ether have been used as solvents without any purification, and the results are the same.

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Thermal Decomposition of Ammonium Nitrate

BY J. T. KUMMER

Recent interest in the decomposition of ammonium nitrate seems to make it worthwhile to call attention to an observation made recently during the preparation of a $N^{14}N^{14}$, $N^{14}N^{15}$, $N^{15}N^{15}$ mixture from a sample of NH_4NO_3 (Eastman Kodak Co.) in which the ammonium group contained 62 atom per cent. N^{15} and 38 atom per cent N^{14} and the nitrate group contained the 0.38% N^{15} of normal nitrogen. This NH_4NO_3 was decomposed, after it had melted, at 290° to give nitrous oxide. The nitrous oxide was then permitted to react quantitatively with a reduced iron catalyst at room temperature to give nitrogen and iron oxide. The nitrogen, when analyzed by a mass spectroscope, was found to contain 0.35% $N^{15}N^{15}$. If the ammonium nitrate molecule decomposed by the reaction of the ammonium group with the nitrate group, the percentage of $N^{15}N^{15}$ would be 0.24; whereas if all the nitrogen atoms present in the ammonium nitrate combined at random, the percentage of $N^{15}N^{15}$ would be 9.6. These results show that the decomposition of the ammonium nitrate to give N_2O proceeds practically entirely by a bond formation between the two nitrogen atoms of the two different groups present, and not by the interaction of similar groups.

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An Extension of the Scope of the Hammick Reaction

BY KURT MISLOW

The synthesis of α-pyridylcarbinols by the decarboxylation of picolinic acid in an excess of aldehyde or ketone was first reported by Hammick and co-workers.[1,2] These authors, after an apparently exhaustive investigation of a large number of decarboxylating acids, reported that "... the decarboxylation of pyridine and quinoline acids other than those containing the carboxyl group α to the nitrogen atom yielded no products of interaction with aldehydes and ketones."[2]

The similarity of the reactivity of the α- and γ-positions on the pyridine ring suggested, however, that this reaction might not necessarily be restricted to picolinic, quinaldinic and isoquinaldinic acids, but that it might be extended to include acids such as isonicotinic acid.

When isonicotinic acid was decarboxylated in boiling benzophenone, a small yield of diphenyl-γ-pyridylcarbinol was indeed realized. Benzophenone was selected as the solvent reagent because it had been shown[2] to react with decarboxylating picolinic acid and because its boiling point roughly coincides with the decarboxylating temperature of isonicotinic acid.

This result indicates that the Hammick reaction is of greater generality than has hithertofore been assumed.

Experimental[3]

A mixture of 19.8 g. (0.16 mole) of recrystallized isonicotinic acid and 250 g. (1.37 mole) of benzophenone was refluxed for nine and one-half hours, an air condenser being employed. A sealed-in plunger arrangement helped to scrape sublimed crystals of isonicotinic acid back into the reaction mixture. After five hours, 3600 ml. of carbon dioxide had been evolved (90% of the theory), and in the subsequent four and one-half hours, only 50 ml. more of the gas was evolved. The dark brown solution was allowed to cool to room temperature, diluted with 500 ml. of benzene and extracted with 2.5 *N* hydrochloric acid (more concentrated acid precipitates a tar, which redissolves on dilution). The acid extracts were made alkaline and extracted with benzene. The solid A at the interface was removed by centrifugation and the benzene layer was evaporated to dryness. The partially crystalline residue was freed of oil by washing with acetone, leaving 0.85 g. of crystals, m. p. 192–232°; recrystallization of A from benzene–pyridine gave an additional 0.6 g. of tan prisms, m. p. 205–232°. The total yield of crude carbinol thus amounted to 3.5%. Further recrystallization from benzene–pyridine afforded colorless microscopic prisms, m. p. 237–238°.

Anal. Calcd. for $C_{18}H_{15}ON$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.94; H, 5.79; N, 5.09.

Tschitschibabin and Benewolenskaja,[4] who prepared this compound by the action of phenylmagnesium bromide on phenyl-γ-pyridylketone, report a melting point of 235°.

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[1] Dyson and Hammick, *J. Chem. Soc.*, 1724 (1937).

[2] Ashworth, Daffern and Hammick, *ibid.*, 809 (1939).

[3] All melting points are corrected; microanalysis by Dr. G. Oppenheimer and Mr. G. A. Swinehart.

[4] Tschitschibabin and Benewolenskaja, *Ber.*, **61**, 547 (1928).

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Correlation of Surface Area and Dehydrogenation Activity for a Chromia–Alumina Catalyst

BY J. R. OWEN

In connection with dehydrogenation of normal butane at Plains Butadiene Plant, which is operated by Phillips Petroleum Company for Reconstruction Finance Corporation—Office of Rubber Reserve, a laboratory study was made of dehydrogenation activity and surface area of several samples of chromia–alumina catalyst A[1] that were used in the plant.

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[1] G. H. Hanson and H. L. Hays, *Chem. Eng. Progress*, to be published.