Reactions of 1,2-Dialkyl-3-pyrazolidinones

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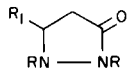
The condensation of 1,2-dialkyl-3-pyrazolidinones (I) with a series of aldehydes, ketones and esters in the presence of sodium hydride is described. Alkylation of I with several alkyl bromides gave 4-alkyl substitution products in modest yield and reaction of 1,2,4-trimethyl-3-pyrazolidinone with *n*-butyl bromide gave a 4,4-dialkylation product. Compound I reacted with aryl Grignard reagents to form 3-aryl-3-pyrazolines whereas the corresponding products were not realized in the case of alkyl Grignards. The reduction of a single example of I as well as the reduction of two 3-pyrazolines to pyrazolidines is also reported.

Previously, the preparation of some ethyl 3-(1,2-dialkylhydrazino)propanoates and their sodium methoxide catalyzed cyclization to 1,2-dialkyl-3-pyrazolidinones (I) has been reported from these laboratories (1). This report is concerned primarily with the aldol and Claisen condensations as well as the alkylation and Grignard reactions of I. For the most part, Ib was utilized in these reactions.



I

a, R=CH_3, R_1=H
b, R=C_2H_5, R_1=H
c, R=CH_3, R_1=CH_3
d, R=C_2H_5, R_1=CH_3
e, R=nC_3H_7, R_1=H
f, R=$isoC_3H_7$, R_1=H

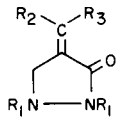
Aldol condensations of I were successful with benzaldehyde, isobutyraldehyde, 2-thiophenecarboxaldehyde, cyclohexanone and methyl ethyl ketone with sodium hydride as the condensing agent (Table I). Cyclopentanone, on the other hand, failed to give a mixed aldol product and furnished instead a 48% yield of a tricyclic self-condensation product, 2-[2′-(cyclopentylidene)cyclopentylidene]-1-cyclopentanone (2). This compound was characterized by its melting point, elemental analysis, infrared and ultraviolet spectrum.

A number of esters, including ethyl carbonate, methyl isobutyrate, ethyl oxalate, ethyl benzoate and ethyl nicotinate were condensed with I under the same conditions employed in the aldol condensations (Table II). The reaction was carried out in dry tetrahydrofuran using two equivalents of sodium hydride. Korte and coworkers (3) used only one and one-half equivalents of this base in the acylation of 1-methyl-2-pyrrolidinone with ethyl oxalate. Swamer and Hauser (4) in their studies on the acylation of ketones and esters have pointed out that two equivalents of base are necessary since one equivalent is neutralized in the conversion of the product to its sodio derivative. Fair yields of the condensation products were obtained except for the condensations involving ethyl carbonate. Ethyl acetate gave only ethyl acetoacetate and none of the mixed condensation product. No mixed condensation product could be obtained from Ib and ethyl formate at varying reaction temperatures (ice-salt bath to refluxing tetrahydrofuran). It has been reported (5) that ethyl formate is cleaved by sodium hydride in refluxing 1,2-dimethoxyethane within twenty minutes to carbon monoxide and ethanol (70% yield). Apparently, the cleavage reaction occurs more readily than the abstraction of an active hydrogen from Ib.

The alkylation of Ib with several different alkyl halides in the presence of sodium hydride in tetrahydrofuran was accomplished. Using a 20% excess of *n*-butyl bromide, *n*-pentyl bromide and *N,N*-dimethylaminopropyl chloride gave the corresponding 4-monoalkyl-3-pyrazolidinones in yields of about 40% (Table III). The reaction of Ib with *n*-propyl bromide in a molar ratio of 1:2 afforded a mixture of 1,2-diethyl-4-propyl-3-pyrazolidinone (33% yield) and 1,2-diethyl-4,4-dipropyl-3-pyrazolidinone (4% yield). The two compounds were separated by fractional distillation. An attempt to alkylate Ib with *sec*-butyl bromide proved

TABLE I

Aldol Condensation Products of I

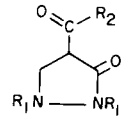


R_1	R_2	R_3	B.P. °C (mm. Hg)	n_D (°C)	Method	Yield %	Formula	Anal. Calcd./Found C	H	N
CH_3CH_2 (a)	H	C_6H_5	149-151 (0.18)	1.5621 (21.5)	A	63.1	$C_{14}H_{18}N_2O$	73.01 72.85	7.88 7.92	12.16 12.17
CH_3CH_2 (b)	H	$(CH_3)_2CH$	94-96 (0.25)	1.4928 (21.0)	A	60.9	$C_{11}H_{20}N_2O$	67.31 67.46	10.27 10.33	14.27 14.04
$(CH_3)_2CH$ (c)	H		156-158 (0.7) (d)	1.5530 (24.0)	B	60.1	$C_{14}H_{20}N_2OS$	63.60 63.69	7.63 7.63	10.60 10.61
CH_3CH_2 (e)	$-(CH_2)_5-$		106-109 (0.15)	1.5208 (23.8)	A	35.8	$C_{13}H_{22}N_2O$	70.23 70.20	9.97 10.00	12.60 12.48
CH_3CH_2 (f)	CH_3	CH_3CH_2	133-135 (9)	1.5028 (23.5)	A	9.4	$C_{11}H_{20}N_2O$	67.31 67.50	10.27 10.41	14.27 14.46

(a) IR (film), μ: 3.25, 3.29 (=CH), 6.10 (amide C=O), 6.25, 6.70 (C=C). (b) IR (film), μ: 3.25 (=CH), 6.13 (amide C=O), 6.25 (shoulder, C=C). (c) IR (KBr), μ: 3.23, 3.27 (=CH), 6.15 (amide C=O), 6.26 (C=C). (d) M.p. 91-92.5° after recrystallization from hexane. (e) IR (film), μ: 5.99 (amide C=O), 6.05 (C=C), no absorption at 3.10-3.33 (=CH). (f) IR (film), μ: 5.99 (amide C=O), 6.05 (C=C), no absorption at 3.10-3.33 (=CH).

TABLE II

Ester Condensation Products of I

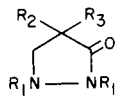


R_1	R_2	B.P. °C (mm. Hg)	n_D(°C)	Method	Yield %	Formula	Anal. Calcd./Found C	H	N
CH_3CH_2 (a)		(b)	–	A	45.6	$C_{13}H_{17}N_3O_2$	63.14 63.31	6.93 6.92	16.99 17.18
CH_3CH_2 (c)	$CO_2CH_2CH_3$	122-125 (0.3)	1.5201 (26.5)	A	38.8	$C_{11}H_{18}N_2O_4$	54.53 54.70	7.49 7.63	11.56 11.81
CH_3CH_2 (d)	C_6H_5	135-135.5 (0.2)	1.5562 (25.0)	A	68.9	$C_{14}H_{18}N_2O_2$	68.27 68.06	7.37 7.56	11.37 11.42
$CH_3CH_2CH_2$ (e)	OCH_2CH_3	119-121 (0.3)	1.4648 (24.0)	A	25.3	$C_{12}H_{22}N_2O_3$	59.48 59.40	9.15 9.05	11.56 11.68
CH_3CH_2 (f)	OCH_2CH_3	104-107 (0.3)	1.4674 (26.5)	B	27.3	$C_{10}H_{18}N_2O_3$	56.06 56.19	8.47 8.28	13.07 12.96
CH_3CH_2 (g)	$CH(CH_3)_2$	93-95 (0.4)	1.4711 (25.0)	B	70.2	$C_{11}H_{20}N_2O_2$	62.24 62.25	9.50 9.40	13.20 13.05

(a) IR (KBr), μ: 5.99 (amide C=O), 6.31 (pyridine ring). (b) M.p., 69.5-71° after recrystallization from hexane. (c) IR (film), μ: 5.78 (ester C=O), 5.85 (ketone C=O), 6.03 (enolic β-dicarbonyl), 6.10 (enolic C=C). (d) IR (film), μ: 5.94 (ketone C=O), 6.00 (enolic β-dicarbonyl), 6.29, 6.34 (C=C). (e) IR (film), μ: 5.79 (ester C=O), 5.95 (amide C=O). (f) IR (film), μ: 5.79 (ester C=O), 5.95 (amide C=O). (g) IR (film), μ: 5.88 (ketone C=O), 6.00 (enolic β-dicarbonyl).

TABLE III

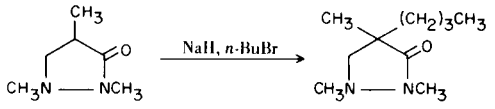
Alkylation Products (a) of I



R_1	R_2	R_3	B.P. °C (mm. Hg)	n_D (°C)	Method	Yield %	Formula	Anal. Calcd./Found C	H	N
CH_3CH_2	H	$CH_2CH_2CH_2CH_3$	135-136 (11) (b)	1.4640 (21.0)	A	42.5	$C_{11}H_{22}N_2O$	66.62 66.63	11.18 11.20	14.13 14.07
CH_3CH_2	H	$CH_2CH_2CH_3$	122-125 (10) (c)	1.4626 (23.4)	A	33.1 (d)	$C_{10}H_{20}N_2O$	65.18 65.41	10.94 10.96	15.20 15.20
CH_3CH_2	H	$(CH_2)_3N(CH_3)_2$ (e)	96.5-98.5 (0.25)	1.4733 (21.6)	B	40.9	$C_{12}H_{25}N_3O$	63.40 63.65	11.08 11.15	18.48 18.24
CH_3CH_2	H	$(CH_2)_4CH_3$	90-92.5 (0.25)	1.4640 (24.4)	B	41.8	$C_{12}H_{24}N_2O$	67.88 67.77	11.39 11.50	13.19 13.29
CH_3	CH_3	$(CH_2)_3CH_3$	61-63 (0.22)	1.4654 (25.0)	B (f)	46.3	$C_{10}H_{20}N_2O$	65.18 65.29	10.94 10.91	15.20 15.29

(a) Exhibited IR absorption maxima at 5.94-5.96 μ (amide C=O). (b) Analysis (VPC) indicated a purity of 86%; the analytical sample was obtained by preparative VPC. (c) Analysis (VPC) indicated a purity of 92%; anal. sample obtained by prep. VPC. (d) In this experiment, the molar ratio of *n*-propyl bromide to the 3-pyrazolidinone was 2:1. In addition to the described monoalkylation product, a dialkylation product, $R_2=R_3=CH_3CH_2CH_2$, b.p. 139-143° (11 mm.) was obtained in 4% yield (71% pure by VPC analysis). The anal. sample was obtained by prep. VPC; $n^{26.8}_D$ 1.4641. *Anal.* Calcd. for $C_{13}H_{26}N_2O$: C, 68.98; H, 11.58; N, 12.38. Found: C, 68.99; H, 11.67; N, 12.53. (e) A picrate was prepared and recrystallized from absolute ethanol, m.p. 115.5-116.5°. *Anal.* Calcd. for $C_{18}H_{28}N_6O_8$: C, 47.36; H, 6.18; N, 18.41. Found: C, 47.10; H, 5.97; N, 18.50. (f) Prepared from 0.073 mole of II, 0.145 mole of *n*-butyl bromide and 0.159 mole of sodium hydride (50% oil dispersion) in 75 ml. of anhydrous 1,2-dimethoxyethane.

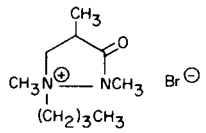
unsuccessful. Refluxing 1,2,4-trimethyl-3-pyrazolidinone (II) with *n*-butyl bromide and sodium hydride in 1,2-dimethoxyethane gave a 46% yield of 1,2,4-trimethyl-4-butyl-3-pyrazolidinone (III).



II III

This result indicates that the introduction of a second alkyl group into a 4-alkyl-3-pyrazolidinone is feasible. The NMR spectrum of III contains a singlet at δ 2.57 which corresponds to the NCH_3 protons and a singlet at δ 2.93 which is due to the $O{=}CNCH_3$ protons. These same protons are found at δ 2.58 and δ 2.96, respectively, in the NMR of II. The protons of the butyl group and the 4-methyl group of III appear further upfield as a broad multiplet at δ 0.63-1.85 with the 4-methyl group as a singlet at δ 1.17 and a deformed triplet due to the methyl protons of the butyl group at δ 0.90.

The alkylations undoubtedly proceed with the removal of an acidic proton from the 4-position of I by sodium hydride, followed by the attack of the resultant resonance stabilized carbanion on the alkyl bromide. However, an alternate reaction pathway is conceivable which involves *N*-alkylation of I as the first step. Thus, *N*-butylation of II would give the quaternary intermediate IV which could serve as an intramolecular or intermolecular alkylation

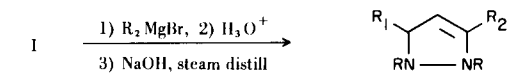


IV

agent. Transfer of a methyl group from IV, which is generally favored over the transfer of a butyl group, would give 1-butyl-2,4,4-trimethyl-3-pyrazolidinone. This compound, however, could not be found in the reaction mixture. Therefore, intermediates such as IV are probably not involved in the described alkylations of I.

The use of sodium hydride as a 50% oil dispersion necessitated removal of the oil prior to distillation of the reaction products. Two procedures were used to obtain oil-free products in the aldol, acylation and alkylation reactions. In method A, the weakly basic character of the products allowed their extraction into dilute mineral acid leaving the mineral oil in ether. In method B, the oil was removed prior to carrying out a reaction by washing with hexane. Method B is preferred over method A since it is less time-consuming.

The 1,2-dialkyl-3-pyrazolidinones (I) reacted with aromatic Grignard reagents to give 1,2-dialkyl-3-aryl-3-pyrazolines (V). Compounds Va, b and d were obtained in 1.4, 20 and 60% yields, respectively. All three 3-pyrazolines



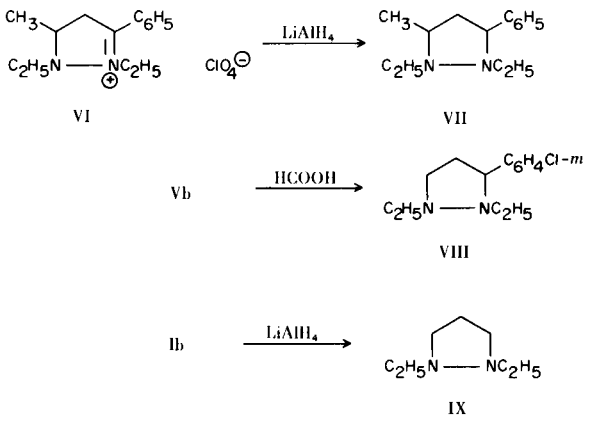
V

a, R=CH_3, R_1=H
b, R=C_2H_5, R_1=H
d, R=C_2H_5, R_1=CH_3

a, R=CH_3, R_1=H, R_2=α-$C_{10}H_7$
b, R=C_2H_5, R_1=H, R_2=*m*-ClC_6H_4
d, R=C_2H_5, R_1=CH_3, R_2=C_6H_5

gave crystalline perchlorate salts. The low yield of Va is apparently the result of a steric effect. The reaction of Ib with an aliphatic Grignard reagent, butylmagnesium bromide, gave only intractable polymeric material. Similar results were obtained from the reaction of Ic with methylmagnesium chloride. By contrast, 1-methyl-3-pyrrolidinone reacts with alkyl or aryl Grignard reagents to give 2-alkyl- or 2-aryl-2-pyrrolines (6). A recent communication (7) describes the reaction of some 1,2-disubstituted-3-pyrazolidinones with alkyl and aryl Grignards, but these 3-pyrazolidinones possessed a phenyl group on one of the nitrogen atoms. 1,2-Dialkyl-3-pyrazolines (V) have been obtained from 1,2-dialkylhydrazines, formaldehyde and ketones (8-10 and from 1,2-dialkylhydrazines and α,β-unsaturated ketones (9). In addition, lithium aluminum hydride reduction of either 3-pyrazoline-5-ones (11) or 1,2-dialkylpyrazolium salts (12, 13) leads to 3-pyrazolines.

Several reductions were also carried out. Treatment of 1,2-diethyl-3-phenyl-5-methyl-2-pyrazolinium perchlorate (VI) with lithium aluminum hydride gave an 88% yield of 1,2-diethyl-3-phenyl-5-methylpyrazolidine (VII). Reduction of Vb was effected by formic acid and afforded



1,2-diethyl-3-(*m*-chlorophenyl)pyrazolidine (VIII) in 44% yield. Lithium aluminum hydride reduction of 1,2-diethyl-3-pyrazolidinone (Ib) resulted in the formation of 1,2-diethylpyrazolidine (IX) (14) in 74% yield. Previously, IX was prepared by the alkylation of 1,2-diethylhydrazine with trimethylene bromide or by the desulfurization of 1,2-diethyl-4-pyrazolidinethiol with Raney nickel (14). Both of these latter methods gave poor yields of IX which was only obtained in a pure state as the picrate derivative.

EXPERIMENTAL

Microanalyses were performed by Dr. Kurt Eder, Geneva, Switzerland. Infrared spectra were recorded on a Beckman IR-8 infrared spectrophotometer. NMR spectra were recorded on a Varian A-60A spectrometer with tetramethylsilane as the internal reference. Melting points were taken on a Fisher-Johns apparatus and are corrected while boiling points are uncorrected. The VPC analyses were obtained with an Aerograph A-700 Autoprep gas chromatograph using a 20 ft. x 3/8 in. aluminum column packed with 30% Silicone Gum Rubber SE 30 on Chromosorb W (45-60 mesh); helium was used as the carrier gas and percentage compositions refer to the relative areas observed for the different components. Magnesium sulfate was employed as the drying agent.

General Procedure for the Aldol and Ester Condensations.

Method A.

To 5.39 g. (0.112 mole) of a 50% sodium hydride dispersion in mineral oil suspended in 65 ml. of anhydrous tetrahydrofuran (THF) was added a solution of 0.0562 mole of I and 0.112 mole of the aldehyde, ketone or ester in 10 ml. of THF. After adding 1 ml. of the solution, the reaction mixture was warmed to about 50° whereupon hydrogen evolution was observed. After completion of the addition, the mixture was refluxed for 16-20 hours, cooled in an ice-bath and decomposed with 15-20 ml. of a saturated aqueous ammonium chloride solution. The THF was decanted and the inorganic sludge was extracted three times with 25 ml. portions of THF. The combined THF solution was evaporated under reduced pressure and the residue was dissolved in 30 ml. of ether. The ether solution was extracted initially with 15 ml., then twice with 10 ml. portions of 10% hydrochloric acid. The acid extracts were combined, washed once with ether, neutralized with solid sodium bicarbonate and extracted into ether. The ether solution was dried, evaporated under reduced pressure and the residue was distilled *in vacuo*.

Method B.

Sodium hydride (50% mineral oil dispersion) in the amount of 5.93 g. (0.124 mole) was rapidly weighed, washed three times with hexane, once with THF, suspended in 65 ml. of THF and charged into a reaction flask. The remainder of the procedure was the same as method A except that the acid extraction and basification were omitted.

General Procedure for the Alkylation Reactions.

Method A.

This method is analogous to that described in method A under aldol condensations with the exception that for 0.0562 mole of I, 0.0674 mole of alkyl bromide and 3.24 g. (0.0674 mole) of sodium hydride (50% oil dispersion) were used.

Method B.

This method is the same as method B used for the aldol condensations, except that for 0.0562 mole of I, 0.0674 mole of the alkyl bromide and 3.56 g. (0.0741 mole) of sodium hydride (50% oil dispersion) were used.

1,2-Diethyl-3-phenyl-5-methyl-3-pyrazoline (Vd).

To phenylmagnesium bromide prepared in the usual way from 2.4 g. (0.1 g.-atom) of magnesium and 15.7 g. (0.1 mole) of bromobenzene in 40 ml. of anhydrous ether was added dropwise at room temperature 7.80 g. (0.05 mole) of 1,2-diethyl-5-methyl-3-pyrazolidinone (Id) in 10 ml. of anhydrous ether. The reaction mixture was stirred overnight at room temperature and decomposed with saturated aqueous ammonium chloride. The ether layer was decanted and the inorganic sludge was extracted three times with 25 ml. portions of ether. The combined ether solution was extracted twice with 25 ml. portions of 10% hydrochloric acid. The acid solution was made strongly alkaline with 40% aqueous sodium hydroxide and steam distilled. The distillate was saturated with potassium hydroxide, extracted with ether and the ether extract was dried. After removal of the ether under reduced pressure, the residue was distilled and afforded 6.60 g. (61.1%) of a colorless liquid (86% pure by VPC), b.p. 138-140° (18 mm.). Preparative VPC gave an analytical sample: $n^{25.7°}_{D}$ 1.5343; IR (film) 6.14 μ (C=C-N), no absorption at 5.88 μ (amide C=O).

Anal. Calcd. for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 78.02; H, 9.47; N, 13.11.

A crystalline perchlorate (VI) was prepared by neutralizing a solution of Vd in dry ether with a 1:1 mixture of perchloric acid (70%) and absolute ethanol against Congo red. After evaporating the mixture under reduced pressure and recrystallization of the remaining solid from absolute ethanol, the pure salt was obtained, m.p. 111-112.5°.

Anal. Calcd. for $C_{14}H_{21}ClN_2O_4$: C, 53.08; H, 6.68; N, 8.84. Found: C, 53.38; H, 6.60; N, 9.01.

1,2-Diethyl-3-(*m*-chlorophenyl)-3-pyrazoline (Vb).

In a similar manner, Vb was obtained from 8.0 g. (0.0562 mole) of 1,2-diethyl-3-pyrazolidinone (Ib), 2.69 g. (0.112 g.-atom) of magnesium and 21.5 g. (0.112 mole) of *m*-chlorobromobenzene. The reaction mixture was not extracted with acid, but was instead evaporated, made alkaline and steam distilled to give 2.70 g. (20.3%) of a liquid, b.p. 94-96.5° (0.45 mm.); $n^{25°}_{D}$ 1.5608; IR (film) 6.16 μ (C=C-N), no absorption at 5.88 μ (amide C=O).

Anal. Calcd. for $C_{13}H_{17}ClN_2$: C, 65.95; H, 7.24; N, 11.83. Found: C, 66.11; H, 7.35; N, 11.82.

The perchlorate was prepared and recrystallized from absolute ethanol, m.p. 118.5-119.5°.

Anal. Calcd. for $C_{13}H_{18}Cl_2N_2O_4$: C, 46.30; H, 5.38; N, 8.30. Found: C, 46.48; H, 5.55; N, 8.38.

1,2-Dimethyl-3-(α-naphthyl)-2-pyrazolinium Perchlorate.

α-Naphthylmagnesium bromide was prepared in the usual way (15) from 3.13 g. (0.131 g.-atom) of magnesium and 27.0 g. (0.131 mole) of α-bromonaphthalene in 78 ml. of absolute ether. The Grignard reagent was diluted with 35 ml. of dry benzene and treated with a solution of 7.45 g. (0.0653 mole) of 1,2-dimethyl-3-pyrazolidinone (Ia) in 13 ml. of absolute ether. The subsequent procedure was similar to that used for Vd. Distillation of the residue remaining after the evaporation of ether gave a liquid, b.p. 106.5-109° (23 mm.) which solidified upon cooling and was identified as naphthalene. The residue from this distillation was

converted into the perchlorate. Recrystallization from absolute ethanol afforded 0.30 g. (1.4%) of white fluffy crystals, m.p. 136-140°.

Anal. Calcd. for $C_{15}H_{17}ClN_2O_4$: C, 55.47; H, 5.28; N, 8.63. Found: C, 55.79; H, 5.24; N, 8.70.

1,2-Diethyl-3-phenyl-5-methylpyrazolidine (VII).

To a stirred suspension of 2.0 g. (0.0528 mole) of lithium aluminum hydride in 50 ml. of THF was added in small portions 3.93 g. (0.0124 mole) of VI over a period of 8 minutes. The reaction mixture was refluxed for 10 hours, stirred overnight at room temperature and decomposed with 40% aqueous potassium hydroxide solution with ice-bath cooling. The THF was decanted, the inorganic sludge was extracted with THF and the combined THF solutions were dried. After removal of the solvent by distillation at atmospheric pressure, the residue was distilled and gave 2.39 g. (88.5%) of a colorless liquid, b.p. 147-148.5° (19 mm.); $n_D^{25°}$ 1.5109; no absorption at 6.14 μ (C=C-N) in the infrared spectrum. VPC analysis showed the presence of diastereomers as two peaks of equal proportion.

Anal. Calcd. for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83. Found: C, 77.04; H, 10.36; N, 12.91.

1,2-Diethyl-3-(*m*-chlorophenyl)pyrazolidine (VIII).

A magnetically stirred mixture of 1.78 g. (0.0071 mole) of Vb and 0.36 g. (0.0078 mole) of formic acid (97%) was heated at 60° for two hours. Vigorous carbon dioxide evolution was observed during the first thirty minutes. The brownish-red mixture was cooled, treated with 20 ml. of ether and made alkaline (*p*H~11) with 40% aqueous potassium hydroxide. The ether layer was separated and the aqueous phase was extracted several times with ether. The solution was dried and the ether was distilled under reduced pressure. Distillation of the residue afforded 0.74 g. (43.8%) of liquid, b.p. 90.5-92° (0.4 mm.); $n_D^{22.3°}$ 1.5432; no absorption at 6.16 μ (C=C-N) in the infrared spectrum.

A crystalline methiodide was prepared and recrystallized from absolute ethanol, m.p. 177-179°.

Anal. Calcd. for $C_{14}H_{22}ClIN_2$: C, 44.18; H, 5.83; N, 7.36. Found: C, 44.66; H, 5.92; N, 7.57.

1,2-Diethylpyrazolidine (IX).

A solution of 10.0 g. (0.070 mole) of Ib in 30 ml. of anhydrous ether was added dropwise to a mechanically stirred suspension of 1.99 g. (0.0525 mole) of lithium aluminum hydride in 70 ml. of anhydrous ether and the mixture was refluxed for 15 hours. Decomposition of the complexes was effected by 40% aqueous potassium hydroxide with ice bath cooling. The ether was decanted and the inorganic sludge was extracted three times with 30 ml. portions of ether. The combined ether solution was dried and fractionally distilled through a 7 x ½ in. column packed with glass helices and led to 6.71 g. (74%) of a colorless liquid, b.p. 138°; $n_D^{27.8°}$ 1.4409. VPC analysis indicated the presence of a single component.

Anal. Calcd. for $C_7H_{16}N_2$: C, 65.57; H, 12.58; N, 21.85. Found: C, 65.62; H, 12.67; N, 21.95.

A picrate derivative was prepared and recrystallized from absolute ethanol, m.p. 148-151°, (lit. (14) m.p. 149-151°). The infrared spectrum was identical in every respect with that of an authentic sample (14).

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