

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

The Synthesis of 9-Phenyl-1,2-benzanthracene and the Three Isomeric 9-Monomethylphenyl-1,2-benzanthracenes<sup>1,2</sup>

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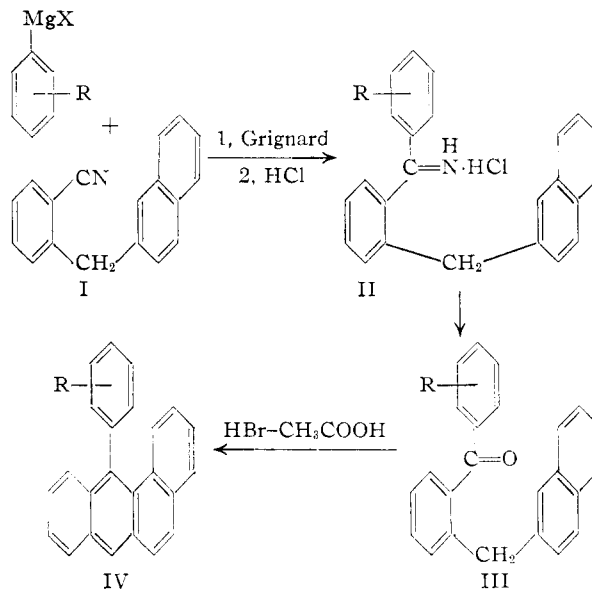
RECEIVED MARCH 10, 1955

Using a previously described method, the synthesis of four new ketimine hydrochlorides, four new ketones and three new hydrocarbons has been accomplished. Bradsher's aromatic cyclodehydration reaction<sup>3</sup> has been extended to the 9-aryl-1,2-benzanthracene system.

Recently Vingiello, Bořkovec and Shulman<sup>4</sup> have extended Bradsher's aromatic cyclodehydration reaction<sup>3</sup> to the preparation of hydrocarbons in the 10-aryl-1,2-benzanthracene system. The preparation of 9-aryl-1,2-benzanthracenes seemed to be a challenging extension of this reaction since the geometry of this system suggests that dehydrogenation to the corresponding 1,2,3,4-dibenzopyrenes,<sup>5</sup> whose structures are greatly stabilized by resonance,<sup>6</sup> might preclude the possibility of isolating the immediate product of cyclodehydration in good yield. Further, the ketones which are cyclized to give the 9-aryl-1,2-benzanthracenes might undergo cyclization in such a way as to give 9-aryl-2,3-benzanthracenes. This latter possibility does not exist in the synthesis of the 10-aryl-1,2-benzanthracenes.

We have now demonstrated that it is indeed possible to prepare hydrocarbons in the 9-aryl-1,2-benzanthracene system by aromatic cyclodehydration since we have prepared 9-phenyl-1,2-benzanthracene and the three isomeric 9-monomethylphenyl-1,2-benzanthracenes in excellent yield.

A new and more economical method has been found for obtaining the 2-(2-cyanobenzyl)-naphthalene (I) required in the synthesis. Bradsher<sup>7</sup> used a Grignard reaction followed by reduction to obtain *o*-chlorobenzyl naphthalene. We found that although we were able to isolate the intermediate carbinol the reduction step gave variable results. The new method involves the direct condensation of *o*-chlorobenzyl chloride with naphthalene in nitrobenzene using aluminum chloride as a catalyst. In this way yields of 61% of a mixture of monobenzyl derivatives (based on the halide) were obtained. This material contained 50% of 2-(2-chlorobenzyl)-naphthalene. As in the case of 1-(2-chlorobenzyl)-naphthalene<sup>4</sup> it was found that the mixture of isomers could not be separated conveniently, so it was converted directly to a mixture of nitriles by the Rosenmund-von Braun method with isolation of



the pure 2-(2-cyanobenzyl)-naphthalene (I) being accomplished by fractional crystallization from 90% ethanol.

The reaction between the nitrile I and the appropriate Grignard reagent led to an excellent yield of the ketimine which was isolated as the hydrochloride. This was hydrolyzed quantitatively to the ketone III using dilute sulfuric acid and subsequently cyclodehydrated to the hydrocarbon IV using a mixture of hydrobromic and acetic acids.

The ultraviolet spectra of the hydrocarbons were taken and the maxima are recorded after Table III. These spectra imply that the 9-phenyl group is not coplanar with the 1,2-benzanthracene group.<sup>8</sup>

**Acknowledgment.**—This work was sponsored by the Office of Ordnance Research, U. S. Army.

Experimental<sup>9,10</sup>

**2-Chlorophenyl-2-naphthylcarbinol.**<sup>11</sup>—The Grignard reagent prepared from 11.6 g. (0.48 mole) of magnesium, 100 g. (0.48 mole) of  $\beta$ -bromonaphthalene in 250 ml. of dry ether was allowed to react with 65 g. (0.46 mole) of *o*-chlorobenzaldehyde. The addition compound then was decomposed with 50 ml. of 20% ammonium chloride solution and the ether-soluble material was extracted, washed with water, dried over Drierite, and finally concentrated. The residue was fractionated under reduced pressure and the fraction distilling at 208–210° (1.5 mm.) was collected, yield 71 g.

(8) R. N. Jones, *ibid.*, **67**, 2127 (1945).

(9) All melting points are corrected.

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

(11) This compound is a previously unisolated intermediate in the synthesis of 2-(2-chlorobenzyl)-naphthalene by the method of Bradsher, ref. 7.

(1) Presented before the Division of Organic Chemistry at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March, 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) E. Clar, "Aromatische Kohlenwasserstoffe Polycyclische System," Zweite Auflage, Springer-Verlag, Berlin, 1952, p. 340.

(6) The occurrence of a yellow band on the chromatography column, when the cyclization product was chromatographed, suggests that a small amount of the dibenzopyrene is formed. Presumably the initial cyclodehydration reaction is followed by a small amount of cyclodehydrogenation.

(7) C. K. Bradsher, *THIS JOURNAL*, **62**, 1077 (1940).

(57%). A portion of this viscous oil was refractionated and a sample was collected after half the material had distilled; b.p. 200–201° (1 mm.).

*Anal.* Calcd. for  $C_{17}H_{13}OCl$ : C, 75.98; H, 4.88. Found: C, 76.37; H, 4.88.

**2- and 1-(2-Chlorobenzyl)-naphthalene.**—A mixture of 384 g. (3 moles) of naphthalene, 650 ml. of nitrobenzene and 6 g. of aluminum chloride was stirred in a two-necked flask with a magnetic stirrer. The mixture was maintained at a pressure of approximately 30 mm. while 242 g. (1.5 moles) of *o*-chlorobenzyl chloride was added dropwise. After all the reagent had been added, the mixture was decomposed with 100 ml. of 20% hydrochloric acid, washed three times with water and dried over calcium chloride. After the nitrobenzene and unreacted naphthalene had been removed, the residue was fractionated under reduced pressure and the fraction distilling at 220–223° (10 mm.) was collected. The yield of 2- and 1-(2-chlorobenzyl)-naphthalene was 230 g. (61%).

**2-(2-Cyanobenzyl)-naphthalene (I).**—A mixture of 200 g. of the isomeric chloro compounds prepared above, 100 g. of cuprous cyanide, 60 ml. of pyridine and 0.2 g. of anhydrous cupric sulfate was heated in a metal-bath maintained at 260° for 17 hours under an air-cooled condenser. The reaction mixture then was cooled and subjected to a crude distillation in a von Braun flask (1 mm.). The distillate was poured into about 500 ml. of 1:1 ammonium hydroxide, stirred well and extracted with ether. The combined ether extracts were washed twice with 2 *N* hydrochloric acid, then with water and finally dried over calcium chloride. The ether was distilled, leaving a mobile liquid which was fractionated. The portion distilling at 190–192° (1 mm.) weighed 178 g. (92%). This fraction was dissolved in hot 90% ethanol, allowed to cool to room temperature, seeded with a pure crystal of the desired compound, and placed in a refrigerator (5°). After the solution stood for 2 days colorless prisms formed and were filtered: 36 g., m.p. 80–84°. The filtrate was concentrated and the crystallization process repeated a total of four times yielding a grand total of 65 g. (41%) of I. When twice recrystallized from ethanol, this material melted at 84–85°, lit.<sup>7</sup> 84.5–85.5°.

**2-(2-Naphthylmethyl)-2'-methylphenylketimine Hydrochloride (II, R = 2'-CH<sub>3</sub>).**—A Grignard reagent was prepared from 12.9 g. (0.075 mole) of *o*-bromotoluene and 1.8 g. (0.075 mole) of magnesium in 150 ml. of dry ether. Most of the ether was distilled and a solution of 12.2 g. (0.050 mole) of 2-(2-cyanobenzyl)-naphthalene in 100 ml. of dry toluene was added. The mixture was heated under reflux with stirring for 6 hours. It then was cooled and decomposed with an equivalent amount of 20% ammonium chloride solution. The toluene layer was decanted and the residue extracted with benzene. The toluene and benzene solutions were combined and concentrated hydrochloric acid was added to precipitate the ketimine hydrochloride. This gave 17.2 g. (92%) of a slightly yellow solid which was washed with petroleum ether (60–90°), then acetone and finally recrystallized from a mixture of 95% ethanol and acetone giving slightly brown large prisms whose m.p. was 185° dec.

*Anal.* Calcd. for  $C_{25}H_{22}NCl$ : C, 80.73; H, 5.98. Found: C, 80.78; H, 5.92.

TABLE I

R	NEW KETIMINE HYDROCHLORIDES (II)					
	Yield, %	M.p., °C., dec.	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
H	80	181	80.54	80.28	5.65	5.82
2'-CH <sub>3</sub>	92	185	80.73	80.78	5.98	5.92
3'-CH <sub>3</sub>	70	175	80.73	80.65	5.98	6.10
4'-CH <sub>3</sub>	55	194	80.73	80.37	5.98	6.03

The other ketimine hydrochlorides were prepared in a similar way.<sup>12</sup>

**2-(2-Naphthylmethyl)-3'-methylbenzophenone (III, R = 3'-CH<sub>3</sub>).**—A mixture of 10 g. of the ketimine hydrochloride, 40 ml. of 25% sulfuric acid and 30 ml. of toluene was heated under reflux for 2 hours. The toluene layer was separated, washed with water, dried over calcium chloride, filtered through charcoal and concentrated. The residue was fractionated under reduced pressure giving 8.4 g. (90%) of a viscous oil which distilled at 136–138° (1.5 mm.). Our attempts to crystallize this oil failed.

*Anal.* Calcd. for  $C_{25}H_{20}O$ : C, 89.25; H, 5.98. Found: C, 89.34; H, 6.19.

The other ketones were prepared in a similar way.

TABLE II

R	Yield, %	B.p. or m.p., °C.	Mm.	NEW KETONES (III)		Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
H	99	236–238	1.3	89.41	89.14	5.63	5.68		
2'-CH <sub>3</sub>	80	88.5–89.5		89.25	89.24	5.99	6.15		
3'-CH <sub>3</sub>	90	136–138	1.5	89.25	89.34	5.99	6.19		
4'-CH <sub>3</sub>	86	237–240	1.5	89.25	89.18	5.99	6.15		

**9-(3'-Methylphenyl)-1,2-benzanthracene (IV, R = 3'-CH<sub>3</sub>).**—A mixture of 1 g. of the ketone, 15 ml. of 48% hydrobromic acid and 30 ml. of glacial acetic acid was sealed in a Carius tube and heated in a Carius furnace for 3 hours at 180°. The whole was extracted with benzene, washed with water and dried over calcium chloride. The solution was filtered, diluted with 30–60° petroleum ether and chromatographed on a column 12 × 300 mm. packed with Fisher alumina (80–200 mesh) using 30–60° petroleum ether as the eluent. Later 30% of benzene was added to the eluting solution. On evaporating the solvents from the combined percolates, the hydrocarbon was obtained as colorless silky needles, m.p. 131–132°, 0.90 g. (95%). After four recrystallizations from a mixture of ethanol and acetone, crystals were obtained whose m.p. was 132.5–133.5°.

*Anal.* Calcd. for  $C_{23}H_{18}$ : C, 94.30; H, 5.70. Found: C, 93.93; H, 5.66.

The other hydrocarbons were prepared in a similar way.

TABLE III

R	Yield, %	M.p., °C.	NEW HYDROCARBONS <sup>a</sup> (IV)		Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
H	95	154–155 <sup>b</sup>						
2'-CH <sub>3</sub>	80	103.5–104.5	94.30	94.01	5.70	5.67		
3'-CH <sub>3</sub>	95	132.5–133.5	94.30	93.93	5.70	5.66		
4'-CH <sub>3</sub>	85	116.5–117.5	94.30	94.58	5.70	5.41		

<sup>a</sup> The ultraviolet spectra of the hydrocarbons were taken with a Beckman spectrophotometer (model DU, 1-cm. silica cell) at a concn. of 10 mg./l. using 95% EtOH as the solvent. The curves for all four hydrocarbons are practically identical. The wave length maxima for IV where R = 4'-CH<sub>3</sub> are:  $\lambda$ , 225 m $\mu$ , 259 m $\mu$ , 268 m $\mu$ , 279 m $\mu$ , 289 m $\mu$ , 335 m $\mu$ , 347 m $\mu$ , 360 m $\mu$ . <sup>b</sup> This hydrocarbon was prepared by E. Clar and D. Stewart, *J. Chem. Soc.*, 687 (1951).

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(12) The one exception was 2-(2-naphthylmethyl)-diphenylketimine hydrochloride which hydrolyzes too easily to be prepared by this method. It was prepared by liberating the free imine and then precipitating the hydrochloride from an ethereal solution with gaseous HCl.