# Synthesis of 1,3-Dipyrrolidino-2-nitropropane

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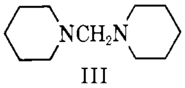
**Dipyrrolidinomethane has been prepared by the reaction of pyrrolidine and formaldehyde. 1,3-Dipyrrolidino-2-nitropropane has been prepared by the Mannich reaction of pyrrolidine, formaldehyde, and nitromethane.**

Attempts to prepare *N*-(2-nitroethyl)amines (I) by

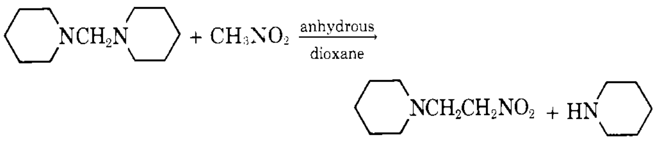
$R_2NCH_2CH_2NO_2$ I

$(R_2NCH_2)_2CHNO_2$ II



III

Mannich reactions employing dialkylamine, formaldehyde, and nitromethane have invariably led to bis(*N,N*-dialkylaminomethyl)nitromethanes (II) (*1, 2*). Recently, it was discovered (*3*) that *N*-(2-nitroethyl)piperidine could be prepared by employing dipiperidino methane (III), under anhydrous conditions, in place of piperidine and formaldehyde:



Our present study of this reaction shows that it is not a general method of preparing the monoalkylated products (I). Even under the above conditions, only the dialkylation products (II) were obtained. Polarographic analysis of reaction mixtures showed no *N*-(2-nitroethyl)di-*n*-propylamine, *N*-(2-nitroethyl)pyrrolidine, or *N*-(2-nitroethyl)morpholine, but that a significant amount of *N*-(2-nitroethyl)-*N*-methylaniline was probably present.

Two new compounds were prepared: dipyrrolidinomethane and 1,3-dipyrrolidino-2-nitropropane.

## EXPERIMENTAL

**Dipyrrolidinomethane.** One mole of 40% formalin (75 grams) (U.S.P. from Fisher Scientific Co.) was added over a period of 1 hr to 2 moles of pyrrolidine (142 grams) (Matheson, Coleman, and Bell). After a cooling to room temperature, the organic layer was separated, the water layer was salted out with $K_2CO_3$, and the combined organic layers were dried—first over $MgSO_4$, then with CaO. Fractional distillation under vacuum yielded 82 grams (55%) of a colorless oil: bp 60° C (3.5 mm Hg). Anal. Calcd. for $C_9H_{18}N_2$: C, 70.07; H, 11.76; N, 18.17. Found: C, 69.88; H, 11.92; N, 18.27.

**1,3-Dipyrrolidino-2-nitropropane.** One mole (71 grams) of pyrrolidine was mixed with 0.5 mole (37.5 grams) of formalin. To this mixture was added 0.25 mole (15.3 grams) of nitromethane (redistilled, bp 101–102° C). After several minutes, a light tan precipitate began to form. The solid 1,3-dipyrrolidino-2-nitropropane was filtered from the reaction mixture and recrystallized from methanol: mp 66–66.5° C, 20.8 grams (77.4%). Anal. Calcd. for $C_{11}H_{21}N_3O_2$: C, 58.14; H, 9.25; N, 18.50. Found: C, 57.91; H, 9.37; N, 18.53.

## LITERATURE CITED

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# Studies on Ultraviolet Absorption Spectra and Taste of Substituted Benzonitriles

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Regarding the relationship between sweet taste and chemical structure, one of the authors obtained conclusive evidence of the relationship of ultraviolet spectroscopic studies to some dulcin derivatives (*18*).

Ferguson and Childers (*5*), by studying the ultraviolet absorption spectra of substituted *m*-nitroanilines, found that some intense sweetness is associated with flat-shaped molecules whose charge distribution is like that found in *p*-disubstituted benzene. This is in accordance with the tentative resonance theory of sweet taste in aromatic molecules (*17*).

The present paper is primarily concerned with distinguishing the types of sweetness in the various substituted benzonitriles (with a hydrogen free "saccharophore" group, CN), as an approach to elucidate the correlation between the molecular electronic state of those compounds and sweetness.

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