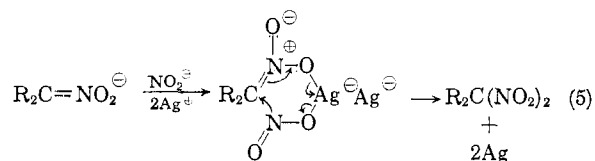


stituted for silver nitrate; however, it has the disadvantages that it is acidic,⁶ its action is slower and more difficult to reproduce, and lower yields of desired products are obtained. Other cationic oxidizing agents have been investigated in the presence of nitrites; however, none is effective in yielding *gem* dinitro compounds. Reaction of salts of 2-nitropropane with cupric ammonium hydroxide yields 2,3-dimethyl-2,3-dinitrobutane⁷; with cuprous chloride, cuprous acetate, ammoniacal cuprous chloride, or Fehling solution, the principal product is acetone. Cupric chloride, an acidic reagent, gives propyl pseudonitrole; ferric chloride yields 2,3-dimethyl-2,3-dinitrobutane and ferric 2-propanenitronate. Anionic oxidants such as ammonium persulfate and sodium peroxide oxidize primary⁸ and secondary⁷ nitronates to *vicinal* dinitro compounds (oxidative dimers) and carbonyl derivatives; neutral potassium permanganate gives the aldehyde^{9a} or ketone^{9b} as the principal product. Since the effects of silver or mercuric ions seem specific in effecting oxidative nitration of a nitronate, it is possible that introduction of a second nitro group during oxidation-reduction may depend on an intermediate complex salt (Equation 5) whose decomposition into the corresponding dinitro compound is sterically favored.¹⁰



A typical procedure for oxidative nitration is illustrated for the preparation of 1,1-dinitroethane. A fresh solution of nitroethane (15.0 g., 0.2 mole), sodium nitrite (4.0 g., 97% assay) and aqueous sodium hydroxide (8.5 g., 80 ml.) was poured into a stirred mixture of aqueous silver nitrate (70.5 g., 0.41 mole in 120 ml.), sodium hydroxide (2-3 drops until silver oxide appeared) and ether (150 ml.) at 0-5°. A cream-colored solid formed immediately and the temperature rose to 10°. The solid decomposed rapidly with blackening and reduction of volume; the temperature rose to 20°. After a few minutes, the cooling bath was removed and the mixture was stirred for 30 minutes. The silver was filtered and washed with ether-

(6) The desired nitration reaction does not occur in acid solution, the nitrous acid produced reacts with the primary or secondary nitro compounds to yield the corresponding nitrolic acids or pseudonitroles.

(7) See also H. Shechter and R. B. Kaplan, *J. Am. Chem. Soc.*, **75**, 3980 (1953).

(8) A. L. Pagano, Ph.D. Dissertation, The Ohio State University, 1960.

(9) (a) F. T. Williams, Ph.D. Dissertation, The Ohio State University, 1958; (b) S. Nametkin and E. Posdnjakova, *J. Russ. Phys. Chem. Soc.*, **45**, 1420 (1913).

(10) A similar mechanism may be involved in electrolysis of nitronates and nitrite ions at platinum anodes to give *gem* dinitro compounds along with *vicinal* oxidative dimers.^{1d} (b) *gem* Dinitro compounds also are formed upon precipitating silver salts of mononitronates in the presence of preformed silver nitrite; *gem* dinitro compounds also are obtained by related processes in the Victor Meyer reaction for preparing mononitro compounds from alkyl halides and silver nitrite. (c) Silver salts of primary nitronates decompose in aqueous suspension to *gem* dinitroalkanes, *vicinal* dinitro compounds, aldehydes, the parent nitroalkane, silver, and nitrous acid, the nitrite generated competes so effectively that *gem* dinitro compounds are the major products formed in such systems.⁸

benzene. The combined filtrate, on distillation, gave colorless 1,1-dinitroethane (18.9 g., 78%); b.p. 55.5-56° (4.5 min.), n_D^{20} 1.4341-1.4346, d_4^{20} 1.355, MR_D (calcd.) 22.68, MR_D (found) 23.01, neut. equiv. (calcd.) 120, neut. equiv. (found) 122; lit.^{1b} b.p. 55-57° (4 mm.), n_D^{20} 1.4322.

(11) Organic Chemicals Department, Jackson Laboratories, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

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RALPH B. KAPLAN¹¹
HAROLD SHECHTER

RECEIVED JUNE 14, 1961

A NEW INTRACRYSTALLINE CATALYST

Sir:

An acid (hydrogen) form of synthetic sodium mordenite having high intracrystalline catalytic activity (Table I) has been prepared. Its measured surface area is in the range 400-500 m.²/g. (B.E.T. method). To our knowledge, this is the first complete acid form of an open zeolite (Found: Na, 0.08) with high thermal stability (800°).

The adsorption of only small molecules by other various cation forms of mordenite has been determined by the studies of Barrer.¹ In contrast to their results this new acid form mordenite has adsorption properties intermediate between zeolite "A" and faujasite and catalytic properties similar to zeolite "10X".^{2,3,4} Our results are compatible with the crystal structure of mordenite as recently determined by Meier.⁵ Preliminary results show that this material is a unique cation exchanger, operating over the entire pH range. Exchanges of di and tri-valent cations, such as Mg⁺⁺, Ba⁺⁺, Al⁺⁺⁺ can be accomplished without change in crystal structure from the parent material.

The catalytic cracking properties of the acid mordenite are similar to those described for "10X"⁴ including a higher paraffin-olefin ratio than that observed with a silica-alumina catalyst in our experiments.

TABLE I

Cracking of *n*-decane; 1 hr., 450°, L.H.S.V. 0.5

Catalyst	% Conversion	Ratios	
		Isobutane- <i>n</i> -butane	Paraffin-olefin
Acid mordenite	36	1.3	4.6
Silica alumina	19	3.3	3.3

In the 450° temperature range, a somewhat higher catalyst deposit observed with decane cracking over mordenite as compared with that from silica-alumina and silica-magnesia in our work, suggested possible catalytic activity at lower temperatures. Indeed this was observed, when cracking of *n*-hexadecane occurred at temperatures as low as 300°. When *n*-hexadecane was cracked at 350° over acid mordenite and silica-alumina under nearly identical conditions, 6 times more light hydrocarbon (up to C₅) was obtained from the former.

(1) R. M. Barrer, *Trans. Faraday Soc.*, **40**, 555 (1944).

(2) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *J. Am. Chem. Soc.*, **78**, 5963 (1956).

(3) R. M. Barrer, W. Buser and W. F. Grutter, *Chimia*, **9**, 118 (1955).

(4) P. B. Weisz and V. J. Frilette, *J. Phys. Chem.*, **64**, 382 (1960).

(5) W. M. Meier, private communication.

Further evidence of low temperature activity was revealed by micro-scale dehydration of ethanol, in which an activated alumina at 340° gave about equal quantities of ethylene and ether, while our catalyst gave ethylene exclusively at 250°.

We have observed cracking with a magnesium exchanged acid mordenite, and isomerization of cyclohexene over acid mordenite and its aluminum exchanged derivative.

Further work is in progress on several of the more interesting aspects of this material.

RESEARCH AND DEVELOPMENT DEPARTMENT
NORTON COMPANY ALLEN H. KEOUGH
WORCESTER, MASSACHUSETTS L. B. SAND

RECEIVED JUNE 28, 1961

LITHIUM N-DIHYDROPYRIDYLALUMINUM HYDRIDE—A SELECTIVE REDUCING AGENT FOR HIGHLY ELECTROPHILIC CARBONYL COMPOUNDS
Sir:

We have reported previously that pyridine is an excellent solvent for the reduction of ketones and the metalation of certain weakly acidic hydrocarbons by lithium aluminum hydride.¹ Carboxylic acids and esters also are cleanly reduced to alcohols in this medium. In contrast to the above results, which are obtained when lithium aluminum hydride is added to pyridine solutions of substrate, a highly selective reducing agent is formed when the hydride and pyridine are allowed to interact before addition of the substrate. This species,² lithium N-dihydropyridylaluminum hydride (I), acts as a weak hydride donor, reacting only with highly electrophilic carbonyl groups. Its rate of formation is quite rapid (but not as fast as the reduction of a ketone when one is present¹), as indicated by the results of a series of benzophenone reductions carried out by aliquots taken periodically from a solution of lithium aluminum deuteride in pyridine and analyzing the resultant mixture of benzhydrol and benzhydrol- α -D by infrared spectroscopy.

TABLE I

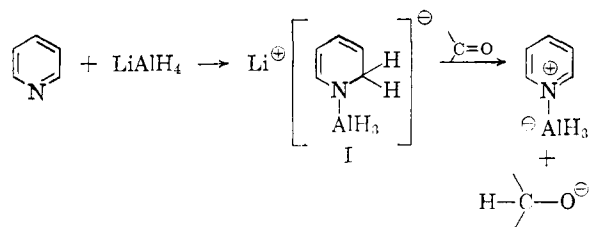
REDUCTIONS OF BENZOPHENONE BY LiAlD ₄ IN PYRIDINE	% C-H
"Age" of solution	
6 min.	2
10	7
30	21
2 hr.	50
24	71
50	77

The postulate that hydride transfer from the dihydropyridine ring is the path involved in carbonyl reduction is strengthened by the above data, as well as by the novel behavior of the complex (see below). This latter factor rules out the possibility that the results shown in Table I are due merely to reversal of the nucleophilic addition of the hydride to the pyridine ring. Such isotope scrambling could account for the observed C-H/C-D ratios, but the selectivity of I, as compared with the powerful reducing action of lithium aluminum hydride, is not explainable in terms of such an hypothesis.

(1) P. T. Lansbury, *J. Am. Chem. Soc.*, **83**, 429 (1961).

(2) F. Bohlmann, *Chem. Ber.*, **85**, 390 (1952).

The tentative assignment of a 1,2-dihydropyridine structure to the complex is based on the previously observed orientation in closely-related nucleophilic additions of organometallics and metal hydrides to N-heteroaromatics.^{2,3}



The specific reducing properties of I are illustrated by the facile reductions of benzophenone, 2,4'-dichlorobenzophenone and hexachloroacetone to the carbinols, whereas 1-naphthoic acid and methyl 1-naphthoate are recovered unchanged even after overnight exposure to excess complex. On the other hand, the reduction of such acids and esters in pyridine solution proceeds normally to alcohols when lithium aluminum hydride is added. This selective action of I may be used advantageously for reduction of ketone groups in certain polyfunctional compounds. Several examples, in which the simplicity of execution is illustrated, are recorded: To a 60-ml. serum bottle containing 50 ml. of anhydrous pyridine is added 0.50 g. of powdered lithium aluminum hydride. After the initial exothermic reaction, during which the solution acquires a dull orange coloration, the bottle is stoppered tightly and aged for at least one day, after which the lithium aluminum hydride is essentially consumed (see above). A ten milliliter aliquot (containing ca. 2.6 mmoles of I) of this solution⁴ is withdrawn by a hypodermic syringe and transferred to 1-1.5 mmoles of substrate, dissolved in pyridine, the solution then being kept overnight before hydrolysis and work-up in the usual manner.¹ Under such conditions of prolonged contact with excess reducing agent, *o*-(α -naphthoyl)-benzoic acid gave 76% 3- α -naphthylphthalide, whereas the methyl ester gave a 78% yield of this lactone. In both cases, infrared examination of the crude products showed only lactone absorption (1745 cm.⁻¹) in the carbonyl region.⁵ Furthermore, *o*-benzoylbenzoic acid and its methyl ester were reduced to 3-phenylphthalide in 93% and 62% yields, respectively. As above, the crude reduction products consisted essentially only of the lactone (carbonyl absorption at 1740 cm.⁻¹).

If a ratio of lithium aluminum hydride to *o*-(α -naphthoyl)-benzoic acid comparable to that used in the above reductions involving I is employed, according to the earlier procedure,¹ the conversion to diol is complete within 15 minutes. This con-

(3) (a) K. Ziegler and R. Zeiser, *Ber.*, **63**, 1847 (1930); (b) E. A. Braude, J. Hannah and R. P. Linstead, *J. Chem. Soc.*, 3249 (1960), and references cited therein; (c) H. S. Mosher, "Heterocyclic Compounds," R. C. Elderfield, editor, John Wiley and Sons, Inc., New York, N. Y., 1950, Volume 1, Chap. 8.

(4) Solutions aged for up to ten days still retain their reducing powder.

(5) This method of reducing this ketoacid appears to be far superior to sodium borohydride in methanol, from which the starting material is recovered unchanged after five hours at room temperature.