

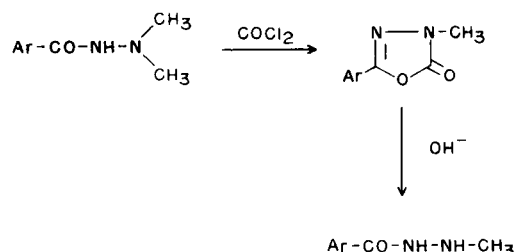
Parke, Davis and Company

A Convenient Synthesis of 1-Acyl-2-methylhydrazines

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The acylation of alkyhydrazines, methylhydrazine especially, has been reviewed by Hinman and Fulton (1) who noted that despite the low yield (8%) "the reaction of methylhydrazine and methyl benzoate is the only useful method for preparing 1-benzoyl-2-methylhydrazine. Attempts to reduce 1-benzoyl-2-methylenehydrazine were unsuccessful." Recently Theuer and Moore (2) reported the preparation of 2-methyl-1-phenylacetylhydrazine from ethyl phenylacetate and methylhydrazine in 76% yield, which seems to be a special case.

We found that 2-aryl-4-methyl- Δ^2 -1,3,4-oxadiazolin-5-ones, which are readily accessible from the corresponding 1-acyl-2,2-dimethylhydrazines by phosgene ring closure (3) may be opened readily by aqueous base to give 1-acyl-2-methylhydrazines:



Thus, 1-benzoyl-2-methylhydrazine was obtained in 71% yield from 1-phenyl-4-methyl- Δ^2 -1,3,4-oxadiazolin-5-one. This procedure is of preparative value, but care should be taken to avoid further hydrolysis of the 1-benzoyl-2-methylhydrazine. In one run where the ring opening was carried out by refluxing for 20 hours with two equivalents of aqueous potassium carbonate a poor yield of 1-benzoyl-2-methylhydrazine was obtained. The bulk of the

product was benzoic acid. Best results were obtained by short boiling with two equivalents of sodium hydroxide in water.

EXPERIMENTAL (4)

1-Benzoyl-2-methylhydrazine.

Ten g. (0.057 mole) of 2-phenyl-4-methyl- Δ^2 -1,3,4-oxadiazolin-5-one (3) was added to 114 ml. (0.114 mole) of 1 N sodium hydroxide solution. The suspension was heated to boiling with stirring. In a few minutes a clear solution was obtained. It was immediately cooled with ice and the pH adjusted to about 8 with glacial acetic acid. Most of the water was evaporated on a rotary evaporator, the last traces by azeotropic distillation with benzene. The benzene solution (~200 ml.) was filtered and the filtrate evaporated to give 8.2 g. of crude product, m.p. 81-83°. One recrystallization from hexane gave 6.05 g. (71%), m.p. 85-86° (reported 86-88° (1)).

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$: C, 63.97; H, 6.71; N, 18.65. Found: C, 64.26; H, 6.87; N, 18.73.

1-(*p*-Chlorobenzoyl)-2-methylhydrazine.

To a hot solution of 40 g. (1 mole) of sodium hydroxide in 500 ml. of water was added in one lot 105 g. (0.5 mole) of 2-(*p*-chlorophenyl)-4-methyl- Δ^2 -1,3,4-oxadiazolin-5-one (3). The suspension was stirred and heated to reflux until all the solid had disappeared (~10 minutes). The reaction mixture was neutralized with 60 ml. of glacial acetic acid. It was cooled in ice, the product collected by filtration, washed with ice water and recrystallized from about 200 ml. of benzene to give 66.2 g. (=72%), m.p. 132-133°.

Anal. Calcd. for $\text{C}_8\text{H}_9\text{ClN}_2\text{O}$: C, 52.05; H, 4.91; N, 15.18. Found: C, 52.01; H, 5.08; N, 15.08.

For the conclusive proof of structure this product was recycled with phosgene (3) in 86% yield to give 2-(*p*-chlorophenyl)-4-methyl- Δ^2 -1,3,4-oxadiazolin-5-one, identical in every respect with authentic material (3).

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REFERENCES

- (1) R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).
- (2) W. J. Theuer and J. A. Moore, *J. Org. Chem.*, **29**, 3734 (1964).
- (3) R. F. Meyer and B. L. Cummings, *J. Heterocyclic Chem.*, **1**, 186 (1964).
- (4) Melting points were observed on a Fisher-Johns block with a calibrated thermometer.

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