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Metal Nitrides in Organic Reactions. I. Reactions of Lithium Nitride with Acid Chlorides. Preparation of N,N-Diacylamides[1,2]

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Lithium nitride reacts with acid chlorides under mild temperature conditions to produce N,N-diacylamides (tertiary amides) and other products. The reactions indicate considerable reactivity of lithium nitride toward acid chlorides, contrary to earlier reports in the literature. The preparation of the previously unreported N,N-bis-*p*-nitrobenzoyl-*p*-nitrobenzamide is described.

The metal nitrides have been reported[5-7] to be quite unreactive with organic compounds other than the alcohols,[8-11] which merely liberate ammonia. Certain acid anhydrides have been observed to react with nitrides: magnesium nitride with acetic and benzoic anhydrides gave the corresponding nitriles in 15 and 42% yields, respectively,[12] and reaction of lithium nitride with acetic anhydride in refluxing carbon tetrachloride produced N,N-dilithioacetamide and the lithium salt of diacetamide.[13] Emmerling[12] noted specifically, however, that acetyl chloride would not react with magnesium nitride. Reactions of acid chlorides with lithium nitride apparently have not been previously studied.

We have found that acid chlorides react readily with lithium nitride at or near room temperature; aromatic acid chlorides form the tertiary amide, or triacylamine.[14] After removal of the tertiary amide, hydrolysis of the residual reaction mixture readily produces the simple amide and the corresponding imide, together with other products not yet characterized; probably the N-lithium derivatives observed by Beck[13] are formed to some degree in the course of the reaction. Acetyl chloride gave no triacetamide but yielded instead acetamide and diacetamide and a tarry material which appeared to be aldol resin, possibly indicating that lithium nitride can effect reduction of the acid chloride to acetaldehyde. Other work in this laboratory[1,17] has shown that the aldol condensation is strongly catalyzed by lithium nitride.

The rather surprising lack of reactivity of the ionic nitrides with organic compounds, reported by previous investigators, may be due, at least in part, to the nearly complete insolubility of the nitrides in nonreacting solvents. The reactions must proceed heterogeneously, and the nitride ion may well be quite unavailable for reaction at the surface of the solid nitride particles. Although in some cases reactions with lithium nitride proceed readily in carbon tetrachloride[1,13,17] or in various other media, reactions involving acid chlorides appear to be carried out most readily in diglyme or pyridine—although these compounds exhibit no apparent solvency for the nitrides, nor do they react significantly with the nitrides at reflux temperatures. During attempted reactions between lithium nitride and liquid acid chlorides in the absence of added solvents, the nitride particles appeared to become coated, presumably with reaction products. The function of the diglyme or pyridine may be, at least partly, to maintain an exposed surface of nitride by aiding removal of adhering product(s).

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(1) A preliminary communication describing a portion of this investigation appeared in *J. Org. Chem.*, **26**, 4777 (1961). Presented in part at the Combined Regional Meeting of the American Chemical Society, New Orleans, La., Dec. 1961. Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963.

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(14) The designation "tertiary amide" is well established and approved by the IUPAC for the N,N-diacylamides[24,25] but has occasionally been used[15,16] to designate N,N-dialkylamides. The name "triacylamine" seems inappropriate because of the dissimilarity between these compounds and true amines. Throughout this paper we have used the term "tertiary amide" in its approved sense, to designate N,N-diacylamides.

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(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 176, 182.

(17) R. B. Dunmire, J. M. Morris, and P. E. Koenig, paper in preparation.

The tertiary amides available from this reaction are with few exceptions[18] difficult to prepare by the ordinary methods of acylation of ammonia or amides. Triacetamide[19] and tribenzamide[20,21] have been prepared by reaction of the sodium salts of the corresponding imides with the appropriate acid chlorides or anhydrides. The reaction of nitriles with acid anhydrides,[22] which is apparently considered a general method of synthesis of the tertiary amides,[23,24] is not always especially convenient; an attempted preparation of triacetamide by this method gave only traces, if any, of the desired product, and the reaction proceeded very slowly. One of the most satisfactory methods of preparation of tertiary amides, particularly those with mixed acyl groups, is Thompson's diacylation of amides by acid chlorides in excess pyridine.[25] This method, however, was found by Thompson to be unsuitable for the synthesis of trinitrotribenzamide and other tertiary amides bearing powerful electron-withdrawing groups, the chief reaction being dehydration of the primary amide. The reaction of lithium nitride with *p*-nitrobenzoyl chloride, on the other hand, proceeds smoothly to give the corresponding tertiary amide, although in rather low yield. 4,4′,4″-Trichlorotribenzamide and the corresponding trimethoxy derivative were also prepared from the nitride, as was tribenzamide.

The tertiary amides showed a strong sharp carbonyl absorption in the range 1690–1730 cm.$^{-1}$ and a strong absorption in the region 1220–1280 cm.$^{-1}$; the latter may be characteristic of aromatic tertiary amides, although insufficient evidence is available at present to warrant a firm assignment of this band. The significance of the location of the carbonyl peak will be the subject of a separate communication.

The formation of tertiary amides from lithium nitride with acid chlorides presumably proceeds by addition of some nucleophilic species (perhaps Li_2N^-) to the unsaturated carbon, followed by displacement of the halogen in the usual manner for nucleophilic reactions. The presence of electron-withdrawing groups on the ring should facilitate reaction; in fact, *p*-chlorobenzoyl chloride reacted more readily and gave a higher yield of tertiary amide than did benzoyl chloride. *p*-Nitrobenzoyl chloride yielded relatively little of the tertiary amide, probably because of interference by the nitro group itself. Work in this laboratory has shown[26] that the nitro group is quite easily reduced by lithium nitride. In the reaction of *p*-nitrobenzoyl chloride with lithium nitride there were produced several relatively insoluble high-melting products which may have been formed by reduction of the nitro group to amino, and subsequent interaction between the amino and acid chloride groups, or by interaction of the N,N-dilithioamido group with the nitro group.

Experimental[27]

Tribenzamide.—In a 200-ml. three-necked flask fitted with a condenser, stirrer, and an addition funnel were placed 1.0 g. (0.029 mole) of lithium nitride in 30 ml. of dry diglyme. Stirring was started and 20 g. (0.142 mole) of benzoyl chloride in 20 ml. of dry diglyme was added over a 1.5-hr. period. Stirring was then continued for an additional 48 hr. The mixture was then filtered and the white precipitate was washed with two 100-ml. portions of petroleum ether (30–60°) and recrystallized from benzene. The yield was 3.9 g., m.p. 206–207°.[21] The filtrate was placed in an ice bath and 100 ml. of petroleum ether was added. The resulting precipitate was separated by filtration and recrystallized from benzene. There was obtained an additional 1.9 g. of tribenzamide, m.p. 206–207°.[21] The total yield of tribenzamide was 61%.

The same reaction was also carried out in pyridine, as follows. In a 200-ml. four-necked flask fitted with a condenser, stirrer, thermometer, and an addition funnel were placed 0.5 g. (0.014 mole) of lithium nitride in 20 ml. of dry pyridine. Stirring was started and 10 g. (0.071 mole) of benzoyl chloride in 50 ml. of pyridine was added over a 2-hr. period, the temperature being maintained at 35–40°. After the addition of reagents and an additional hour of stirring, a further 10-g. portion of benzoyl chloride in 30 ml. of pyridine was added and stirring was continued for 2 hr. more. The mixture became dark red in color; it was poured into 200 ml. of 1 *N* hydrochloric acid and the resulting precipitate was separated by filtration, washed with 20 ml. of petroleum ether (20–40°), and recrystallized from 100 ml. of benzene. There was obtained 1.7 g. (36%) of tribenzamide, m.p. 206–207°. The infrared spectra of the two samples of tribenzamide were identical.

4,4′,4″-Trinitrotribenzamide.—In a four-necked flask fitted as described above were placed 2.0 g. (0.056 mole) of lithium nitride in 40 ml. of dry diglyme. Over a period of 3 hr., a solution of 30 g. (0.16 mole) of *p*-nitrobenzoyl chloride in 70 ml. of diglyme was added with stirring; the temperature of the reaction mixture was held at 35–36°. When addition was complete, stirring was continued for 3 hr. and an additional 10 g. of *p*-nitrobenzoyl chloride in 20 ml. of diglyme was added. Stirring was then continued for an additional 3 hr. A yellow precipitate was present; this was removed by filtration, washed with two 100-ml. portions of 5% sodium carbonate solution, and recrystallized from tetrahydrofuran containing petroleum ether (20–40°). A second recrystallization gave 6.6 g. (25%) of 4,4′,4″-trinitrotribenzamide, m.p. 231–232°.

Anal. Calcd. for $C_{21}H_{12}N_4O_9$: C, 54.3; H, 2.6; N, 12.1. Found: C, 54.27; H, 2.73; N, 12.04.

4,′4,4″-Trichlorotribenzamide.—With the apparatus described above, 25 g. (0.142 mole) of *p*-chlorobenzoyl chloride dissolved in 25 ml. of dry diglyme was added over 2 hr. to 1.2 g. (0.034 mole) of lithium nitride suspended in 40 ml. of diglyme. Stirring was continued for 6 hr. The precipitate which had formed was washed with 100 ml. of 5% sodium carbonate solution, then with water, then recrystallized successively from tetrahydrofuran and chloroform. The yield was 6.84 g. (48.7%), m.p. 234–235°. Thompson[25] reported a melting point of 259–260° for this compound, with the comment that the melting point varies with rate of heating.

Anal. Calcd. for $C_{21}H_{12}Cl_3NO_3$: C, 58.29; H, 2.80; N, 3.23. Found: C, 58.38; H, 2.90; N, 3.35.

4′4,4″-Trimethoxytribenzamide.—In the manner previously described, 10.5 g. (0.062 mole) of *p*-methoxybenzoylchloride in 20 ml. of diglyme was added over 2 hr. to 0.525 g. (0.015 mole) of lithium nitride in 10 ml. of diglyme. An additional 5 g. of *p*-methoxybenzoyl chloride was added and stirring was continued for 20 hr. The resulting precipitate was separated and washed as before, and recrystallized from acetone. There were obtained 2.8 g. of a white solid, m.p. 159–160°, and 0.4 g. of white needles, m.p. 196–198°. Both materials showed acceptable elementary analyses for trimethoxytribenzamide.

Anal. Calcd. for $C_{24}H_{21}NO_6$; C, 68.73; H, 5.05; N, 3.34. Found (for 160° compound): C, 68.64; H, 5.13; N, 3.53. Found (for 198° material): C, 68.91; H, 5.20; N, 3.47.

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(27) All melting points are corrected and were taken on a Fisher-Johns block unless otherwise indicated. Analyses were performed by Galbraith Laboratories, Inc., Knoxville 21, Tenn. Except as otherwise noted, the lithium nitride employed in these experiments was generously supplied by Foote Mineral Co., West Chester, Pa.

Infrared spectra of the two samples were nearly identical, varying only in the relative intensities of two bands in the vicinity of 1500 cm.$^{-1}$. Thompson[25] reported m.p. 197–198° for this compound. The 160° melting point is apparently that of a second crystalline modification; polymorphism is not uncommon in the tertiary amides.[25]

Reaction of Lithium Nitride with Acetyl Chloride.—The lithium nitride employed in this experiment was prepared by the method of Masdupuy and Gallais[28] as a black crystalline solid which was then ground to a fine powder in a mortar. Acetyl chloride (54 g., 0.23 mole) was added over 15 min. to a dispersion of 7.67 g. (0.22 mole) of lithium nitride in 50 ml. of diglyme. The mixture was stirred mechanically and warmed on a steam bath for 4 hr. The mixture was then filtered to remove lithium chloride and unchanged lithium nitride and the filtrate was cooled. A precipitate of 1.5 g. of diacetamide, m.p. 77–78°, was obtained and identified by its molecular weight and infrared spectrum. No triacetamide was observed.

In another experiment employing Foote Mineral lithium nitride,[27] 23.2 g. (0.25 mole) of acetyl chloride was added over a period of 2 hr. to 3 g. (0.086 mole) of lithium nitride in 5 ml. of diglyme. The mixture was stirred for 6 hr. and allowed to stand overnight, when an additional 5 g. of acetyl chloride was added without observable effect. To the mixture was added 100 ml. of 5% sodium hydroxide solution and the resulting mixture was extracted with ether. Removal of the ether by distillation left 0.8 g. of a dark red resinous material which melted over a range of 118–126° and appeared to be an aldol resin. Acidification of the aqueous layer produced a small amount of a precipitate which was assumed to be diacetamide but which was not investigated.

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The Reaction of Alkyl Benzenesulfonates with Sodium Methoxide in Dimethyl Sulfoxide and Dimethylformamide. Scope and Stereochemistry.

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Benzenesulfonates of typical primary and secondary alcohols react rapidly at room temperature with sodium methoxide in dimethyl sulfoxide to give high yields of alkenes and/or alkyl methyl ethers. Except for cyclohexyl benzenesulfonate, the ether–alkene ratio is significantly higher in reactions with sodium methoxide than with potassium *t*-butoxide. Although 2-octyl benzenesulfonate reacts more slowly with sodium methoxide than with potassium *t*-butoxide in dimethylformamide, product ratios are essentially identical in both solvents. Mechanistic implications are discussed for the predominance of Hofmann elimination from 2-octyl benzenesulfonate and for the conversion of 2-octyl *p*-brosylate to 2-methoxyoctane of inverted configuration.

Aryl sulfonates have been shown to react readily with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) to yield alkenes and alkyl *t*-butyl ethers.[1] Continued interest in the reaction has led to an investigation of other nucleophiles in DMSO and other aprotic media. Results of investigations involving both sodium methoxide[2] and dimethylformamide (DMF) are reported here.

Benzenesulfonate esters were treated with an excess of sodium methoxide in DMSO at 20–25° for 30 min. and the products were analyzed by gas chromatography as described previously.[1] Table I presents a comparison of results obtained in this investigation with corresponding results reported earlier for potassium *t*-butoxide. In Table II are results obtained in DMF for reactions of benzenesulfonates of a typical primary and secondary alcohol with both sodium methoxide and potassium *t*-butoxide.

Generally the data are consistent with a recent report that both *n*-octadecyl bromide and 2-mesitylethyl tosylate give a larger substitution–elimination ratio with sodium methoxide in refluxing methanol than with potassium *t*-butoxide in refluxing *t*-butyl alcohol.[3]

More specifically, predominant Hofmann elimination obtained with 2-octyl benzenesulfonate and potassium *t*-butoxide (65% Hofmann in DMSO; 66% in DMF) compared with this ester and sodium methoxide (59% and 57% Hofmann in DMSO; 56% and 55% in DMF) appears to be another example of the steric influence of the nucleophile in controlling the direction of elimination.[4]

Because isomerization of alkenes has been reported under conditions similar to these, a control experiment was run using 0.5 M 1-octene and 1.0 M potassium *t*-butoxide in DMSO at 20°. The observation of less than 4% isomerization to 2-octene, together with reported equilibrium constants, in a similar system but at 55°, of 7.83 and 25.9 for isomerization of 1-pentene to *cis*- and *trans*-2-pentene, respectively,[5] indicates almost exclusive kinetic control of alkene ratios here.

Predominantly Hofmann elimination observed in this study, even with methoxide anion, contrasts remarkably with predominantly Saytzeff elimination (58–59% Saytzeff in five runs) observed in the E2 elimination of 2-pentyl arenesulfonates with sodium ethoxide in ethanol.[6] In the present study similarities of product proportions in both DMSO and DMF suggest that the predominance of Hofmann elimination here may be due to a general solvent effect. A simple explanation is based on the inability of DMSO and DMF (but ability of ethanol) to solvate anions by hydrogen bonding. Thus, in Colter and Johnson's study, the solvent ethanol can stabilize the departing anion readily by hydrogen bonding in a *trans* elimination. In this work, however, hydrogen bonding to the sulfonate anion can occur only from alcohol *generated in the elimination itself.* The stabilization gained by hydrogen bonding of the generated anion with simultaneously generated alcohol may be a sufficient driving

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