The Pyrolytic Defluorination of Perfluoropyrrolidine.—This reaction was carried out in a 3-ft. length of $^3/_8$-in. o.d. stainless steel retubing, of which the central section (2 ft.) was packed with steel wool and electrically heated. Before each reaction the tube was heated to the required temperature and hydrogen passed through it for a few hours, after which it was purged with dry nitrogen. The reactant was vaporized slowly from a cooled trap and carried through the tube on a stream of nitrogen (9 l./hr.). In this manner perfluoropyrrolidine (1.7 cc.) at 500° yielded approximately 1 cc. of product, which on examination by analytical chromatography and infrared was shown to contain about 80% of heptafluoro-1-pyrroline, which was subsequently purified by preparative chromatography.

The pure $\underbrace{CF_2CF_2CF_2CF{=}N}$ was a colorless liquid, b.p. 22° (extrapolated), mol. wt., 198 ± 4 (calcd. 195), obtained in approximately 50% yield. The infrared spectrum exhibited a sharp band at 5.81 μ (C=N). Other strong bands were located at 7.02, 7.42, 7.69, 8.07, 8.32, 8.76, 9.64, and 10.30 μ. When it was treated with an excess of 10% sodium hydroxide in a sealed tube at room temperature for 24 hr. it was completely hydrolyzed to ammonia and sodium tetrafluorosuccinate. The free acid, obtained by the acidification and ether extraction of the hydrolysis product gave a dianilinium salt, m.p. 223–225° (lit.[17] m.p. 223–225°). A mixture melting point with an authentic sample showed no depression.

The Pyrolytic Defluorination of Perfluoropiperidine.—This compound (3.5 cc.) was defluorinated in an analogous manner to that just described to yield the previously reported nonafluoro-1-piperideine[12,13] in 50 to 60% yield. After purification by preparative chromatography, it was found to be a colorless liquid, b.p. 42.5° (extrapolated), av. mol. wt., 243 ± 3 (calcd. 245), ΔH_{vap} 6.87 kcal./mole and Trouton's constant 21.8. The infrared spectrum exhibited a strong absorption at 5.70 μ (C=N). Other strong absorptions were located at 7.37, 7.58, 8.01, 8.31, 8.58, 9.26, and 10.42 μ. The mass spectrum exhibited the following principal m/e values in order of decreasing relative intensity: 69 (CF_3^+), 31 (CF^+), 145 ($C_3F_5N^+$), 50 (CF_2^+), 100 ($C_2F_4^+$), 76 ($C_2F_2N^+$), 95 ($C_3F_3N^+$), 131 ($C_3F_5^+$), 93 ($C_3F_3^+$), 176 ($C_4F_6N^+$), and a weak parent ion at 245 ($C_5F_9N^+$). The F^{19} n.m.r. spectrum showed five peaks at −24.1 p.p.m. (=CF), +17.1 p.p.m. (CF_2–N), +46.2 p.p.m. (CF_2–CF=), +58.8 p.p.m. (CF_2), and +59.9 p.p.m. (CF_2), referred to CF_3COOH, the relative areas of which were in accord with the assigned structure.

A small sample (0.2 cc.) of this unsaturate was hydrolyzed at room temperature in a sealed tube by an excess of 10% sodium hydroxide. The resulting basic solution liberated ammonia on boiling, but did not effervesce when acidified. The ether extract of the acid solution readily yielded the anilinium salt of hexafluoroglutaric acid, m.p. 221–222° (lit.[18] m.p. 218–220). The other products of this defluorination were found to be identical with the mixture of perfluoro-N-methylpyrrolidine and the unsaturate produced by the fluorination of hexafluoroglutaronitrile with argentic fluoride.

Acknowledgment.—We are indebted to Dr. Wallace S. Brey of the University of Florida for the n.m.r. data and to Dr. Charles Colburn and Dr. Grover Paulett for the mass spectra presented here. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

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[17] M. W. Buxton, *et al.*, *J. Chem. Soc.*, 3830 (1952).

[18] D. E. Evans and J. C. Tatlow, *ibid.*, 1184 (1955).

The Cyclization of Propynyl Carbanilates to 2-Oxazolidones

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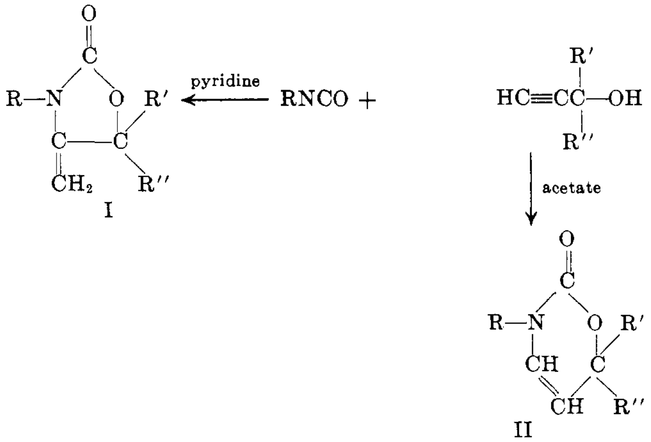
Propynyl carbanilates undergo facile cyclization to 4-methylene-2-oxazolidones with basic catalysts or by simply heating the appropriate isocyanate and alcohol. A discussion of the proof of structure as determined by nuclear magnetic resonance data is included.

The ease with which propynylureas cyclized intramolecularly to 2-imidazolones[1] with a wide variety of reagents (strong acids, phosphorus pentachloride, and base) encouraged us to speculate on the mechanism of cyclization of analogous propynyl carbanilates. Recent literature disclosed the formation of 2-oxazolidones I with pyridine as a catalyst[2] and 1,3-oxazin-2-ones II with sodium acetate.[3]

On repeating this work with *m*-chlorophenyl isocyanate and 1-ethynylcyclohexanol, the same product Ie was obtained with pyridine, sodium acetate, or more simply by heating the isocyanate and alcohol or the pre-formed carbanilate. Mixture melting points were not depressed and infrared and nuclear magnetic resonance spectra were identical. Similar results were obtained with Ia–g.

Five-membered heterocyclic carbonyl compounds derived from ureas and carbanilates can be differentiated from the corresponding six-membered rings by the carbonyl shift to higher frequency for the smaller ring.[1b] Infrared spectra of the products prepared by any of the methods gave the characteristic absorption band for C=O at 5.70–5.75 μ indicative of the five-membered ring. The spectra also showed absorption for $>C{=}CH_2$



a, R = phenyl; R′ = R″ = H
b, R = 3,4-dichlorophenyl; R′ = R″ = H
c, R = phenyl; R′R″ = pentamethylene
d, R = 3,4-dichlorophenyl; R′ = ethyl; R″ = methyl
e, R = 3-chlorophenyl; R′R″ = pentamethylene
f, R = 3,4-dichloro; R′ = R″ = methyl
g, R = 3,4-dichloro; R′R″ = pentamethylene

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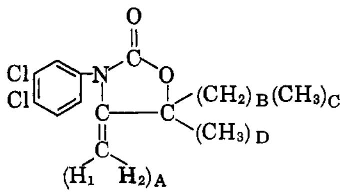
[1] (a) P. J. Stoffel and A. J. Speziale, *J. Am. Chem. Soc.*, **84**, 501 (1962); (b) *J. Org. Chem.*, **27**, 3079 (1962); (c) in press.

[2] M. D. Cameron, U. S. Patent 2,844,950 (July 22, 1958).

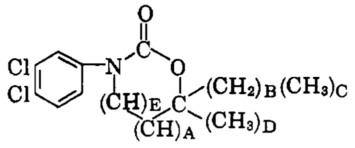
[3] S. L. Shapiro, V. Bandurco, and L. Freedman, *J. Org. Chem.*, **26**, 3710 (1961).

at 5.95–6.05 μ while bands for NH at 2.95 μ and C≡CH at 3.0 μ associated with the carbanilates were absent.

N.m.r. data of the cyclized carbanilates confirms the oxazolidone structure I unequivocally and excludes the oxazinone structure II regardless of the method of preparation. In a typical example, Id, chemical shifts were observed as a quartet $(CH_2)_A$ at 5.85 τ, a quartet $(CH_2)_B$ at 8.20 τ, a triplet $(CH_3)_C$ at 9.05 τ, a singlet $(CH_3)_D$ at 8.48 τ, and the benzene complex at 1.35 τ. The protons of the exocyclic methylene group show a symmetrical 1:2:2:1 quartet in excellent agreement with Roberts'[4] assignment for nonequivalent protons on a doubly bonded carbon atom. The coupling constant, $J_{H_1H_2}$ = 3.5 c.p.s., is compatible with protons of the exocyclic methylene group, whereas a *cis* double bond of IId would predict a value of 10–15 c.p.s. Integration with reference to the three phenyl protons gives the correct intensity ratio 3:2:3:5 in agreement with Id as opposed to 3:1:1:3:5 for IId.

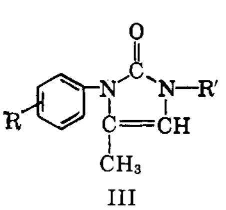


Id

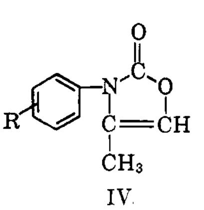


IId

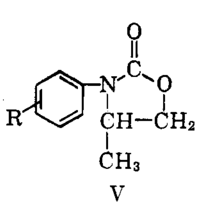
Although Shapiro[3] did not report the cyclization of an α,α-unsubstituted carbanilate, Cameron[2] showed that cyclization of propargyl carbanilate gave the 4-methyleneoxazolidone Ia[5] and no methyloxazolone IVa. It seemed pertinent to reexamine all data since the cyclization of the analogous propynyl ureas gave only the rearranged endocyclic imidazolones III.



III



IV



V

IV-Va, R = H
b, R = 3,4-dichloro

N.m.r. data of Ib prepared from 3,4-dichlorophenyl isocyanate and propargyl alcohol gave a characteristic quartet for an exocyclic methylene group at 5.80 τ and a triplet at 4.95 τ assigned to the remaining endocyclic CH_2 group. The assignment for the latter group at such low field is not unreasonable considering its juxtaposition to both oxygen and the carbon double bond.[6] The lack of a methyl group necessarily excludes IVb and confirms Ib, as does the proton intensity ratio of 3:2:2 for Ib as opposed to 3:3:1 for IVb.

Final confirmation of structure Ib was obtained on hydrogenation to Vb. The characteristic quartet for the exocyclic methylene group at 5.80 τ had disappeared and was replaced by a typical doublet for CH_3 at 8.70 τ. Since Vb is representative of an ABC system, two multiplets appeared at 5.50 and 5.90 τ, representing the CH and CH_2 protons, respectively.

As this paper was being written, Sisido, *et al.*,[7a] reported the cyclization of propynyl carbanilates. We are in complete agreement on physical properties and n.m.r. data in the case Ic. We also have given conclusive data that Ia and b do not rearrange to IVa and b, respectively, although the urea analogs do rearrange to III. However, Sisido, *et al.*,[7a] reported that treatment of propargyl carbanilate with methanolic potassium hydroxide gave the isomerized product IVa with supporting n.m.r. data.[7b] In one experiment, which they could not replicate,[7c] they obtained a product, m.p. 97–98°, whose n.m.r. spectra showed two multiplets at 5.90 and 5.00 τ; the assignment we have given to the exo- and endocyclic CH_2 groups of Ia and b, respectively. Following their procedure we ran nine experiments, starting with the propargyl carbanilate or propargyl alcohol and phenyl isocyanate. In all cases we recovered starting material or only a compound identical to Ia which was also obtained with pyridine or sodium acetate. N.m.r. spectra show multiplets at 5.85 and 5.05 τ but no absorption at 8.1 τ. The spectra gave the correct intensity ratio 5:2:2. Spectra of Va and b (hydrogenated Ia and b) gave the expected doublet for a methyl group at 8.70 τ. For comparison, the n.m.r. data of the corresponding nitrogen analogs III and IIIa are included in Table I.

Experimental[8]

1-Ethynylcyclohexyl 3-Chlorocarbanilate. Method A.—A solution of *m*-chlorophenyl isocyanate (15.4 g., 0.1 mole) and 1-ethynylcyclohexanol (12.4 g., 0.1 mole) was warmed and held at 80–90° for 4 hr. The carbanilate crystallized on cooling. Four recrystallizations from hexane gave fine colorless needles, m.p. 119.2–119.7°, 19.0 g., 68.5% yield.

Method B.[2]—The same charge as in A was added into 50 ml. of pyridine, and following a mild exothermic reaction was held at 90° for 4 hr. The reaction mixture was quenched in 500 ml. of water. The solid was repeatedly recrystallized from hexane to give fine colorless needles, m.p. 118.0–118.8°, 14.5 g., 52.4% yield.

The infrared spectra is superimposable with those from A.

3-(3-Chlorophenyl)-4-methylene-1-oxo-3-azaspiro[4.5]decan-2-one (Ie). Method C.—A solution of *m*-chlorophenyl isocyanate (15.4 g., 0.1 mole) and 1-ethynylcyclohexanol (12.4 g., 0.1 mole) was warmed as in method A, but heating was continued to 120–140° at which point an extremely vigorous reaction set in. When the reaction subsided, the mass was recrystallized from methanol as small colorless plates, m.p. 141.9–142.6°, 24.6 g., 88.8% yield.

Method D.[3]—On adding 0.25-g. of sodium acetate to a solution of *m*-chlorophenyl isocyanate (15.4 g., 0.1 mole) and 1-ethynyl-

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(4) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 56.

(5) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **27**, 2927 (1962).

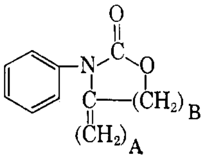
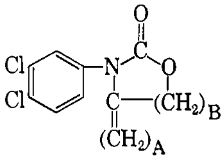
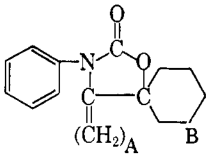
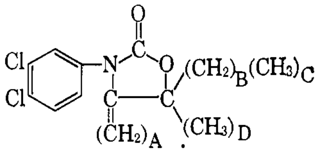
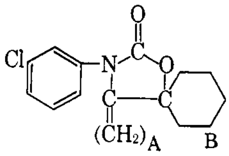
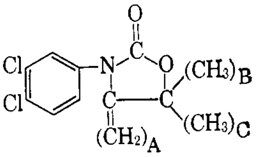
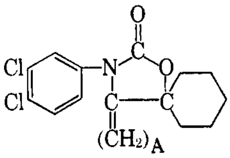
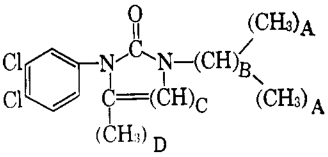
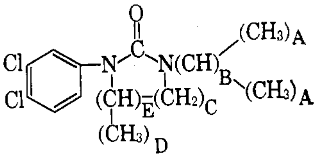
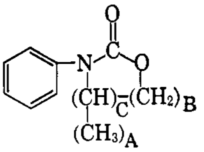
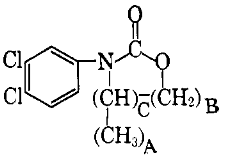
(6) "High Resolution Nuclear Magnetic Resonance," Varian Associates, National Press, 1962.

(7) (a) R. Sisido, K. Hukuoka, M. Tuda, and H. Nozaki, *J. Org. Chem.* **27**, 2663, 1962. (b) A doublet and a quartet were observed at 8.1 and 3.4 τ, respectively, in an intensity ratio of 3:1 with a coupling constant of 2.0 c.p.s. They assigned the 8.1 τ absorption to CH_3 protons and 3.4 τ quartet to olefinic proton of IVa, m.p. 97.5–98.0°. (c) In addition to the multiplets at 5.90 and 5.00 τ, their sample, m.p. 97–98°, showed absorption at 8.1 and 3.4 τ indicating contamination with IVa. Our melting point for Ia is 97.1–97.7°.

(8) See Tables II and III for data regarding propynyl carbanilates and 4-methylene-2-oxazolidones.

TABLE I

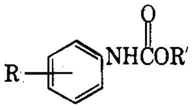
CHEMICAL SHIFTS AND SPIN–SPIN COUPLING OF 2-OXAZOLIDONES[a]

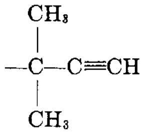
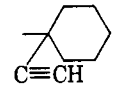
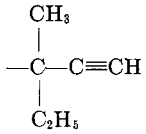
		Chemical shifts, τ	Coupling constants, c.p.s.
Ia		$(CH_2)_A$ Quartet, 5.85 $(CH_2)_B$ Triplet, 5.05	$J_{CH_{2A}CH_{2B}}$, 2.5
Ib		$(CH_2)_A$ Quartet, 5.80 $(CH_2)_B$ Triplet, 4.95	$J_{CH_{2A}CH_{2B}}$, 2.5
Ic		$(CH_2)_A$ Quartet, 5.95 ⬡$_B$ Complex, 8.35	$J_{CH_{2A}}$, 3.0
Id		$(CH_2)_A$ Quartet, 5.85 $(CH_2)_B$ Quartet, 8.20 $(CH_3)_C$ Triplet, 9.05 $(CH_3)_D$ Singlet, 8.48	$J_{CH_{2A}}$, 3.5 $J_{CH_{2B}CH_{2C}}$, 7.5
Ie		$(CH_2)_A$ Quarter, 5.95 ⬡$_B$ Complex, 8.35	$J_{CH_{2A}}$, 3.0
If		$(CH_2)_A$ Quarter, 5.85 $(CH_3)_{BC}$ Singlet, 8.40	$J_{CH_{2A}}$, 3.5
Ig		$(CH_2)_A$ Quartet, 5.95 ⬡$_B$ Complex, 8.35	$J_{CH_{2A}}$, 3.3
III		$(CH_3)_A$ Doublet, 8.72 $(CH)_B$ Septet, 5.69 $(CH)_C$ Quartet, 4.00 $(CH_3)_D$ Doublet, 8.06	$J_{CH_CCH_{3D}}$, 1.6
IIIa		$(CH_3)_A$ Doublet, 8.75 $(CH)_B$ Septet, 5.80 $(CH_2)_C$ Multiplet, 7.10 $(CH_3)_D$ Doublet, 8.85 $(CH)_E$ Multiplet, 6.50	$J_{CH_{3A}CH_B}$, 6.5 $J_{CH_{2C}CH_{3D}CH_E}$, 5.0
Va		$(CH_3)_A$ Doublet, 8.70 $(CH_2)_B$ Complex, 6.10 $(CH)_C$ Complex, 5.60	$J_{CH_{3A}}$, 6.0
Vb		$(CH_3)_A$ Doublet, 8.70 $(CH_2)_B$ Complex, 5.90 $(CH)_C$ Complex, 5.50	$J_{CH_{3A}}$, 6.0 $J_{CH_2BCH_2C}$, 2.5

[a] All n.m.r. spectra were measured on a Varian A-60 spectrometer at 60 Mc./sec. using tetramethylsilane standard.

TABLE II

PROPYNYL CARBANILATES[a]

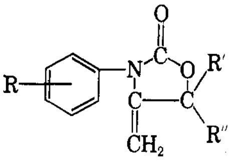


R	R′	Method[b]	% Yield	M.p., °C.	Analyses: % Nitrogen Calcd.	Analyses: % Nitrogen Found	Analyses: % Chlorine Calcd.	Analyses: % Chlorine Found
3,4-Dichloro	$CH_2C\equiv CH$	A	80.5	79.5–80.2	5.74	5.77	29.10	29.25
		B	65.5	78.7–79.5	5.74	5.80	29.10	29.07
3,4-Dichloro	 $-C(CH_3)_2-C\equiv CH$	A	58.5	116.8–117.2	5.15	5.22	26.05	26.00
		B	70.5	116.6–117.2	. .	. .	26.05	26.11
3-Chloro		A	68.5	119.2–119.7	5.05	5.10	12.45	12.38
		B	52.4	118.8–119.4	5.05	5.01	12.45	12.50
H	$CH_2C\equiv CH$	A	71.5	63.7–64.2	8.00	7.95	. . .	. . .
		B	75.5	62.5–63.2	8.00	8.15	. . .	. . .
3,4-Dichloro	 $-C(CH_3)(C_2H_5)-C\equiv CH$	A	98.5	69.2–70.0	. .	. .	24.80	24.76
		B	87.5	69.4–70.1	. .	. .	24.80	24.88

[a] All carbanilates show characteristic absorption λ_{NH} 2.95, $\lambda_{C\equiv CH}$ 3.00, and $\lambda_{C=O}$ 5.85–5.95 μ. [b] The products prepared by A or B in each case gave superimposable infrared spectra and mixture melting points were not depressed.

TABLE III

4-METHYLENE-2-OXAZOLIDONES[a]



	R	R′	R″	Method[b]	% Yield	M.p., °C.	Analyses: % Nitrogen Calcd.	Analyses: % Nitrogen Found	Analyses: % Chlorine Calcd.	Analyses: % Chlorine Found
Ia	H	H	H	C	82.5	97.1–97.5	8.00	8.04	. . . .	. . .
				D	95.5	97.2–97.7	8.00	8.11	. . .	. . .
				E	72.8	97.2–97.7	8.00	8.05	. . .	. . .
Ib	3,4-Dichloro	H	H	C	92.5	152.2–153.0	5.74	5.63	29.10	29.18
				D	74.3	151.9–152.8	5.74	5.74	29.10	29.08
Ic	H	Pentamethylene		C–D	88.8	167.1–167.6	5.76	5.81	. . .	. . .
Id	3,4-Dichloro	CH_3	C_2H_5	D	82.5	88.1–88.9	. .	. .	24.80	24.65
Ie	3-Chloro	Pentamethylene		C	88.8	141.9–142.5	5.05	5.01	. . .	. . .
				D	82.5	142.2–142.7	5.05	5.11	. . .	. . .
				E	68.5	142.0–143.0	5.05	5.17	. . .	. . .
If	3,4-Dichloro	CH_3	CH_3	E	62.5	134.0–134.7	5.15	5.22	26.05	26.17
				D	46.5	134.2–135.1	5.15	5.12	26.05	26.14
Ig	3,4-Dichloro	Pentamethylene		C	67.3	161.7–162.1	. .	. .	22.70	22.65
				D	61.3	161.5–162.1	. .	. .	22.70	22.71

[a] The cyclized oxazolidones show characteristic absorption $\lambda_{C=O}$ 5.7 and $\lambda_{C=CH_2}$ 5.95–6.05 μ and no longer show λ_{NH} 2.45 and $\lambda_{C\equiv CH}$ 3.0 μ. [b] The products prepared by methods C, D, and E in each set gave superimposable infrared spectra and mixture melting points were not depressed.

cyclohexanol (12.4 g., 0.1 mole) an extremely vigorous reaction set in, the temperature rising to 180–190°. The molten product was poured into methanol from which the product crystallized in small white plates, m.p. 142.2–142.7°, 24.9 g., 82.5% yield.

Method E.[2]—The same charge as in C was refluxed in 200 ml. of pyridine for 36–40 hr. The charge was quenched in 500 ml. of water and the solids were filtered and recrystallized four times from methanol to give small colorless plates, m.p. 142.0–143.0°, 19.0 g., 68.5% yield.

3-(3,4-Dichlorophenyl)-4-methyl-2-oxazolidone (Vb).—3-(3,4-Dichlorophenyl)-4-methylene-2-oxazolidone (24.4 g., 0.1 mole) and 0.5 g. of platinum oxide in 100 ml. of methanol was charged into a Parr hydrogenator. The reduction was completed in 4 hr. at 30° and 50 p.s.i. The solution was filtered and distilled giving the product as a pale yellow oil, b.p. 180–185° (3.0 mm.), which solidified in the receiver. Two recrystallizations from methanol gave fine colorless needles, m.p. 88.7–89.5°, 18.1 g., 73.3% yield.

Anal. Calcd. for $C_{10}H_9Cl_2NO_2$: C, 48.75; H, 3.66; Cl, 28.82; N, 5.70. Found: C, 48.71; H, 3.59; Cl, 28.87; N, 5.66.

3-Phenyl-4-methyl-2-oxazolidone (Va) was prepared following the procedure for Vb. The product was distilled at 155–160°, (0.7 mm.) and recrystallized from ether as fine colorless needles, m.p. 49–50°, in 65.5% yield.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 68.00; H, 6.26; N, 7.93. Found: C, 68.16; H, 6.21; N, 7.92.