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

DEPARTMENT OF CHEMISTRY
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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.

Methods and Results.—Dehydrogenation activity was determined by passing normal butane (Pure Grade) through a portion of catalyst supported vertically in an electrically heated tube furnace, under the following conditions: hydrocarbon space velocity of 500 volumes (STP) per volume of catalyst per hour, pressure of one atmosphere (absolute), average internal catalyst temperature of 1100° F., and on-stream period of sixty minutes. The catalyst was flushed for two minutes before and after each dehydrogenation period with nitrogen, and was revivified for fifty-six minutes with air at a space velocity of 1000 volumes per volume of catalyst per hour. The single-pass conversion to normal butenes plus butadiene during each of 5 to 8 cycles was determined with a hydrogen-sensitive, thermal-conductivity gas analyzer and these values were averaged. The gas analyzer was calibrated by data from low-temperature fractional analyses of total dehydrogenation effluent.

Surface area of each catalyst was determined after the dehydrogenation test by the low-temperature nitrogen-adsorption method developed by Brunauer and Emmett,[2] in an apparatus similar to that described by Krieger.[3] The area was calculated by a two-point substitution in the BET equation. The data obtained are in Fig. 1; they show that there is a definite correlation between surface area and dehydrogenation activity for the chromia–alumina catalyst.

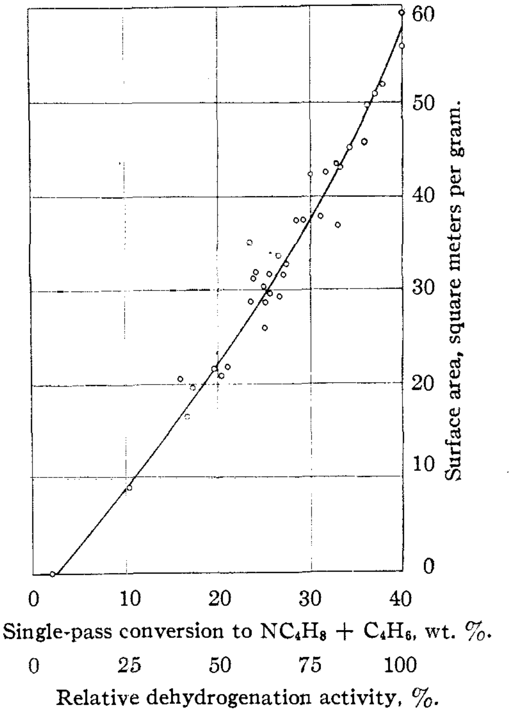

Fig. 1.—Correlation of surface area and dehydrogenation activity for chromia–alumina catalyst A.

Acknowledgment.—The author wishes to thank Phillips Petroleum Company and Reconstruction Finance Corporation—Office of Rubber Reserve for permission to publish these data.

PHILLIPS PETROLEUM COMPANY
RESEARCH DEPARTMENT
BARTLESVILLE, OKLAHOMA

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[2] S. Brunauer and P. H. Emmett, THIS JOURNAL, **57**, 1754 (1935); *et seq.*

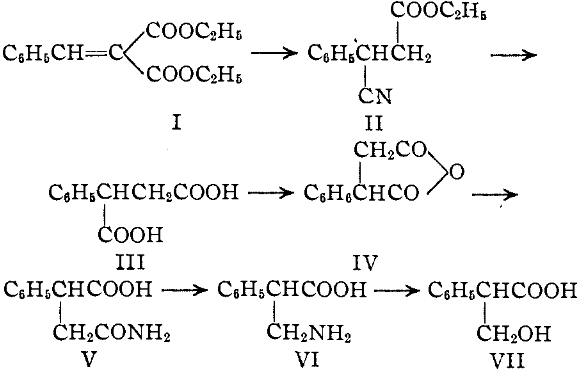
[3] K. A. Krieger, *Ind. Eng. Chem., Anal. Ed.*, **16**, 398 (1944).

A New Synthesis of *dl*-Tropic Acid

BY M. R. NATARAJAN AND S. SWAMINATHAN[1]

Tropic acid (VII) is formed through hydrolysis of atropine and related alkaloids. The earliest synthesis of this acid was by Ladenburg and Rügheimer[2] and this preparation was later improved by McKenzie and Wood.[3] In addition, syntheses have been reported by Müller[4] and by Chambon.[5]

The scheme of synthesis herein reported is essentially as follows:



$$\underset{\text{I}}{C_6H_5CH{=}C(COOC_2H_5)_2} \longrightarrow \underset{\text{II}}{C_6H_5\underset{CN}{CH}\overset{COOC_2H_5}{CH_2}} \longrightarrow$$

$$\underset{\text{III}}{C_6H_5\underset{COOH}{CH}CH_2COOH} \longrightarrow \underset{\text{IV}}{C_6H_6\overset{CH_2CO}{CH}CO}\!>\!O \longrightarrow$$

$$\underset{\text{V}}{C_6H_5\underset{CH_2CONH_2}{CH}COOH} \longrightarrow \underset{\text{VI}}{C_6H_5\underset{CH_2NH_2}{CH}COOH} \longrightarrow \underset{\text{VII}}{C_6H_5\underset{CH_2OH}{CH}COOH}$$

β-Amino-α-phenylpropionic acid (VI) was obtained by McKenzie and Strathern[6] by interaction of atropic acid and hydroxylamine in alcoholic solution, and, more recently, by Craig and Henze[7] through reduction of β-amino-α-hydroxy-α-phenylpropionic acid. The conversion of VI to tropic acid was achieved by adopting the method outlined by McKenzie and Strathern.[6]

Experimental

Phenylsuccinic acid was prepared from benzalmalonic ester,[8] and the anhydride obtained therefrom either by distilling under reduced pressure,[8] or by treating with three equivalents of acetyl chloride at 110° for three hours and subsequently distilling after removal of acetic acid, acetic anhydride and acetyl chloride at reduced pressure. The pure product distilled at 191–192° (12 mm.). The ammonium salt of α-phenylsuccinamic acid was obtained by interaction of dry ammonia and an ether solution of phenylsuccinic anhydride; the amido acid was precipitated in almost quantitative yield by addition of hydrochloric acid;[9] it melted at 145–146°.

β-Amino-α-phenylpropionic Acid.—To a cooled solution of 11.6 g. of potassium hydroxide in 105 cc. of water, 4 g. of bromine was added gradually with thorough stirring, the temperature being maintained at 0–5°. Four and one-half grams of α-phenylsuccinamic acid was added portionwise, and the mixture was warmed at 70° for four hours. After neutralization with hydrochloric acid, the solution was evaporated, the residue shaken with 60 cc. of water, and separated by filtration. The undissolved portion was

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[1] Lady Tata Research Scholar, Indian Institute of Science.

[2] Ladenburg and Rügheimer, *Ber.*, **13**, 2041 (1880); **22**, 2590 (1889).

[3] McKenzie and Wood, *J. Chem. Soc.*, **115**, 830 (1919).

[4] Müller, *Ber.*, **51**, 252 (1918); Wislicenus and Bilhuber, *ibid.*, **51**, 1237 (1918).

[5] Chambon, *Compt. rend.*, **186**, 1630 (1928).

[6] McKenzie and Strathern, *J. Chem. Soc.*, **127**, 85 (1925).

[7] Craig and Henze, *J. Org. Chem.*, **10**, 19 (1945).

[8] Bredt and Kallen, *Ann.*, **293**, 344–349 (1896); Wegscheider and Hecht, *Monatsh.*, **24**, 418 (1903).

[9] Hahn and Walter, *Ann.*, **354**, 132 (1907).