Applications of Metal Nitrides in Organic Syntheses

Sir:

To the extent that the "ionic" nitrides contain the N^{-3} ion,[1] they would be expected to react with a variety of organic compounds, showing strong basic, nucleophilic, and reducing properties. Early investigators, however, reported that no reaction occurs with alkyl halides,[2] acid chlorides,[3] and other compounds.[2,3,4] Nitrides with acid anhydrides have been reported to give nitriles[2] or imides.[5] We now report several additional reactions of ionic nitrides with organic substrates which indicate broad utility of the nitrides as powerful basic catalysts, nucleophiles, and reducing agents.

If, as seems likely, the pK_a of the NH^{-2} ion is larger than that of the OH^- ion, then the N^{-3} ion may well be the strongest and most convenient base available under ordinary conditions and may be capable of abstracting a proton even from a saturated hydrocarbon. The nitrides are, however, almost completely insoluble in nonreacting solvents, so that the nitride ion is not readily available for reaction; this fact may account for the failure of previous investigators to observe appreciable reactivity. We have found that diglyme and certain other ethereal solvents strongly enhance the reactivity of the nitrides, possibly by partial solution of the nitrides. Fluorene, which would not react with lithium nitride in ethyl ether or without a solvent at the melting point of fluorene, reacted on refluxing overnight in diglyme to produce a deep red solution; carbonation gave 31% of 9-fluorenecarboxylic acid, which on purification melted at 205–207°,[6] neut. equiv. 217 (Calcd. 210). Similarly 5 g. phenylacetylene and 1 g. lithium nitride, which would not react in mixed benzene-ether, reacted when dioxane was added; the mixture was refluxed (77°) for 8 hr. and carbonated to give 5.5 g. (72%) impure phenylpropiolic acid, m.p. 120–138°, which on recrystallization from carbon tetrachloride melted at 136–139°.[7]

Acetaldehyde and propionaldehyde reacted very vigorously at 15–20° with small amounts of lithium nitride to give mostly resinous products and small amounts of aldols and related products; 8 g. crotonaldehyde was obtained from 100 g. acetaldehyde in this manner. Isobutyraldehyde (100 g.) containing 3 g. of lithium nitride was kept at room temperature 3 days, then filtered and distilled to give 17.7 g. of the monoisobutyrate of 2,2,4-trimethyl-1,3-pentanediol, b.p. 103–104 (2 mm.), n_D^{25} 1.4392.[8]

The Tischenko reaction was observed with benzaldehyde; 53 g. benzaldehyde with 3 g. lithium nitride reacted rapidly at 80° in carbon tetrachloride to give 35 g. benzyl benzoate and small amounts of benzoic acid. Fourteen grams of benzaldehyde was recovered unchanged.

Although acid chlorides had been reported not to react with lithium nitride, benzoyl chloride and lithium nitride reacted in diglyme to give tribenzamide in good yield, m.p. 208–210° (lit.[9] m.p. 207–208°). Acetyl chloride also reacts with the nitride but thus far has given only diacetamide and none of the tertiary amide. With difunctional acid chlorides it should be possible to prepare imide polymers or related molecules containing tertiary amide linkages, which should show excellent thermal stability. Terephthaloyl chloride with either lithium or magnesium nitride gave an insoluble polymer decomposing at 190–200°; the infrared spectrum of this material is quite similar to that of a vaguely related tertiary amide model compound, *N,N'*-phthaloyldiphthalimide.

Various other reactions have been observed but have not yet been studied appreciably. These include reactions of lithium nitride with nitrobenzene, from which neutral products were obtained together with a gas which appeared to be nitrogen; with organotin halides, which presumably reacted metathetically, since the lithium halide separated; with acetone, which apparently gave condensation products; and with benzyl chloride.

Lithium nitride may be prepared directly from lithium and nitrogen under various reaction conditions; the nitride employed[10] in this investigation was shown by analysis to be 90–95% pure.

We believe the ionic nitrides constitute a class of reagents of wide applicability in synthetic organic chemistry. Investigations currently in progress extend to a variety of additions, displacements, and polymerizations, as well as to the use of dispersions and fused-salt solutions of the nitrides in organic reactions.

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