Synthesis of Nitriles. Use of *N*-Ethylacetonitrilium Fluoroborate for Aldoxime Dehydration

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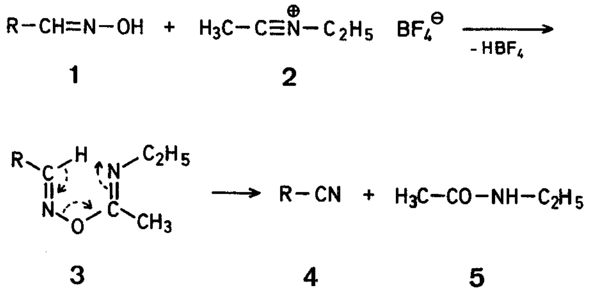
Amongst various methods for converting aldoximes into nitriles, that involving trichloroacetonitrile[1] is one of the mildest. To further exploit this principle of extracting the molecule of water from aldoximes by a nitrile or its derivatives, we have examined the effectiveness of nitrilium salts[2,3], as dehydrants. *A priori*, nitrilium salts are exceedingly electrophilic, their facile reaction with hydroxylic substances being well-known, and it was anticipated that their interaction with aldoximes would inevitably lead to high energy, fragmentation-proned imino esters whose collapse would then generate nitriles and an amide derived from the nitrilium ion.

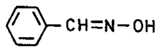
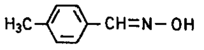
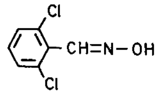
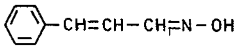
Nitrilium salts have become a class of well characterized compounds since Meerwein's pioneering investigations[2]. They can be readily prepared by *N*-alkylation of nitriles with trialkyloxonium fluoroborate, *inter alia*, or by *C*-alkylation of isonitriles. *N*-Ethylacetonitrilium fluoroborate (**2**) was chosen for our present study because it is simple to make from acetonitrile and the amide (**5**) arisen from which is easily removable by virtue of its solubility in water. In practice, every expectation has been fulfilled and nitriles (**4**) were obtained in good yields.



We have also attempted the addition of aldoximes to *t*-butyl isocyanide with or without acid catalysis. Results were unpromising, however. Formation of nitrilium salts by alkylation of isonitriles has not been pursued because while they serve the same purpose, isonitriles are more difficultly accessible, unpleasant to handle, and afford amides of higher molecular weights and hence lower water solubility.

The commercial availability of the more potent alkylating agents, alkyl fluorosulfonates[4], should further simplify and expedite the preparation of nitrilium salts.

Table. Nitriles from Treatment of Aldoximes with $(C_2H_5)_3O^{\oplus}$ $BF_4^{\ominus}$

Oximes	Nitriles Yield (%)	 B.p. (M.p.)	Lit.[5] B.p. (M.p.)
$n\text{-}C_5H_{11}\text{-}CH{=}N\text{-}OH$	88	162–165°	164°
	76	190–192°	191°
	78	214–216°	217°
	74	(140–143°)	(143°)
	56	253–255°	254°

General Procedure for Aldoxime Dehydration:

To *N*-ethylacetonitrilium fluoroborate[2] (5 mmol) in dry acetonitrile (6 ml) was added the aldoxime (4 mmol) and the mixture was left at room temperature for 8 h and heated at 80° for 0.5 h. It was cooled, poured into saturated sodium hydrogen carbonate and extracted with benzene. The dried benzene solution was evaporated and the residue was distilled or crystallized to give the nitrile, identified by spectral characteristics.

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