Synthesis of 1,3-Dipyrrolidino-2-nitropropane

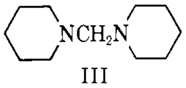
ROBERT F. KORB and JACK E. FERNANDEZ[1]
Chemistry Department, University of South Florida, Tampa, Fla. 33620

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

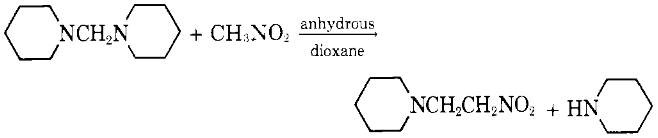
$R_2NCH_2CH_2NO_2$ I

$(R_2NCH_2)_2CHNO_2$ 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

(1) Blomquist, A. T., Shelley, T. H., Jr., *J. Amer. Chem. Soc.*, **70**, 147 (1948).
(2) De Mauny, Cerf, *Bull. Soc. Chim. France*, 4 (5), 1460 (1937).
(3) Fernandez, J. E., Fowler, J. S., Glaros, S. J., *J. Org. Chem.*, **30**, 2787 (1965).

RECEIVED for review March 2, 1970. Accepted September 18, 1970.

---

[1] To whom correspondence should be addressed.

Studies on Ultraviolet Absorption Spectra and Taste of Substituted Benzonitriles

YOJIRO TSUZUKI[1] and YOSHIHIRO ASABE
Department of Chemistry, Science University of Tokyo, Kagurazaka, Tokyo, Japan

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.

---

[1] To whom correspondence should be addressed.