported for ethyl γ-acetoxycrotonate, $n^{20}D$ 1.4445).[36]

Ethyl β-Nitromethyl-γ-acetoxybutyrate.—To a stirred solution of 53 g. (0.875 mole) of nitromethane and 12 g. of freshly prepared benzyltrimethylammonium butoxide in butanol (25% solution) was added dropwise over one-half hour 30 g. (0.175 mole) of ethyl γ-acetoxycrotonate. The reaction mixture was stirred for forty-eight hours at 60–65°, with the addition of 5-g. portions of catalyst after sixteen and thirty-two hours. The product was isolated in the usual manner. Fractional distillation gave 26.3 g. (65%) of ethyl β-nitromethyl-γ-acetoxybutyrate, b. p. 116–119° (0.4–0.5 mm.); $n^{20}D$ 1.4490; d^{20}_4 1.185.

Anal. Calcd. for $C_9H_{15}NO_6$: C, 46.35; H, 6.48; N, 6.01; MR_D, 52.70. Found: C, 46.42; H, 6.59; N, 5.84; MR_D, 52.77.

Diethyl β-Acetoxymethyl-γ-nitropimelate.—To a stirred solution of 22.7 g. (0.097 mole) of ethyl β-nitromethyl-γ-acetoxybutyrate and 4 g. of aqueous 40% benzyltrimethylammonium hydroxide solution with 10 ml. of *t*-butyl alcohol was added 9.7 g. (0.097 mole) of ethyl acrylate. The mixture was stirred for forty-eight hours at 55–60° and was then worked up in the usual manner. The product was distilled through a short-path distillation apparatus and was obtained as a light yellow oil, b. p. 157–160° (0.3 mm.); yield 21.7 g. (67%); $n^{20}D$ 1.4562; d^{20}_4 1.173.

Anal. Calcd. for $C_{14}H_{23}NO_8$: C, 50.44; H, 6.95; N, 4.20; MR_D, 77.45. Found: C, 50.39; H, 6.88; N, 4.43; MR_D, 77.30.

Reductive Cyclization of Diethyl β-Acetoxymethyl-γ-nitropimelate

A. At 265°.—Hydrogenation of VIII in dioxane at 265° and 250 atm. over copper chromite resulted in absorption of more than the theoretical amount of hydrogen necessary for conversion to 1-hydroxymethylpyrrolizidine. Isolation and purification of the product gave at least a 40% yield of 1-methylpyrrolizidine. Treatment with picric acid gave a picrate, m. p. 234–236° (dec.), identical with *dl*-pseudoheliotridane picrate. Attempts to form derivatives of the higher-boiling fraction were unsuccessful.

B. At 180–200°.—A solution of 21.7 g. of VIII in 130 ml. of dioxane was hydrogenated at 180–200° and 200–250 atm. over 22 g. of copper chromite catalyst during three and one-half hours. After filtration of the catalyst and removal of the solvent, it was possible to distil only a small portion of the residue *in vacuo*. A fraction (0.1 g.) was collected at 60–65° (21 mm.) and was converted to a picrate, m. p. 234–236° (dec.) which did not depress the melting point of *dl*-pseudoheliotridane picrate. A second fraction (1.2 g.) was collected at 93–96° (0.5 mm.) and was subjected to purification by chromatographic adsorption on alumina. Ether percolation of the column gave a small amount of basic oil, after evaporation of the ether, which formed a picrate that melted, with decomposition, at 174–175°. By melting point and analysis, the picrate could be ***dl*-trachelanthamidine picrate** (Men'shikov and Borodina[7] reported 174° as the melting point of *l*-trachelanthamidine picrate). A mixture of this picrate with *l*-isoretronecanol picrate (m. p. 193–194°)[11] melted, with decomposition, at 174–175°. Two recrystallizations of *dl*-trachelanthamidine picrate from ethanol–ether failed to alter the melting point of the fine yellow needles.

Anal. Calcd. for $C_{14}H_{18}N_4O_8$: C, 45.40; H, 4.90; N, 15.13. Found: C, 45.42; H, 4.91; N, 15.01.

(36) Kirrmann and Rambaud, *Compt. rend.*, **194**, 1168 (1932).

Summary

1. 1-Methylpyrrolizidine has been separated into its racemic forms, *dl*-heliotridane and *dl*-pseudoheliotridane, with the latter predominating in the Leonard and Felley[3] method of synthesis.

2. 1-Methylpyrrolizidine has also been synthesized starting with nitromethane and diethyl ethylidenemalonate by a three-step method involving two Michael condensations followed by reductive cyclization.

3. *dl*-Pseudoheliotridane has been resolved and the active form isolated is probably the enantiomorph of the alkaloid product "*l*-pseudoheliotridane."[7,8]

4. 1-Hydroxymethylpyrrolizidine has been synthesized by a reductive cyclization method, and the predominant racemate obtained is apparently *dl*-trachelanthamidine.

5. The absolute stereochemical configuration of the naturally occurring 1-substituted pyrrolizidines has been discussed.

URBANA, ILLINOIS RECEIVED NOVEMBER 14, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Synthesis of Pyrrolizidines. VII. Use of the Pyrrole Mannich Base

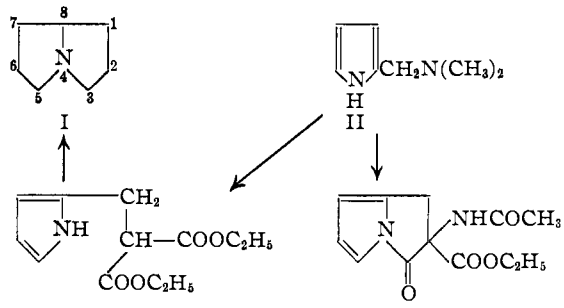
BY NELSON J. LEONARD AND EMMETT H. BURK, JR.[1]

A general method has been developed[2] for the synthesis of pyrrolizidine (I) and substituted pyrrolizidines by reductive cyclization of the corresponding γ-nitropimelic esters. The possibility of the development of a second general method for the synthesis of pyrrolizidines was envisaged as a result of the use of the pyrrole Mannich base II. Herz, Dittmer and Cristol[3] have reported the synthesis of diethyl (2-pyrrylmethyl)-malonate (III) by alkylation of diethyl malonate with 2-dimethylaminomethylpyrrole (II) and the synthesis of the lactam IV by the use of acetamidomalonic ester. The structure of these products and their ready availability suggested that catalytic hydrogenation of such intermediates might be a practical method for the synthesis of pyrrolizidines, especially 2-substituted pyrrolizidines. Accordingly the method has been

(1) Present address: Sherwin-Williams Co., Chicago, Illinois.

(2) (a) Leonard, Hruda and Long, THIS JOURNAL, **69**, 690 (1947); (b) Leonard and Beck, *ibid.*, **70**, 2504 (1948); (c) Leonard and Felley, *ibid.*, **71**, 1758 (1949); (d) Leonard and Shoemaker, *ibid.*, **71**, 1760 (1949); (e) **71**, 1762 (1949); (f) Leonard and Felley, *ibid.*, **72**, 2537 (1950).

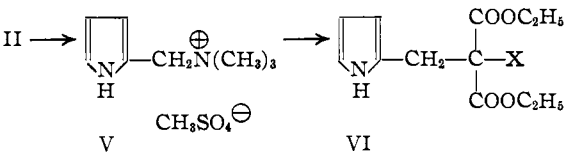
(3) Herz, Dittmer and Cristol, *ibid.*, **70**, 504 (1948).



I II III IV (a, C_6H_5 in place of CH_3)

evaluated by the synthesis and hydrogenation of a series of substituted diethyl (2-pyrrylmethyl)-malonates.

2-Dimethylaminomethylpyrrole (II) was readily prepared from pyrrole by the Mannich reaction with formaldehyde and dimethylamine hydrochloride according to the directions of Herz, Dittmer and Cristol.[4] In order to obtain (2-pyrrylmethyl)-malonic esters, the same workers[3] employed the alkylation procedure used by Albertson, Archer and Suter[5] for gramine with acylaminomalonic esters. Following this procedure, dimethyl sulfate was added slowly to a cold solution of the 2-dimethylaminomethylpyrrole and sodio-malonic ester in absolute ethanol. Yields of 85–90% were realized when the sodio derivatives of diethyl acetamidomalonate and ethyl cyanoacetamidoacetate were used, but Herz, Dittmer and Cristol[3] obtained only a 33% yield of diethyl (2-pyrrylmethyl)-malonate (III) when diethyl malonate was alkylated with the Mannich base (II). We have been able to effect a slight improvement in the yield of III by altering the order in which the reactants are brought together. It was considered that in the previously described order of addition[3,5] both sodio-malonic ester and dimethyl sulfate could be withdrawn from the reaction by a competing methylation reaction, and that dimethyl sulfate could be withdrawn by quaternization of the amine evolved during the course of the alkylation. Therefore, it was thought best to form the methosulfate (V) of II before addition of the sodiomalonic ester. We have used this method (II → V → VI) to prepare a series of substituted (2-pyrrylmethyl)-malonic esters. A solution of



V VI

X = H, III; $COOC_2H_5$, VIa; CH_3, VIb; C_6H_5, VIc; CH_3COO, VId; C_6H_5CONH, VIe

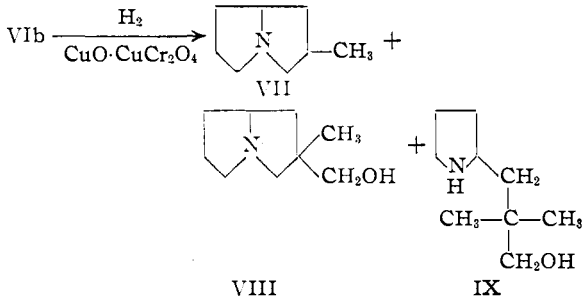
V was first prepared by the addition of dimethyl sulfate to a solution of 2-dimethylaminomethylpyrrole in ethanol, and no difficulty was encountered at this stage if the temperature of the reaction mixture was kept below 40°. The substituted sodio-malonic ester in ethanol was added quickly to the solution of the quaternary salt and the reaction mixture was maintained at 40° under a nitrogen atmosphere until the evolution of amine had practically ceased. A higher temperature accelerated the reaction but also caused considerable tar formation. The final vacuum distillation was found to be the critical step in the preparation and isolation of the esters VI, and best results were achieved by using a short-path distillation apparatus[6] in every case.

By following the general method outlined above, diethyl (2-pyrrylmethyl)-malonate (III) was obtained in 44% yield. The product had the correct composition for III, and ammonia treatment converted the diester to (2-pyrrylmethyl)-malondiamide, identical with the derivative obtained previously by Herz, Dittmer and Cristol.[3] Tricarbethoxymethane was alkylated by 2-dimethylaminomethylpyrrole in the same manner with the purpose of obtaining VIa, but diethyl (2-pyrrylmethyl)-malonate (III) was the main product isolated. The loss of a carbethoxyl group has been encountered previously in the attempted alkylation of tricarbethoxymethane with *o*-nitrobenzyl chloride in the presence of sodium ethoxide[7] and in the reaction of tricarbethoxymethane with ammonia.[8] The loss of a carbethoxy group has also been observed in the closely analogous reaction of gramine with diethyl nitromalonate and sodium ethoxide.[9] By contrast, alkylation of diethyl methylmalonate using V and sodium ethoxide proceeded normally to give diethyl (2-pyrrylmethyl)-methylmalonate (VIb) in 55% yield, and diethyl (2-pyrrylmethyl)-phenylmalonate (VIc) was obtained from diethyl phenylmalonate in 63% yield. Diethyl (2-pyrrylmethyl)-acetamidomalonate (VId) was obtained similarly from diethyl acetamidomalonate (27% yield) and diethyl (2-pyrrylmethyl)-benzamidomalonate (VIe), from diethyl benzamidomalonate (85% yield).

The reductive cyclization of esters of type VI was attempted following the conditions—hydrogenation over copper chromite at high temperature and pressure—which were shown to be effective for the conversion of γ-nitropimelic esters to pyrrolizidines.[2] The loss of one of the carbethoxyl groups during the process was expected inasmuch as Boekelheide and Rothchild[10] have reported the facile conversion of diethyl β-

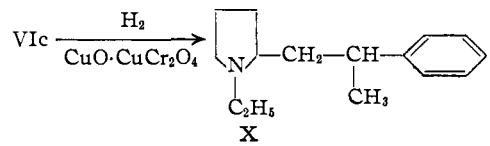
(4) Herz, Dittmer and Cristol, THIS JOURNAL, **69**, 1698 (1947).
(5) Albertson, Archer and Suter, *ibid.*, **67**, 36 (1945).
(6) Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1938, pp. 100, 101.
(7) Reissert, *Ber.*, **29**, 639 (1896).
(8) Phillipi, Hanusch and von Wacek, *ibid.*, **54**, 895 (1921).
(9) Lyttle and Weisblatt, Abstracts, American Chemical Society Meeting, New York, N. Y., September, 1947, p. 35L.
(10) Boekelheide and Rothchild, THIS JOURNAL, **69**, 3149 (1947); **71**, 879 (1949).

(2-pyridyl)-ethylmalonate to the homologous quinolizidine ring system under the same conditions. Hydrogenation of a solution of diethyl (2-pyrrylmethyl)-malonate (III) in dioxane over copper chromite at 260° and 230–240 atmospheres gave a 59% yield of pyrrolizidine (I), a yield commensurate with that realized by the earlier reductive cyclization process.[2a,2f] The pyrrolizidine was characterized by its physical properties and by the analysis and properties of its picrate.[2a] The use of a more active copper chromite catalyst[11] resulted in a decrease of the time required for hydrogenation but also in the production of a mixture of pyrrolizidine and 2-methylpyrrolizidine (VII). The latter product was isolated in 20% yield and must have resulted from hydrogenolysis, rather than elimination, of the carbethoxyl group. 2-Methylpyrrolizidine was identified by the formation of derivatives which were identical with those prepared from an authentic sample of VII.[2d] 2-Methylpyrrolizidine



was produced in 50% yield by the reductive cyclization of diethyl (2-pyrrylmethyl)-methylmalonate, along with two other products which had the compositions denoted by VIII and IX. However, the structures have not been established unequivocally as 2-hydroxymethyl-2-methylpyrrolizidine (VIII) and 2,2-dimethyl-3-(α-pyrrolidyl)-1-propanol (IX) although their formation from VIb by hydrogenation-hydrogenolysis would not be unusual in the light of experience with the hydrogenolysis of 1,3-glycols and 1,3-aminoalcohols.[2f,12]

Presumably, on the basis of the successful reductive cyclizations leading to pyrrolizidine and 2-methylpyrrolizidine, it would appear that other 2-alkylpyrrolizidines could be prepared by the same method from the appropriate alkylmalonic esters (VI, X = C_2H_5, C_3H_7, etc.). In an attempt to form a 2-arylpyrrolizidine, diethyl (2-pyrrylmethyl)-phenylmalonate (VIc) was hydrogenated in dioxane over copper chromite at 260° and 215-310 atmospheres, but instead of 2-phenylpyrrolizidine, a liquid of composition $C_{15}H_{23}N$ was obtained in 75% yield. A structure X was tentatively assigned to this product on the basis of the direct evidence of analysis, infrared spectrum, and qualitative N-ethyl determination, and on the basis of analogy to known N-ethyla-



tion,[2b] carbon–carbon hydrogenolysis,[13] and carbon–oxygen hydrogenolysis[13] under the conditions employed. Hydrogenolysis also interfered with the production of 2-hydroxy- and 2-aminopyrrolizidine in the reductive cyclization of diethyl (2-pyrrylmethyl)-acetoxymalonate (VId) and diethyl (2-pyrrylmethyl)-benzamidomalonate (VIe). Accordingly, this method of reductive cyclization of intermediates readily available from the pyrrole Mannich base (II) appears to be applicable mainly to the synthesis of 2-*alkyl*-pyrrolizidines.

Experimental

Preparation of Diethyl (2-Pyrrylmethyl)-malonates (VI).—The same general method was employed for the preparation of all of the (2-pyrrylmethyl)-malonic esters of type VI, and the yield, properties, and analysis of each are given in Table I. The general method is illustrated below in the specific case of diethyl (2-pyrrylmethyl)-malonate (III).

Diethyl (2-Pyrrylmethyl)-malonate (III).—To a solution of 40 g. (0.32 mole) of 2-dimethylaminomethylpyrrole[4] in 100 ml. of absolute ethanol maintained under nitrogen and cooled in an ice-bath was added 39.5 g. (0.32 mole) of dimethyl sulfate at such a rate that the internal temperature did not exceed 40°. Following the addition, the solution was stirred for one-half hour. A solution of sodio-malonic ester was prepared by dissolving 9.16 g. (0.40 mole) of sodium in 200 ml. of absolute ethanol and then adding 64.1 g. (0.40 mole) of diethyl malonate. The resulting sodio-malonic ester solution was added quickly to the solution of the methosulfate of 2-dimethylaminomethylpyrrole. The reaction mixture was placed in an oil-bath maintained at 40° and was stirred for seven days under a nitrogen atmosphere. The precipitation of inorganic sulfate and the liberation of volatile amine had ceased after this period of time. The ethanol was removed under reduced pressure, and 200 ml. of water was added to the viscous residue. The mixture was extracted with ether, the ether extracts were dried, and the ether was removed. The residue was distilled under reduced pressure using a short-path distillation apparatus, and the fraction boiling at 135–145° (1.6 mm.) was collected and redistilled at 122° (0.3 mm.) for determination of physical properties and analysis. The diester was converted to the diamide for identification, and this derivative melted at 202°, with previous darkening, as described for (2-pyrrylmethyl)-malondiamide by Herz, Dittmer and Cristol.[3] The product obtained from the alkylation of tricarbethoxymethane had the correct analysis and properties (see Table I) for diethyl (2-pyrrylmethyl)-malonate and was likewise converted to the diamide, m. p. 202°.

Lactam from Diethyl (2-Pyrrylmethyl)-benzamidomalonate (IVa).—The procedure used by Herz, Dittmer and Cristol[3] in the alkylation of diethylacetamidomalonate was employed to prepare the lactam of diethyl (2-pyrrylmethyl)-benzamidomalonate. To a boiling suspension of 0.5 g. of powdered sodium hydroxide in 60 ml. of moist toluene maintained under nitrogen was added 8.4 g. (0.03 mole) of diethyl benzamidomalonate followed by 3.8 g. (0.03 mole) of 2-dimethylaminomethylpyrrole. After refluxing for eight hours, the suspension was filtered, and the filtrate was allowed to stand at room temperature for several days. Large prisms separated and after recrys-

(11) Riener, THIS JOURNAL, **71**, 1130 (1949).

(12) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 88.

(13) Adkins, *ibid.*, pp. 71, 103, 104-112.

TABLE I

(2-PYRRYLMETHYL)-MALONIC ESTERS

Ester	Formula	Yield, %	Boiling pt. °C.	Mm.	$n^{20}D$	d^{20}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
III. Diethyl (2-pyrryl-methyl)-malonate	$C_{12}H_{17}NO_4$	44	122	0.3	1.4825	1.114	60.23	60.65	7.16	7.16	5.85	6.04
VIb. Diethyl 2(-pyrrylmethyl)-methylmalonate	$C_{13}H_{19}NO_4$	55	133–135	1.0	1.4830	1.096	61.64	61.81	7.56	7.82	5.53	5.72
VIc. Diethyl (2-pyrrylmethyl)-phenylmalonate	$C_{18}H_{21}NO_4$	63	164[a]	0.6	....	...	68.55	68.73	6.71	6.89	4.44	4.70
VId. Diethyl (2-pyrrylmethyl)-acetoxymalonate	$C_{14}H_{19}NO_6$	27	132	0.4	1.4891	1.167	56.56	56.74	6.44	6.73	4.71	4.79
VIe. Diethyl (2-pyrrylmethyl)-benzamidomalonate	$C_{19}H_{22}N_2O_5$	84	...[b]	...	....	...	63.67	63.87	6.19	6.36	7.82	7.75
IVa. Lactam from diethyl (2-pyrrylmethyl)-benzamidomalonate	$C_{17}H_{16}N_2O_4$	38	...[c]	...	....	...	65.37	65.17	5.16	5.40	8.97	8.89
III. Diethyl (2-pyrryl-methyl)-malonate[d]	$C_{12}H_{17}NO_4$	26	130	0.9	1.4825	1.110	60.23	59.92	7.16	7.03	5.85	5.64

[a] M. p. 68–69°, prisms from petroleum ether. [b] M. p. 95–96°, prisms from aqueous acetone. [c] M. p. 136–137°, prisms from aqueous ethanol. [d] Product of alkylation of tricarbethoxymethane with 2-dimethylaminomethylpyrrole methosulfate in the presence of sodium ethoxide.

tallization from aqueous ethanol were observed to melt at 136–137°; yield, 3.6 g. (38%) (see Table I).

Hydrogenation of Diethyl (2-Pyrrylmethyl)-malonate.—A solution of 26.02 g. (0.11 mole) of diethyl (2-pyrrylmethyl)-malonate in 100 ml. of purified dioxane was hydrogenated over 18 g. of copper chromite catalyst at 260° and 230–340 atmospheres. The theoretical quantity of hydrogen was absorbed after five and one-half hours. The solution was filtered and the filtrate was distilled very slowly through a packed column at atmospheric pressure until most of the dioxane was removed and then under reduced pressure. The fraction which boiled at 57–59° (22 mm.) was collected; yield, 7.18 g. (59.4%). A picrate was formed in ether solution and was recrystallized from ethanol, from which it separated as yellow elongated prisms, m. p. 245° (d.). The derivative had the composition of **pyrrolizidine picrate** and was undepressed in melting point on mixing with an authentic sample.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: C, 45.86; H, 4.74; N, 16.46. Found: C, 45.63; H, 4.71; N, 16.61.

Different results were obtained when the time necessary for hydrogenation was decreased from five and one-half hours to one and one-quarter hours by the use of a more active copper chromite catalyst prepared according to the directions of Riener.[11] The behavior of the product on distillation indicated the presence of a mixture since the temperature of distillation rose gradually to 160° (748 mm.). A fraction boiling at 160–164° was collected in order to identify the higher boiling constituent; $n^{20}D$ 1.4613; yield, 1.4 g. (19%). The liquid formed a picrate, m. p. 184–185°, identical with that reported (m. p. 183–184°)[2d] for **2-methylpyrrolizidine picrate**.

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: C, 47.46; H, 5.12; N, 15.81. Found: C, 47.28; H, 5.54; N, 15.66.

Hydrogenation of Diethyl (2-Pyrrylmethyl)-methylmalonate.—The reductive cyclization was carried out as with III (see above). The product boiling at 52–56° (18 mm.) was collected in 24% yield and was identified as **2-methylpyrrolizidine** by conversion to a picrate and a picrolonate, each of which was undepressed in melting point when mixed with an authentic sample of the corresponding derivative of 2-methylpyrrolizidine.[2d] No attempt was made to obtain both racemates represented by formula VII. An increase in the yield of 2-methylpyrrolizidine (to 50%) was realized by the use of copper chromite catalyst prepared according to the directions of Riener.[11]

A second fraction was collected upon distillation of the reduction product, b. p. 78–79° (0.5 mm.); $n^{20}D$ 1.4818; d^{20}_4 1.000. It had the correct composition for **2-hydroxymethyl-2-methylpyrrolizidine** (VIII), but was not further identified as such.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.79; H, 11.06; N, 9.04. Found: C, 69.51; H, 11.25; N, 9.18.

A third fraction was also collected, b. p. 90–93° (0.5 mm.), $n^{20}D$ 1.4883, d^{20}_4 1.010. It had the correct composition for **2,2-dimethyl-3-(α-pyrrolidyl)-1-propanol** (IX) but was not further investigated.

Anal. Calcd. for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.58; H, 11.71; N, 8.83.

Hydrogenation of Diethyl (2-Pyrrylmethyl)-phenylmalonate.—The reductive cyclization was attempted by the same method which led successfully to pyrrolizidine and 2-methylpyrrolizidine. The product boiled at 87° (0.5 mm.), $n^{20}D$ 1.5120, d^{20}_4 0.942, and had the correct composition for $C_{15}H_{23}N$; yield, 21.2 g. (75%).

Anal. Calcd. for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.45. Found: C, 82.74; H, 10.66; N, 6.64.

A qualitative N-ethyl determination was positive, and the infrared spectrum[14] indicated the presence of a monosubstituted phenyl group and the probable absence of OH and NH groups in the molecule. Tentative assignment of structure X to the $C_{15}H_{23}N$ compound has been made. No satisfactory derivatives were readily obtainable.

Hydrogenation of Diethyl (2-Pyrrylmethyl)-acetoxymalonate and Diethyl (2-Pyrrylmethyl)-benzamidomalonate.—When either of these compounds was hydrogenated under the conditions generally applied, only the hydrogenolysis products, pyrrolizidine and 2-methylpyrrolizidine, could be isolated and identified.

Summary

1. A number of substituted (2-pyrrylmethyl)-malonates have been prepared and subjected to hydrogenation over copper chromite at high temperature and pressure.

2. Pyrrolizidine can be synthesized efficiently by the reductive cyclization of diethyl (2-pyrrylmethyl)-malonate, and 2-methylpyrrolizidine, from diethyl (2-pyrrylmethyl)-methylmalonate.

URBANA, ILLINOIS RECEIVED NOVEMBER 21, 1949

(14) The authors are indebted to Miss Elizabeth M. Petersen for determination of the infrared absorption spectrum.