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THE PREPARATION OF N-CYANOAMMONIUM SALTS

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N-Cyanotrialkylammonium salts have been previously postulated only as reactive intermediates in the von Braun cyanogen bromide reaction (2-4). The reaction is presumed to proceed by formation of the N-cyanotrialkylammonium ion which in a subsequent but rapid step is attacked by the counter ion, bromide, to give a cyanamine and an alkyl bromide (4). If the second step could be prevented by exchange of the counter ion for one that is a less potent nucleophile then the intermediate N-cyanotrialkylammonium salt might be sufficiently stable for isolation.

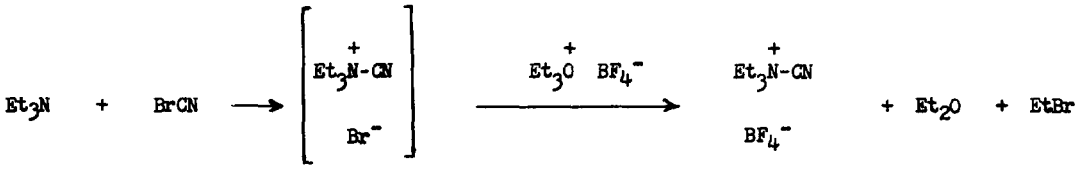
We wish to report that we have isolated several N-cyanotrialkylammonium fluroborates and have examined the reactivity of this new class of ammonium salts (Table 1). All of the salts are stable up to a month at 0° and I and II are stable for several months at room temperature. All of the salts decompose rapidly in a moist atmosphere.

TABLE 1

Salt	Yield (%)[5]	M.p.(°C)
N-Cyanotriethylammonium fluroborate (I)	98	63-4
N-Cyanotri-n-butylammonium fluroborate (II)	97	79-80
N-Cyano-N-methylpiperidinium fluroborate (III)	80	144-5
N-Cyano-N-n-butylpiperidinium fluroborate (IV)	86	68-9

The preparations were accomplished by treatment at -70° of the trialkylamine in ether with cyanogen bromide. After precipitation of a colorless solid an equivalent amount of triethyloxonium fluoroborate in methylene chloride was added to remove the bromide ion and form the N-cyanotrialkylammonium fluroborate. The course of the reaction is illustrated in the formation of N-cyanotriethylammonium fluroborate. All of the salts exhibited sharp absorption bands in the

2200-2300 cm^{-1} region of the infrared. The presence of more than one band in the N-cyanopiper-



I

idinium fluroborates has not been explained. The n.m.r. spectra also are consistent with an ammonium salt structure for all of the new compounds (Table 2). The chemical shift of 4.02 ppm for I is at 1.0 ppm lower field than that of diethylcyanamide. Such a shift to lower field is typical for ammonium and oxonium salts.

TABLE 2

Compound	ν_{max}^{nujol} cm^{-1}	$\delta(CH_3CN)$ for $CH_2\overset{+}{N}CN$
I	2270	4.02 (q)
II	2265	3.92 (t)
III	2212,2272,2282	4.15 (3.81 for $\overset{+}{N}-CH_3$)
IV	2200,2270	4.1 (broad multiplet)

The chemical shifts (CH_3CN) of possible contaminants (Et_2NCN, 3.02; Et_3O^+ BF_4^-, 4.70; Et_2O, 3.52; $Et_4\overset{+}{N}$, 3.15; $Et_3\overset{+}{N}-H$, 3.18; EtBr, 3.4; Et_3N, 2.4) for the methylene adjacent to nitrogen under identical condition clearly indicated that our product was not any one of the reactants or bi-products that may be associated with this reaction. Elemental analyses and melting points indicate that the compounds are pure substances.

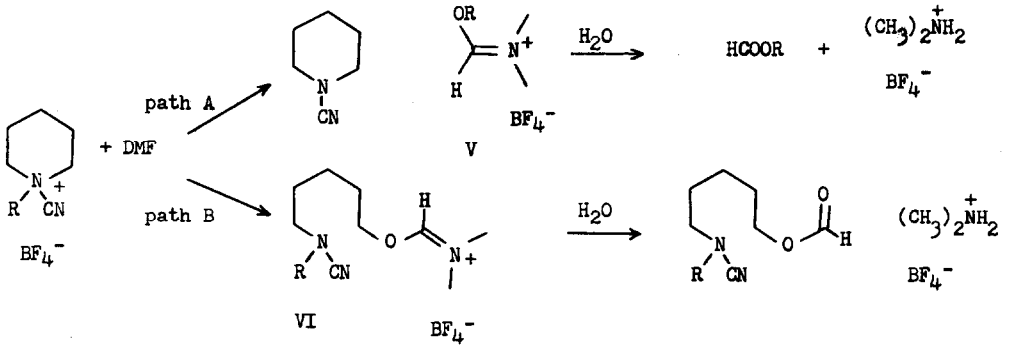
We have found that the stable salts give the same products as the postulated intermediates of the von Braun reaction if the stable salts are subjected to the appropriate nucleophiles such as bromide, iodide, water, alcohols, dimethyl formamide or pyridine. This behavior is consistent with the observations of the reactions of transient intermediater (6,7). N-Cyanotriethylammonium fluroborate reacts completely with water in a few minutes and with pyridine in a few seconds. The kinetics of the reaction of I, II and III with dimethylformamide in acetonitrile at 37° have been examined by n.m.r. Integration of the peaks of the cyanoammonium salt and the product with respect to time, gave reasonable second order kinetics: first order in dimethylforamide and first order

in cyanoammonium salt. Table 3 lists the observed rates which must, at this time, be considered as having ± 10% error limits.

TABLE 3

Compound	k (1 mole^{-1} sec^{-1})
I	4.5×10^{-4}
II	4.9×10^{-4}
III	1.0×10^{-4}

The reaction of dimethylformamide with N-cyano-N-alkylpiperidinium fluroborates can proceed to give either N-cyanopiperidine and V (path A) or by attack of the piperidine ring to give VI (path B). The reactions with N-cyano-N-methylpiperidinium fluroborate (III) proceed by path A exclusively. The reactions of N-cyano-N-n-butylpiperidinium fluroborate proceed to give a mixture



of products arising from reaction along paths A and B. The products were identified by the presence of n-butyl formate (path A) and 5-(N-n-butyl-N-cyanoamino)pentyl formate (path B) on hydrolysis of the reaction mixture. In the von Braun reaction N-methylpiperidine gave demethylation products, N-ethylpiperidine gave 66% de-ethylation and N-n-propylpiperidine gave 40% depropylation and 60% ring opening (8,9).

We have demonstrated that N-cyanotrialkylammonium fluroborates can be prepared in good yield and isolated as stable salts. Even though this method is limited to the preparation of N-cyanotrialkaylammonium salts that are less reactive toward nucleophiles than triethyloxonium fluroborate, it should be useful for the preparation of a large variety of compounds. The reactivity that we have observed shows a great potential for the use of these salts as intermediates in synthesis. All of the salts are good alkylating reagents and can be prepared with much greater

structural variety than, for example, oxonium salts. Other methods of preparation and other reactions of N-cyanotrialkylammonium fluroborates will be reported in the near future (10).

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