4.1 g. of magnesium, 40 g. of the bromide XIV and 28 g. of *p*-propionyltoluene. Distillation gave 26.2 g. of the tertiary alcohol boiling at 160–163° (3 mm.), $n^{20}D$ 1.5540, d^{20}_4 1.0025; MR_D calcd. 88.9, obsd. 90.2.

Anal. Calcd. for $C_{20}H_{26}O$: C, 85.1; H, 9.2. Found: C, 84.3; H, 9.4.

(c) 1-*p*-Tolyl-1-(2-methyl-5-propylphenyl)-propene (XVI).—Prepared by dehydration of compound XV in benzene solution in presence of oxalic acid. The olefin was obtained in 87% yield, b. p. 149–150° (3 mm.), $n^{20}D$ 1.5695, d^{20}_4 0.9616; MR_D calcd. 86.9, obsd. 89.9.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.84; H, 9.16. Found: C, 90.80; H, 9.20.

(d) 1-*p*-Tolyl-1-(2-methyl-5-propylphenyl)-propane (XVII).—The olefin, compound XVI, was hydrogenated under pressure in the presence of a nickel–kieselguhr catalyst at 45°. The hydrocarbon obtained (XVII) boiled at 143–144° (3 mm.), $n^{20}D$ 1.5455, d^{20}_4 0.9480; MR_D calcd. 87.3, obsd. 86.6.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.29; H, 9.80.

The infrared absorption spectra are given in Graph V.

Acetylation followed by treatment with 2,4-dinitrophenylhydrazone gave a solid derivative m. p. 263–265°. A mixed melting point with the dinitrophenylhydrazone of synthetic *p*-methylacetophenone showed no depression.

XI. Reaction of *p*-Xylene with 4-Methylcyclohexene

Forty-two grams (0.4 mole) of *p*-xylene was treated with 19.2 g. (0.2 mole) of 4-methylcyclohexene in the presence of 50 g. of hydrogen fluoride by the usual procedure described above. The hydrocarbon layer after washing and drying weighed 52 g. The following products were separated by fractional distillation through a 20-plate column: (1) 135–137° (750 mm.), 22 g., $n^{20}D$ 1.4960 (*p*-xylene); (2) 131–134° (10 mm.), 18 g., $n^{20}D$ 1.5260; (3) > 135° (4 mm.), 9 g., $n^{20}D$ 1.5310.

Fraction 2 corresponded to (1-methylcyclohexyl)-*p*-xylene, d^{20}_4 0.9363; MR_D calcd. 65.7, obsd. 66.2 (new compound).

Anal. Calcd. for $C_{15}H_{22}$: C, 89.11; H, 10.89. Found: C, 89.05; H, 10.77.

Acetylation yielded a ketone from which 2,4-dinitrophenylhydrazone was prepared. Crystallization from the chloroform–ethanol solution produced orange needles m. p. 172–174° (new compound).

Anal. Calcd. for $C_{23}H_{28}N_4O_4$: N, 13.21. Found: N, 13.70.

Nitration of the hydrocarbon with a solution of 2 volumes of 96% sulfuric acid gave a sirupy product which could not be crystallized.

Acknowledgment.—The authors wish to thank Dr. W. S. Gallaway, Universal Oil Products Company, for the infrared absorption spectra, and Miss Patricia Craig, Northwestern University, for microanalyses.

Summary

When *p*-ethyltoluene and *p*-propyltoluene react with methylcyclohexene in the presence of hydrogen fluoride and sulfuric acid, the main products formed result from a hydrogen transfer in which the aromatic hydrocarbons acted as a hydrogen donor and methylcyclohexene as a hydrogen acceptor.

The products obtained from the respective aromatic hydrocarbons through a hydrogen transfer were: 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane and 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane.

A mechanism for the hydrogen transfer reaction has been proposed; *p*-xylene on reaction with methylcyclohexene yields the expected cycloalkylation products.

The following new compounds and their derivatives were prepared; 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethanol, 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethene, 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane, 3,6-dimethyl-1-*p*-tolylindene, 3,6-dimethyl-1-*p*-tolylindan, 1-bromo-2-methyl-5-propylbenzene, 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propanol, 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propene, 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane and (1-methylcyclohexyl)-*p*-xylene.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 19, 1948

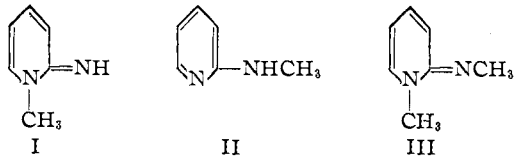
NOTES

2-Triphenylmethylaminopyridine

BY ROGER ADAMS AND JOHN B. CAMPBELL

The direct interaction of 2-aminopyridine and methyl iodide yields almost entirely the hydroiodide of N-methyl-2-pyridoneimide (I).[1] The reaction of the sodio derivative of 2-aminopyridine and methyl iodide yields principally 2-methylaminopyridine (II). The reaction of I or II with methyl iodide gives the dimethyl derivative (III). The same general behavior occurs when benzyl chloride is used rather than methyl iodide.

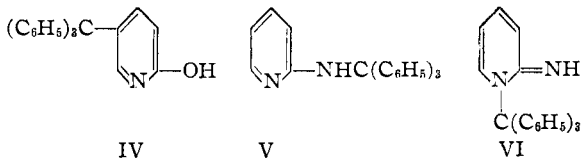
(1) Chichibabin, Konovalova and Konovalova, *Ber.*, **54**, 814 (1921).



I II III

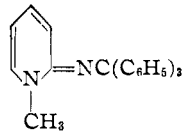
Triphenylcarbinol was condensed with 2-aminopyridine in the presence of a trace of acid in an attempt to obtain 5-triphenylmethyl-2-aminopyridine. Diazotization of the product in an effort to get the known 5-triphenylmethyl-2-hydroxypyridine (IV) resulted in cleavage of the molecule to yield triphenylcarbinol. Cleavage was also readily effected by means of concentrated

sulfuric acid. This behavior indicated that N-alkylation had occurred to produce V or VI. The attempted condensation of triphenylcarbinol with 2-aminopyridine using larger amounts of acidic catalyst gave only dark tarry products which could not be crystallized.



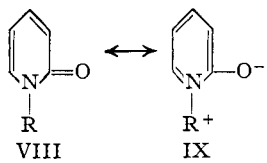
IV V VI

The product obtained was shown to be 2-triphenylmethylaminopyridine (V) by reaction with methyl iodide to yield N-methyl-2-pyridonetriphenylmethylimide(VII), the latter also being obtained in low yield by the reaction of N-methyl-2-pyridoneimide(I) with triphenylchloromethane. Thus, triphenylcarbinol reacts differently than do the methyl and benzyl halides.



VII

It is noteworthy that the free bases having the quinoid structure, as shown by I, III and VII, have a yellow color. The color is lost upon preparing the hydrochlorides. Since color is lacking in N-alkyl-2-pyridones (VIII), the color in the imide-type structures may be because the latter do not have as great a tendency to exist in a "zwitterion" structure as do the N-alkyl-2-pyridones as shown by IX. The zwitterion structure results in the loss of the quinoid structure and the attendant color.



VIII IX

Experimental

2-Triphenylmethylaminopyridine.—A mixture of 40 g. of 2-aminopyridine, 26 g. of triphenylcarbinol and 0.1 g. of *p*-toluenesulfonic acid was refluxed gently for two hours, steam being passed through the condenser to remove the water formed. The cooled mixture was recrystallized from 90% ethanol to yield 18.2 g. (54%) of light cream-colored crystals. Recrystallization from 95% ethanol gave glistening white crystals, m. p. 152–153° (cor.).

Anal. Calcd. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.57; H, 6.02; N, 8.18.

Cleavage of 2-Triphenylmethylaminopyridine. (A) By Nitrous Acid.—A suspension of 4.97 g. of powdered 2-triphenylmethylaminopyridine in 25 ml. of concd. hydrochloric acid was stirred at room temperature as a solution of 1.1 g. of sodium nitrite in 15 ml. of water was dropped in over a period of fifteen minutes. The mixture was stirred for one hour after the addition was complete. The white product was then collected on a filter and washed well with water. The yield was 3.50 g. (91%). Two recrystallizations from 95% ethanol gave pure triphenylcarbinol, m. p. 162°, as shown by the melting point of a mixture with an authentic sample.

(B) By Sulfuric Acid.—Upon dissolving 2-triphenylmethylaminopyridine in concd. sulfuric acid and pouring the solution into water, a nearly quantitative yield of triphenylcarbinol resulted.

N-Methyl-2-pyridonetriphenylmethylimide. (A) From 2-Triphenylmethylaminopyridine.—A solution of 1 g. of 2-triphenylmethylaminopyridine and 5 ml. of methyl iodide in 20 ml. of absolute ethanol was refluxed for five hours and then diluted with 50 ml. of petroleum ether. The precipitate of hydroiodide was collected on a filter and washed well with petroleum ether. It was then dissolved in 50 ml. of a 3:2 mixture of hot ethanol and water and the solution made basic with dilute aqueous sodium hydroxide. The mixture was warmed and stirred a few minutes and then cooled overnight in the ice-box. The yellow crystalline precipitate was collected on a filter and washed well with 50% ethanol. The yield was 0.52 g. (50%). Two recrystallizations from 95% ethanol gave yellow crystals, m. p. 151–152° (cor.). A melting point of this compound mixed with 2-triphenylmethylaminopyridine gave a large depression.

Anal. Calcd. for $C_{25}H_{22}N_2$: C, 85.67; H, 6.33; N, 8.00. Found: C, 85.84; H, 6.46; N, 7.98.

(B) From N-Methyl-2-pyridoneimide.—To a suspension of 2.36 g. of the hydroiodide of N-methyl-2-pyridoneimide[1] in 50 ml. of hot benzene was added 5 ml. of 10% aqueous sodium hydroxide and the mixture quickly shaken. The benzene layer was separated, dried over anhydrous sodium sulfate and the benzene removed on the steam-cone. To the green residual oil was added 2.8 g. of triphenylchloromethane and the mixture heated on the steam-cone one hour. Then 30 ml. of benzene was added and the mixture boiled a few minutes. After cooling overnight in the ice-box, the precipitate of hydrochloride was collected on a filter, washed well with benzene and dried. It was then taken up in 10 ml. of boiling ethanol and the solution made basic with the addition of 10% aqueous sodium hydroxide. After cooling in the ice-box, 0.20 g. of dark yellow crystalline material was collected on a filter. Recrystallization from 95% ethanol gave yellow crystals, m. p. 151–152° (cor.), identical with the product obtained above, as shown by a melting point of the mixture.

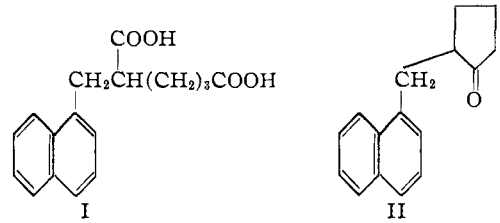
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED JULY 5, 1949

Preparation of the Isomeric 2-(Naphthylmethyl)-cyclopentanones

BY W. E. BACHMANN AND N. C. DENO[1]

Condensation of α-chloromethylnaphthalene with the sodio derivative of 2-carbethoxycyclopentanone gave the substituted cyclic keto ester, which was hydrolyzed by alkali with ring cleavage to α-(1′-naphthylmethyl)-adipic acid (I). Cyclization of the diacid with the aid of acetic anhy-



I II

(1) Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio.