NOTES

1,2-Di-(1′-isoquinolyl)-ethane

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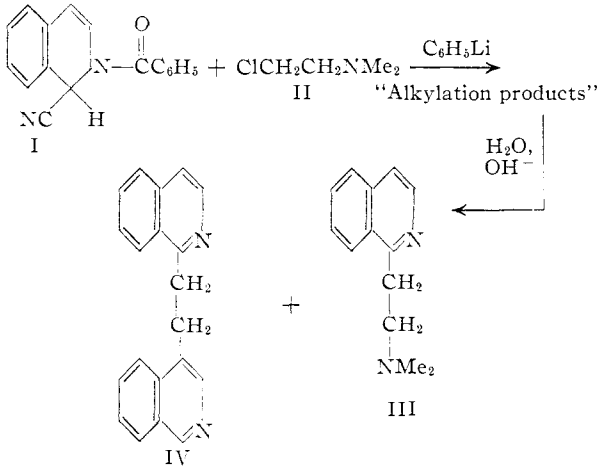
In a recent investigation of 1-vinylisoquinoline and related compounds,[2] we reported that the alkylation of 1-cyano-2-benzoyl-1,2-dihydroisoquinoline (I) with β-chloroethyldimethylamine (II) followed by alkaline hydrolysis of the crude reaction product gave 1-(β-dimethylaminoethyl)-isoquinoline (III). Further investigation of this reaction sequence now has shown that in addition to the main product (III) there can be isolated in small yield a higher boiling, basic side-product. The structural evidence to be discussed below clearly establishes this side product as 1,2-di-(1′-isoquinolyl)-ethane (IV).



The composition and molecular weight of this basic side-product IV were in agreement with the empirical formula $C_{20}H_{16}N_2$. In addition, the ultraviolet absorption spectrum of this compound showed it to be an isoquinoline derivative. Since the only logical structure to accommodate these facts was that of 1,2-di-(1′-isoquinolyl)-ethane (IV), the synthesis of IV was carried out using the procedure developed by Campbell and Teague for preparing 1,2-di-(2′-pyridyl)-ethane.[3] That the 1,2-di-(1′-isoquinolyl)-ethane obtained in this manner was identical with the basic side-product was shown through comparison of the corresponding picrates of the two samples.

Although the isolation of 1,2-di-(1′-isoquinolyl)-ethane from the alkylation of 1-cyano-2-benzoyl-1,2-dihydroisoquinoline was quite unexpected, there are several ways in which its formation can be rationalized. Of these we favor a mechanism involving conversion of III by intramolecular elimination to 1-vinylisoquinoline with subsequent addition of the 1-vinylisoquinoline to a second molecule of 1-cyano-2-benzoyl-1,2-dihydroisoquinoline. The resulting product would then by alkaline hydrolysis yield 1,2-di-(1′-isoquinolyl)-ethane as observed.

(1) Aided by a grant from the United Cerebral Palsy Association.

(2) V. Boekelheide and A. L. Sieg, *J. Org. Chem.*, **19**, 587 (1954).

(3) P. B. Campbell and P. C. Teague, This Journal, **76**, 1371 (1954).

Experimental[4]

1,2-Di-(1′-isoquinolyl)-ethane by the Alkylation of 1-Cyano-2-benzoyl-1,2-dihydroisoquinoline.—The alkylation of 1-cyano-2-benzoyl-1,2-dihydroisoquinoline with β-chloroethyldimethylamine and the alkaline hydrolysis of the resulting crude product is described for a typical experiment in our previous publication.[2] In the course of subsequent repetitions of this experiment on the same scale, it was found that a careful distillation of the final product yielded, in addition to the 7.1 g. (40%) of the main product (1-(β-dimethylaminoethyl)-isoquinoline), 1.5 g. (12%) of a light yellow oil, b.p. 160–163° at 1 mm.

Anal. Calcd. for $C_{20}H_{16}N_2$: C, 84.47; H, 5.67. Found: C, 84.30; H, 5.25.

The picrate of 1,2-di-(1′-isoquinolyl)-ethane was obtained after recrystallization from ethanol as yellow needles, m.p. 159–161°.

Anal. Calcd. for $C_{26}H_{19}N_5O_7$: C, 60.84; H, 3.73; mol. wt., 513.5. Found: C 60.54; H, 3.66; mol. wt. (by the spectrophotometric method[5]), 514.

1,2-Di-(1′-isoquinolyl)-ethane by Synthesis from 1-Methylisoquinoline.—A solution of 1-isoquinolylmethyllithium, prepared from 14.3 g. of 1-methylisoquinoline and 200 ml. of a 0.55 *M* ethereal solution of phenyllithium, was cooled to −40° and then 8.8 g. of bromine was added dropwise with stirring over a period of one hour. After the addition was complete, the reaction mixture was stirred an additional hour at −40° before it was decomposed by addition successively of 30 ml. of water and 30 ml. of 6 *N* hydrochloric acid. The aqueous layer was separated, made basic by addition of an aqueous solution of sodium hydroxide, and extracted with chloroform. When the chloroform extract was concentrated and the residual oil was distilled, there was obtained 3.6 g. (25%) of a light yellow oil, b.p. 160–165° at 1 mm.

The picrate of the 1,2-di-(1′-isoquinolyl)-ethane, obtained in this preparation, was isolated as yellow needles, m.p. 160–161°, after recrystallization from ethanol. A mixture of the picrate from this preparation and that of the preceding experiment showed no depression of melting point.

(4) Analyses by Miss Annett Smith. All melting points given are corrected.

(5) K. G. Cunningham, W. Dawson and F. S. Spring, *J. Chem. Soc.*, 2305 (1951).

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Synthesis of 2-Amino-5-dimethylaminodiphenylamine and Other Derivatives of 3,4-Dinitrodimethylaniline

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2-Amino-5-dimethylaminodiphenylamine (I) is a possible semidine rearrangement product of the hydrazo derivative of the hepatic carcinogen 4-dimethylaminoazobenzene. It is also the only rearrangement product whose formation *in vivo* is not contraindicated by the high carcinogenicities of certain polyfluoro derivatives of this dye.[1] In order to test its carcinogenicity this hitherto unknown

(1) J. A. Miller, E. C. Miller and G. C. Finger, *Cancer Research*, **13**, 93 (1953).