[Contribution from the Biochemical Research Laboratory, The Dow Chemical Company]

Phenylnitromethane. Condensation with Pyridine and Quinoline Aldehydes

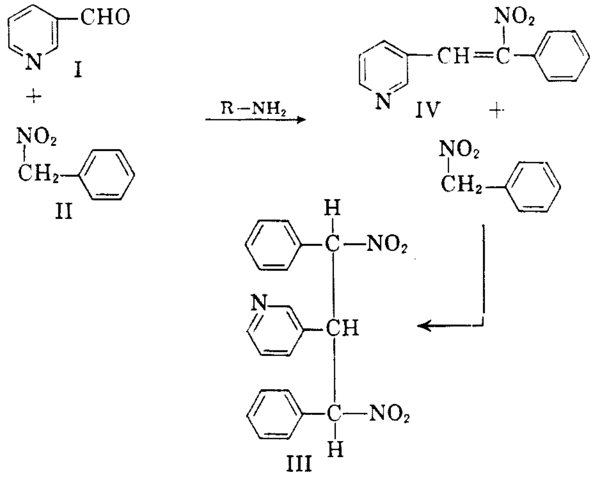
DALE N. ROBERTSON

Received October 21, 1959

The reaction between pyridine-3-carboxaldehyde (I) and phenylnitromethane (II) has been reported to yield 1,3-dinitro-1,3-diphenyl-2-(3-pyridyl)propane (III). Reinvestigation of this reaction has revealed that pyridine and quinoline aldehydes condense with II in a simple aldol manner to give nitroethanols. Dehydration to nitroethylenes, a mandatory intermediate for the dinitropropane III previously reported, could not be accomplished.

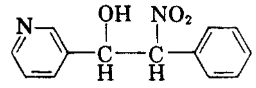
Dornow and Boberg[1] reported that the condensation of pyridine-3-carboxaldehyde (I) with phenylnitromethane (II) gave 1,3-dinitro-1,3-diphenyl-2-(3-pyridyl)propane (III). The assignment of this structure was based on the following elemental analyses: C, 65.65; H, 5.30; N, 11.26. (The theoretical values for structure III, $C_{20}H_{17}O_4N_3$, are: C, 66.10; H, 4.72; N, 11.56. No molecular weight data or infrared spectra were reported.)

The dinitropropane III could only arise by addition of II to the intermediate 1-nitro-1-phenyl-2-(3-pyridyl)-ethylene (IV)[2,3] according to the reaction:



Because of our interest in the α-nitrostilbenes, we attempted to prepare IV *via* the Schiff's base, a method found to be quite reliable with other aromatic aldehydes.[2] In this method, a Schiff's base of an aromatic aldehyde is made to react with phenylnitromethane in glacial acetic acid, giving good yields of α-nitrostilbenes. With a Schiff's base of pyridine-3-carboxaldehyde, only intractable black tars were formed. This led to a reinvestigation of the reaction reported by Dornow and Boberg.[1]

Using *n*-butylamine as catalyst in place of the methylamine in the original work,[1] we were able to isolate a low yield of a white crystalline material melting a few degrees lower than that reported. It was, however, accompanied by large amounts of dark, intractable oils. The infrared spectrum of the white crystals suggested a bonded hydroxyl, pyridine ring, nitro and monosubstituted phenyl. An equivalent weight determination by titration of the pyridine nitrogen (perchloric acid) gave a value of 246.4. The molecular weight of the simple aldol product (V) is 244.25 while that of III is 363.36. The analytical data (C, H, N) also support the simpler structure V.



V

It was found that all three pyridine aldehydes gave excellent yields of adduct when diethylamine or triethylamine was substituted for primary amine catalysts. Quinoline-2-carboxaldehyde gave considerably lower yields. Several other pyridine aldehydes also were employed in the condensation (see Table I).

In contrast to the facile conversion of nitroethanols, in general, to nitroethylenes, the products represented by V could be dissolved in either base or acid and recovered unchanged by neutralization. An attempt to dehydrate one of these adducts to the nitroethylene by heating in acetic acid was unsuccessful, leading again to intractable tars.

It should be pointed out that the lower nitroalkanes often give aldol products with pyridine[4,5] and quinoline aldehydes[6] although the corresponding nitroethylenes are obtained[1,5] at times.

All the compounds of Table I are white solids, quite sensitive to heat (and thus of variable melting point) and are soluble in both dilute acid and alkali.

EXPERIMENTAL

α-(α-Nitrobenzyl)-x-pyridine (and quinoline) methanols. The following general procedure was found to give good yields of quite pure products:

The aldehyde (0.1 mole) and phenylnitromethane (0.1 mole) were mixed in 25 ml. of ethanol or ethyl acetate. A

---

(1) A. Dornow and F. Boberg, *Ann.*, **578**, 101 (1952).

(2) D. N. Robertson, *J. Org. Chem.*, in press.

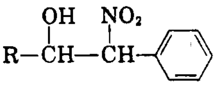
(3) D. E. Worrall, *J. Am. Chem. Soc.*, **57**, 2299 (1935).

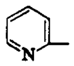
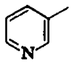
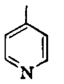
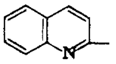
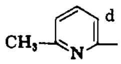
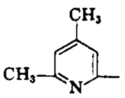
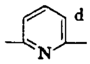
(4) F. Zymalkowski, *Arch. Pharm.*, **289**, 52 (1956).

(5) A. Burger, M. L. Stein, and J. B. Clements, *J. Org. Chem.*, **22**, 143 (1957).

(6) A. P. Phillips, *J. Am. Chem. Soc.*, **70**, 452 (1948).

TABLE I



			Neutral Equivalent[b]		Analyses[c]					
		Yield,			Carbon		Hydrogen		Nitrogen	
R	M.P.[a]	%	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
	106–107	86.7	244.2	247	63.92	64.52	4.95	4.89	11.47	11.30
	117–117.5	86.7	244.2	247.2	63.92	64.15	4.95	4.81	11.47	11.30
	130–130.5 (dec.)	87.9	244.2	246.4	63.92	64.21	4.95	4.88	11.47	10.48
	132.5–133	38.8	—	—	69.38	69.67	4.79	4.72	9.52	9.33
 [d]	99.5–101	90.0	258.31	259.5	—	—	—	—	—	—
	124–127.5	95.6	272.3	274.8	66.16	66.14	5.92	5.54	—	—
 [d] (bis compound)	144.5–147	80.5	409.5	414.0	—	—	—	—	—	—

[a] Since these compounds are sensitive to heat, the melting points are quite variable, depending on rate of heating, residence time in apparatus, etc. The figures presented should be taken only as guides. [b] By titration with perchloric acid in acetic acid. [c] Infrared spectra were consistent with each formula. [d] Since the neutral equivalents and infrared spectra support these structures, further analyses were not conducted.

few drops of either diethyl- or triethylamine were added and the mixture was allowed to stand. In most cases, the solution warmed spontaneously and crystallization began within a few minutes. Although the reactions appeared to be complete within 1 or 2 hr., they were usually allowed to stand overnight. The products were recovered by filtration, washed with small amounts of alcohol and dried *in vacuo* over phosphorus pentoxide.

Analytical samples were prepared by dissolving the compound in ethyl acetate at room temperature, adding Skellysolve A to turbidity and placing in the deep-freeze at −17° This procedure was necessary because heating slowly decomposed most of the products. (Analytical samples could not be dried at 60°, for example.)

The product from quinoline-2-carboxaldehyde was much more stable and could be recrystallized from hot ethanol-ethyl acetate.

Table I lists the products prepared.

MIDLAND, MICH.