

10.5 g. (20%) of yellow oil, b.p. 180–200° (3.0 mm.). (C) **Hydrogenation:** The ester from (B) was shaken under hydrogen (40 lb.) at room temperature for 8 hours in the presence of 2 g. of 5% palladium-charcoal and 100 ml. of ethyl acetate. The product was isolated as usual. Distillation *in vacuo* gave 6.2 g. (58%) of oil, b.p. 160–180° (3.0 mm.). This product gave negative tests with permanganate and with bromine. (D) **Glyoxylation:** Reaction of product C with excess ethyl oxalate in the presence of sodium ethoxide in dry ether according to the usual procedure gave 68% of alkali-soluble, red oil, which gave a red-purple ferric chloride test. (E) **Cyclization and Hydrolysis:** A solution of 5.9 g. of enol from (D) in 20 ml. of 85% phosphoric acid was chilled in ice and treated with a cold solution of 25 ml. of concd. sulfuric acid and 25 ml. of 85% phosphoric acid. The solution was kept at ice temperature for 10 days, and was hydrolyzed with ice and water. The gummy product was washed with dilute sodium hydroxide solution, and the remaining neutral material was warmed with 40 ml. of 5% sodium hydroxide solution on a steam-cone for 20 minutes. The mixture was filtered. The alkaline solution was washed with ether and was acidified with hydrochloric acid. Yellow crystals were deposited upon heating the turbid solution, or after standing several days at room temperature. The crystals were washed with water and triturated with ethanol. There was obtained 1.1 g. of anhydride, m.p. 169–172°. Recrystallization from ethyl acetate gave yellow crystals, m.p. 172–174°. The infrared spectrum

(chf.) had an intense double peak at 5.48 and 5.68  $\mu$  and a moderately strong peak at 6.18  $\mu$ .

*Anal.* Calcd. for  $C_{15}H_{14}O_2$ : C, 65.68; H, 5.15. Found: C, 65.68; H, 5.28.

The ultraviolet spectrum (ethanol) had  $\lambda_{max}$  237 and 362  $m\mu$  ( $\log \epsilon$  3.95 and 3.90, respectively) with minima at 227 and 275  $m\mu$  ( $\log \epsilon$  3.91 and 3.45, respectively) and a point of inflection at 308  $m\mu$  ( $\log \epsilon$  3.61). The spectrum of IX in sodium hydroxide solution had  $\lambda_{max}$  274  $m\mu$  ( $\log \epsilon$  4.11).

**2-Ethylphenol.**—A mixture of 18.0 g. of *o*-hydroxyacetophenone, 5 g. of 10% palladium-charcoal<sup>9</sup> and 400 ml. of ethyl acetate was shaken under hydrogen (40 lb.) at 80°. About 2.5 moles of hydrogen was consumed in 1.4 hours, after which time the reaction became very slow. Shaking was stopped after 2 hours, and the mixture was filtered. The solvent was evaporated. Distillation of the residue afforded 12.6 g. (78%) of colorless oil, b.p. 204–208°. The material had a strong characteristic odor, was soluble in dilute sodium hydroxide solution, and gave a deep blue ferric chloride test. 2-Ethylphenoxyacetic acid was prepared, following the usual procedure; colorless crystals, m.p. 138–140° (lit.<sup>11</sup> m.p. 140–141°).

(11) W. Steinkopf and T. Höpner, *J. prakt. Chem.*, [2] **113**, 140 (1926).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

## The Use of Alumina in Aromatic Cyclodehydration<sup>1,2</sup>

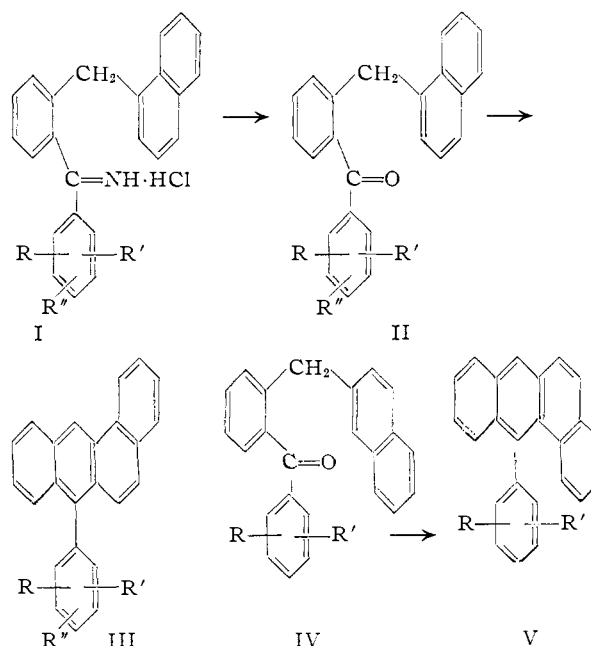
BY FRANK A. VINGIELLO AND ALEXEJ BOŘKOVEC

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A new procedure employing alumina has been successfully applied to the aromatic cyclodehydration of ketones to hydrocarbons.

Although the cyclization of ketones to hydrocarbons has generally proceeded quite well in solution under the influence of heat and acids,<sup>3–7</sup> sterically hindered ketones have failed to cyclize under these conditions.<sup>5,7</sup> So for example 2-(1-naphthylmethyl)-2',6'-dimethylbenzophenone (II, R,R' = 2',6'-dimethyl, R'' = H), 2-(2-naphthylmethyl)-2',6'-dimethylbenzophenone (IV, R,R' = 2',6'-dimethyl) and 2-(1-naphthylmethyl)-2',4',6'-trimethylbenzophenone (II, R,R',R'' = 2',4',6'-trimethyl) are cleaved under the usual cyclizing conditions<sup>5</sup> to give 1,2-benzanthracene. This indicated the necessity of devising a new method or at least of changing the conditions of the cyclization. Cold concentrated sulfuric acid led invariably to sulfonated, water-soluble products. Phosphorus pentoxide and 100% phosphoric acid yielded small amounts of green fluorescent oils which could not be crystallized. Finally a successful method was devised which followed a rather unconventional line. The

previous cyclizations were carried out in solution with catalysis by a strong mineral acid. The new method consists of heating the ketone with powdered aluminum oxide to 240–280° under reduced



pressure. This procedure yielded excellent results in the cases of the hindered ketones (II and IV with

(1) Presented before the Division of Organic Chemistry at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1955.

(2) This paper has been abstracted from the Doctorate thesis presented to the Virginia Polytechnic Institute by Alexej Bořkovec in 1955.

(3) C. K. Bradsher, *This Journal*, **62**, 486 (1940).

(4) F. A. Vingiello, A. Bořkovec and J. Shulman, *ibid.*, **77**, 2320 (1955).

(5) F. A. Vingiello and A. Bořkovec, *ibid.*, **77**, 3413 (1955).

(6) F. A. Vingiello and A. Bořkovec, *ibid.*, **77**, 4823 (1955).

(7) Presented before the Section of Organic Chemistry at the Seventh Southeastern Regional Meeting of the American Chemical Society, Columbia, South Carolina, Nov., 1955.

two *o*-methyl groups). When applied to the cyclization of unhindered ketones, this procedure, in general, proved to be superior to the usual one.<sup>5</sup>

In one series of experiments the optimal reaction time was shown to be about two hours and the optimal reaction temperature about 270°. In a second series of experiments different kinds of alumina were used. Three sorts of Woelm alumina (designated as: "acid," "basic" and "non-alkaline") were compared with Fisher alumina for chromatographic analysis. Under similar conditions, the latter and Woelm "basic" alumina gave the better results, the "acid" alumina being surprisingly inefficient.

It must be emphasized that the alumina cyclization reaction cannot be considered at present as a clean-cut procedure as far as the mechanism, scope and limitations are concerned. It can perhaps be argued that aluminum oxide, being able to act as a "Lewis acid,"<sup>8</sup> simply replaces the function of the hydrobromic acid in the usual cyclization mixture. It is quite difficult, however, to imagine ionic processes in the absence of a solvent. It seems more acceptable to regard the alumina only or mainly from the point of view of a large active surface acting in a similar way to the hydrogenation catalysts.<sup>9</sup> This, on the other hand, is also open to serious objections and much more work will have to be done before this reaction is fully understood.

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#### Experimental<sup>10,11</sup>

**2-(1-Naphthylmethyl)-2',4',6'-trimethyldiphenylketimine Hydrochloride (I, R,R',R'' = 2',4',6'-Trimethyl).**—A Grignard reagent was prepared from 3.7 g. (0.16 mole) of magnesium and 30 g. (0.16 mole) of bromobenzene in 200 ml. of dry ether. The slow reaction was initiated with a small amount of ethylmagnesium iodide. After eight hours all the metal had reacted, the ether was replaced with 12 g. (0.05 mole) of 2-(1-naphthylmethyl)-benzimidazole<sup>4</sup> in 200 ml. of dry toluene, and the mixture heated under reflux overnight. After adding 30 ml. of 20% ammonium chloride solution, the mixture was boiled until it cleared, the deep red, fluorescent liquid was decanted, and the residue washed with benzene. The toluene and benzene solutions were combined and mixed with 20 ml. of concd. hydrochloric acid, whereupon the ketimine salt crystallized after scratching the flask with a glass rod. The crystals were filtered, washed with toluene, then with acetone, and dried; yield 18 g. (88%).

The analytical sample was prepared by decomposing the crude ketimine hydrochloride with sodium hydroxide, extracting the free imine with benzene, and precipitating the hydrochloride with concd. hydrochloric acid. Recrystallization from a mixture of ethanol and acetone (1:10) and a mixture of chloroform and ether (1:5) gave small, colorless crystals, m.p. 195° dec.

*Anal.* Calcd. for C<sub>27</sub>H<sub>26</sub>NCl: N, 3.50. Found: N, 3.33.

**2-(1-Naphthylmethyl)-2',4',6'-trimethylbenzophenone (II, R,R',R'' = 2',4',6'-Trimethyl).**—A suspension of 2.0 g. of the above ketimine hydrochloride in 25 ml. of water and 10 ml. of concd. sulfuric acid was sealed in a Carius tube and heated in a Carius furnace for six hours at 180°. The tube was cooled, opened, and the brown glassy material separated, dissolved in a mixture of benzene and petroleum ether (8:2) and passed through a short column packed with Fisher alumina for chromatographic analysis. On evaporating the solvent from the percolate there was obtained a

slightly yellow oil which was crystallized from ligroin (60–90°), and recrystallized from a mixture of dioxane and ethanol (1:1) and finally from acetone. Colorless crystals were obtained, m.p. 159.5°, yield 1.4 g. (77%).

*Anal.* Calcd. for C<sub>27</sub>H<sub>24</sub>O: C, 88.97; H, 6.44. Found: C, 88.64; H, 6.82.

**10-(2',4',6'-Trimethylphenyl)-1,2-benzanthracene (III, R,R',R'' = 2',4',6'-Trimethyl).** A.—**Attempted Preparation from the Ketimine via Acid Cyclization.**—A mixture of 4.0 g. of the corresponding ketimine hydrochloride, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace for six hours at 220°. The tube was cooled, opened, the contents extracted with benzene and chromatographed<sup>12</sup> on alumina. The first fraction, eluted with petroleum ether, yielded 0.85 g. (37%) of 1,2-benzanthracene which was identified through the following data: m.p. 157–158° (lit.<sup>13</sup> 158–159°); it dissolves in concentrated sulfuric acid with the formation of a red solution which on standing turns blue (lit.<sup>13</sup> reports the same phenomena); picrate, m.p. 140.5–141.5° (lit.<sup>13</sup> 141.5–142.5°); trinitrofluorenone adduct, m.p. 223–223.5° (lit.<sup>14</sup> 223.6–224.0°), the ultraviolet absorption spectrum is the same as that reported by Clar<sup>15</sup> and by Friedel and Orchin.<sup>16</sup> The second fraction, eluted with a mixture of ether and petroleum ether (2:8), gave 1.4 g. of an unidentified red oil. Several other fractions were not eluted.

B. **Preparation from the Ketone via Alumina.**—A mixture of 2.0 g. of the corresponding ketone and 15 g. of Fisher alumina for chromatographic analysis was heated at 240–250° under reduced pressure (0.5 mm.) for two hours. The hydrocarbon was recovered by chromatography<sup>12</sup> on alumina using petroleum ether as the eluent. It formed colorless crystals, m.p. 144.5–145.5°, yield 1.5 g. (83%).

*Anal.* Calcd. for C<sub>27</sub>H<sub>22</sub>: C, 93.61; H, 6.39. Found: C, 93.29; H, 6.70.

The ultraviolet spectrum was taken with a Beckman spectrophotometer (model DU, 1-cm. silica cell) at a concn. of 10 mg./l. using 95% ethanol as the solvent. The curve, as compared with the curve for 1,2-benzanthracene,<sup>13,16</sup> shows the same bathochromic shift as the 10-methylphenyl-1,2-benzanthracenes.<sup>4</sup> The wave length maxima for III where R,R',R'' = 2',4',6'-trimethyl are: λ 222, λ 259, λ 271, λ 281, λ 292, λ 320, λ 335, λ 351 and λ 368 mμ.

**10-(2',6'-Dimethylphenyl)-1,2-benzanthracene (III, R,R' = 2',6'-Dimethyl; R'' = H).** A.—**Attempted Preparation from the Ketimine via Acid Cyclization.**—A mixture of 2.0 g. of the corresponding ketimine hydrochloride, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace for 46 hours at 180°. The tube was cooled, opened, the contents extracted with benzene and chromatographed<sup>12</sup> on alumina. The first fraction, eluted with a mixture of ether and petroleum ether (3:7) yielded 0.40 g. (30%) of 1,2-benzanthracene which was identified as previously described. The second fraction consisted of 0.20 g. of an unidentified deep red solid.

B. **Preparation from the Ketone Using Alumina.**—A mixture of 1.5 g. of the corresponding ketone and 30 g. of Fisher alumina for chromatographic analysis was heated at 240–270° under reduced pressure (1.0 mm.) for three hours. The hydrocarbon was recovered by chromatography<sup>12</sup> as colorless crystals, m.p. 134.5–135.5°, yield 0.66 g. (46%).

*Anal.*<sup>16</sup> Calcd. for C<sub>26</sub>H<sub>20</sub>: C, 93.93; H, 6.07. Found: C, 93.57; H, 6.07.

**9-(2',6'-Dimethylphenyl)-1,2-benzanthracene (V, R,R' = 2',6'-Dimethyl).** A.—**Attempted Preparation from the Ketone via Acid Cyclization.**—A mixture of 2.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace for 21 hours at 180°. The black mixture which formed was extracted with benzene and chromatographed<sup>12</sup> on alumina. The only fraction which

(12) For the details of this procedure see ref. 7.

(13) E. Clar, "Aromatische Kohlenwasserstoffe Polycyclische System," Zweite Auflage Springer Verlag, Berlin, 1952, p. 186.

(14) M. Orchin and R. O. Woolfolk, *This Journal*, **68**, 1727 (1946).

(15) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(16) See ref. 5 for the ultraviolet spectrum.

(8) C. Dufraisse and R. Hoclois, *Bull. soc. chim.*, **3**, 1880 (1936).

(9) R. Linstead, W. Doering, B. Selby, P. Levine and R. Whetstone, *This Journal*, **64**, 1986 (1942).

(10) All melting points are corrected.

(11) All the analyses were carried out by the Micro-Tech Laboratories, Skokie, Ill.

could be identified was a fraction of 0.63 g. (49%) of 1,2-benzanthracene.

**B. Preparation from the Ketone via Alumina.**—A mixture of 1.0 g. of the ketone and 25 g. of alumina was heated at 240–270° under reduced pressure (1.0 mm.) for two hours. The yellow powder was then chromatographed<sup>12</sup> on alumina using a mixture of benzene and petroleum ether (1:4) as the eluent. A yellow fluorescent fraction was collected and rechromatographed on alumina using petroleum ether as the eluent. A colorless, blue fluorescent zone was eluted and concentrated. Crystallization from ethanol gave first colorless prisms, m.p. 193–200°, insoluble in concd. H<sub>2</sub>SO<sub>4</sub>, which were shown spectroscopically not to be the expected benzanthracene derivative. The analysis corresponds well to a dihydro-9-(2',6'-dimethylphenyl)-1,2-benzanthracene.

*Anal.* Calcd. for C<sub>26</sub>H<sub>22</sub>: C, 93.37; H, 6.63. Found: C, 93.47; H, 6.56.

The second product of crystallization was colorless plates, m.p. 123.5°, soluble in concd. H<sub>2</sub>SO<sub>4</sub> with the formation of a red solution which changed to blue and then to brown.

The spectroscopic evidence<sup>7</sup> indicated that this was the expected hydrocarbon.

*Anal.* Calcd. for C<sub>26</sub>H<sub>26</sub>: C, 93.94; H, 6.06. Found: C, 94.00; H, 6.25.

The remaining fractions could not be identified. The yield of 9-(2',6'-dimethylphenyl)-1,2-benzanthracene was 6.0%.

Other hydrocarbons, first prepared by acid cyclization<sup>4,6,7</sup> but now prepared by the alumina method, are listed together with the yields.

Compound III	Yield, %	Compound V	Yield, %
R,R',R'' = H	99	R,R' = H	74
R = 2'-CH <sub>3</sub> ; R',R'' = H	82	R = 2'-CH <sub>3</sub> ; R' = H	42
R = 3'-CH <sub>3</sub> ; R',R'' = H	92	R = 3'-CH <sub>3</sub> ; R' = H	80
R = 4'-CH <sub>3</sub> ; R',R'' = H	96	R,R' = 2',4'-dimethyl	75
		R,R' = 2',5'-dimethyl	46
		R,R' = 3',4'-dimethyl	68

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, WEIZMANN INSTITUTE OF SCIENCE]

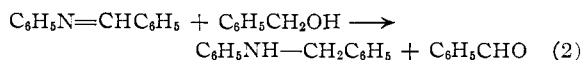
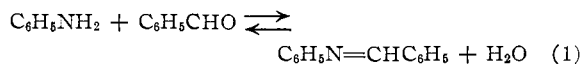
## Reduction and Benzylolation by Means of Benzyl Alcohol. II. N-Benzylolation. The Preparation of Secondary Aromatic Benzylamines

BY YA'IR SPRINZAK

RECEIVED NOVEMBER 7, 1955

A method is described for the monobenzylolation of aromatic amines. It consists in heating the amine with benzyl alcohol in the presence of potassium hydroxide and distilling off the water as it is formed. The reaction is accelerated by the addition of benzaldehyde. With bi-primary amines, each amino group is monobenzylolated. The method is also suitable for the preparation of benzylaminopyridines.

It has been reported in part I of this series<sup>1</sup> that fluorene and its derivatives are readily benzylolated in the 9-position by heating with benzyl alcohol in the presence of potassium hydroxide. The present paper reports the N-benzylolation of a variety of primary aromatic amines (Table I) by a modification of this procedure<sup>2</sup> in which equilibrium (1) is forced to the right by distilling off the by-product water as it forms.



Under these conditions it is to be expected that the potassium hydroxide would be converted to potassium benzylate.<sup>3</sup> A closely related procedure using xylene as a solvent and ordinarily employing a U.O.P. nickel catalyst has been published recently,<sup>4</sup> and an earlier paper<sup>5</sup> describes N-alkylation of aniline using dry alkoxides of aliphatic alcohols.

In certain cases (Table I) it is advantageous to accelerate the reaction by adding a small amount of benzaldehyde.<sup>6</sup> This may be correlated with the reported acceleration by benzalaniline and with the interpretation of the function of the U.O.P. nickel.<sup>4</sup> The rate of reaction may also be increased

by the use of a higher concentration of potassium hydroxide.

The data of Table I emphasize the variety of primary aromatic amines which are readily benzylolated in high yield by this method. It is noteworthy that  $\alpha$ -aminopyridines react as readily, although alkylation of these amines by benzyl halides often gives 1-benzyl-2-pyridoneimines.<sup>7</sup>

### Experimental

**Materials.**—All amines used were commercial products, employed without purification, with the exception of the following, which were redistilled *in vacuo*: *o*-toluidine, *m*-toluidine and *m*-phenylenediamine.

**Apparatus and Procedure.**—The apparatus used consisted of a flask equipped with a separator and a thermometer. As the usual type of trap for separating heavy liquids from water proved inefficient, use was made of the funnel commonly employed for the preparation of alkyl iodides.<sup>8</sup> A "cold finger" passing through its neck and reaching to its bottom served both to condense vapors coming through its side arm and to cool the condensed liquid. To avoid occlusion of water in the narrow depression of the bottom at the beginning of condensation, a few drops of benzyl alcohol were filled into the funnel before reaction was started. The reaction flask was supplemented with a dropping funnel in experiments where benzaldehyde was added during the reaction.

After the reactants had been placed in the flask, the mixture was heated rapidly and kept boiling sufficiently vigorously to enable vapors to condense in the funnel at a moderate rate. The tap of the funnel was opened from time to time to allow the lower layer of the distillate, which consisted of benzyl alcohol, to return to the flask. The benzaldehyde,

(1) Y. Sprinzak, *THIS JOURNAL*, **78**, 466 (1956).

(2) Y. Sprinzak, Israeli Pat. 6492 (April 8, 1953); Brit. Pat., 276545 (Jan. 27, 1953).

(3) A. Wacker, French Patent 653818 (May 3, 1928); *Chem. Zentr.*, **100**, I, 3036 (1929).

(4) E. F. Pratt and E. J. Frazza, *THIS JOURNAL*, **76**, 6174 (1954).

(5) J. U. Nef, *Ann.*, **318**, 137 (1901).

(6) Cf. reference 1.

(7) A. E. Tschitschibabin, R. A. Konowalowa and A. A. Konowalowa, *Ber.*, **54**, 814 (1921); Th. M. Sharp, *J. Chem. Soc.*, 1855 (1939); J. H. Biel, *THIS JOURNAL*, **71**, 1306 (1949).

(8) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 285; H. S. King, "Org. Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 399.