Notes

A department for short papers of immediate interest.

Reaction of Heterocyclic Cyanoformamidines with Some Primary Amines

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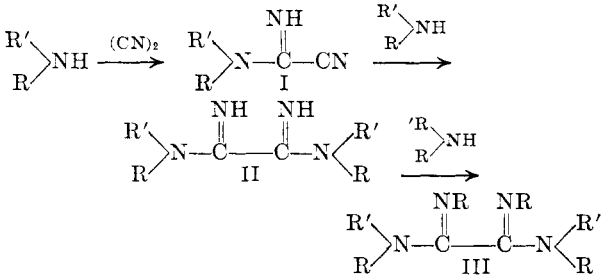
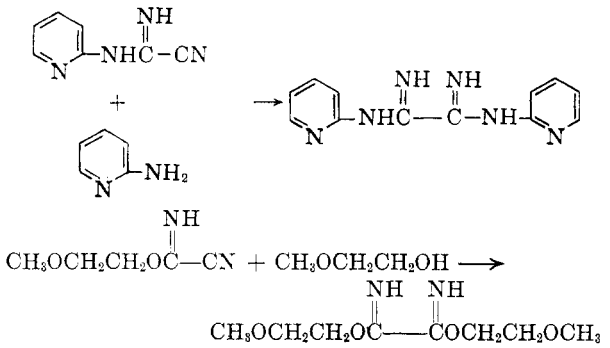
Study of the reaction of cyanogen with a number of classes of organic compounds[1] indicates that the products are formed by a stepwise mechanism, for example:



The actual conversion of the intermediate of type I to that of type II, however, has been accomplished in only a few instances:



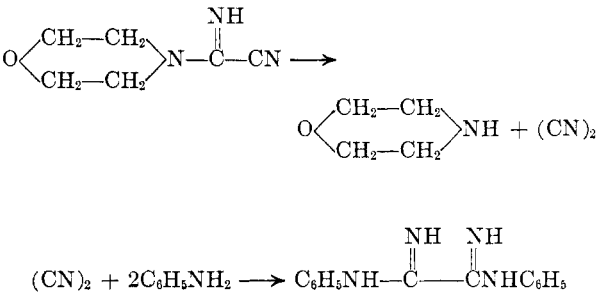
With a number of relatively stable cyanoformamidines of nitrogen-containing heterocycles available,[2] it was of interest to investigate their reactions with primary amines, the possibility existing that unsymmetrical oxamidines might result.

n-Butyl amine and aniline were chosen as typical primary amines whose reactions with cyanogen and cyanogen derivatives were already well known.[3,4] Furthermore, their formula weights were close to those of the heterocyclic portions of the cyanoformamidines available. In the reactions of oxamidines with primary amines II to III, it has been found that substitution occurs when the alkyl group in the amine is heavier than the alkyl group in the oxamidine.[4]

The heterocyclic derivatives studied were

(A) 1-(Cyanoformimino)piperidine
(B) 4-(Cyanoformimino)morpholine
(C) 1,4-Bis(cyanoformimino)piperazine
(D) 1 - (Cyanoformimino)piperidine hydrochloride
(E) 4 - (Cyanoformimino)morpholine hydrochloride

Contrary to expectation the products obtained were not unsymmetrical oxamidines. Instead, the heterocyclic portions of the compounds were removed entirely. Compounds (A), (B), and (C) with aniline gave *sym*-diphenyloxamidine[4]; compounds (D) and (E) with *n*-butyl amine gave tetra-*n*-butyloxamidine.[4] This suggests that the first step in the reaction might have been a dissociation of the cyanoformamidine into heterocycle and cyanogen, followed by a reaction between cyanogen and the primary amine:



However, the interaction of (A), (B), and (C) with *n*-butyl amine gave an entirely different result. The same compound was produced in every case but it was one not previously encountered in our cyanogen studies. A nearly white, crystalline material melting at 33–34°, it corresponded in analysis to *n*-butylcyanoformamidine, $C_4H_9NHC(=NH)CN$. To our knowledge this is the first example of a cyanoformamidine produced from an aliphatic primary amine.

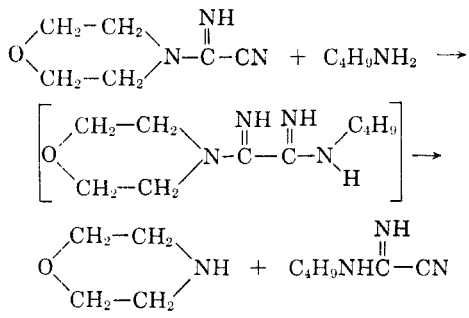
From our experience with primary amines, it seems unlikely that this compound resulted from the interaction of *n*-butyl amine and cyanogen. A possible (though unproved) mechanism involves an unsymmetrical oxamidine as an intermediate:

(1) Papers I–XIII of the Series Reactions of Cyanogen with Organic Compounds by H. M. Woodburn, *et al.* appear in *J. Org. Chem.*, **14** (1949) to **24** (1959).

(2) H. M. Woodburn and W. S. Zehrung, *J. Org. Chem.*, **24**, 1184 (1959).

(3) H. M. Woodburn, B. A. Morehead and M. C. Chen, *J. Org. Chem.*, **15**, 535 (1950).

(4) H. M. Woodburn, B. A. Morehead and M. C. Chen, *J. Org. Chem.*, **15**, 541 (1950).



After the reaction had occurred the three heterocycles were identified in the filtrate by forming their picrates.

EXPERIMENTAL

In the experimental details which follow only general procedures are outlined. There was only slight variation in yield with each compound studied.

Reaction of a heterocyclic cyanoformamidine (free base) with aniline. Two g. of the cyanoformamidine was heated with an excess of aniline at 100° for 6 hr. The hot solution was cooled, poured into 10 ml. of 95% ethanol, and diluted with water until aniline began to separate. Sufficient ethanol was then added to bring it back into solution. After standing at room temperature for 12 hr., a small amount of crystalline material was collected and dried in air. The melting point after recrystallization was 209–210°. Mixed with a known sample of *sym*-diphenyloxamidine the melting point remained the same.

Reaction of a heterocyclic cyanoformamidine hydrochloride with n-butyl amine. One g. of the hydrochloride was refluxed with an excess of *n*-butyl amine for 3 hr. The reaction mixture was allowed to cool and diluted to about 200 ml. with water. After standing for several hours a quantity of white crystals had formed. These were collected, washed with water, and dried. The yield was about 0.2 g. After recrystallization from petroleum ether the crystals melted at 85.5–86°. Admixture with *sym*-tetra-*n*-butyloxamidine[4] resulted in no depression of the melting point.

Reaction of a heterocyclic cyanoformamidine (free base) with n-butyl amine. Two g. of the cyanoformamidine was refluxed with an excess of *n*-butyl amine for 6–8 hr. The reaction mixture was poured over crushed ice and the mixture diluted to approximately 200 ml. with water. After 48 hr. in the ice chest an oil gradually separated and crystallized. The solid product was washed several times with cold water and dried in a vacuum desiccator kept in the ice chest. Yields of crude product ranged from 0.5 to 0.75 g. Recrystallized from petroleum ether, the material became almost white and melted at 33–34°.

Anal. Calcd. for $C_6H_{11}N_3$: C, 57.6; H, 8.8; N, 33.6. Found: C, 57.5; H, 8.9; N, 33.2.

The three heterocycles were proved to be present in the filtrates from the reaction mixtures by isolating their picrates.

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Synthesis of Diarylmethylmalonates and Analogous Compounds

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In connection with the synthesis of polynuclear compounds, β-arylacrylates and diarylmethylmalonates were required. One of the convenient ways for their preparation was thought to be the stepwise reaction of organometallics with α-carbethoxy-β-ethoxyacrylate (diethyl ethoxymethylenemalonate). A recent report regarding the synthesis of diarylmethylmalonates and diarylmethylcyanoacetates[1,2] by alternate procedures prompts us to publish our preliminary results.

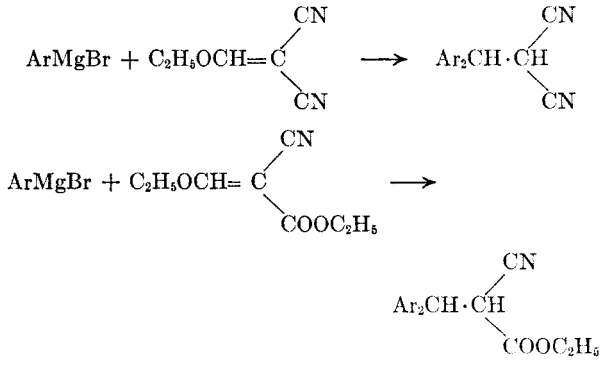
The only reference in the literature to the reaction of an organometallic compound with the acrylate is that of Reynolds[3] who, by carrying out a normal addition, *i.e.*, addition of ester to phenylmagnesium bromide, has obtained diphenylmethylmalonate.

Since we were interested in the preparation of β-acrylates it was of interest to see whether these compounds could be obtained by reverse addition and following the reaction by color tests.[4] However, the products obtained by the above procedure, in all cases, were intractable oils. The reaction of the organometallic compounds with the acrylate carried out by normal addition, *i.e.*, addition of ester to Grignard reagent in equimolar proportions gave in all cases diarylmethylmalonates; formed by the nucleophilic displacement of ethoxide group followed by the conjugate addition of Grignard reagent to β-arylacrylate:

$$ArMg\,Br + C_2H_5OCH{=}C(COOC_2H_5)_2 \longrightarrow Ar_2CH\cdot CH(COOC_2H_5)$$

For structural confirmation of the above products, diphenylmethylmalonate was hydrolyzed with alcoholic potash and the resulting dicarboxylic acid was converted to the known β,β-dipheylpropionic acid by partial decarboxylation with acetic acid.

Next, reactions were carried out with ethoxymethylenemalononitrile and ethoxymethylenecyanoacetate. In these cases also the corresponding diarylmethylmalononitrile and diarylmethylcyanoacetate were obtained.



(1) (a) M. S. Newman and H. R. Flanagan, *J. Org. Chem.*, **23**, 796 (1958). (b) M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, **78**, 4765 (1956).

(2) E. Clar, W. Kemp, and D. G. Steward, *Tetrahedron*, **3**, 325 (1958).

(3) Reynolds, *Am. Chem. J.*, **44**, 305–31 (1910).

(4) H. Gilman and Schulz, *J. Am. Chem. Soc.*, **47**, 2002–5 (1925).