of the isomeric 2-substituted compound. The blue eluate, wt. 0.9 g., was dissolved in ethanol and treated with 0.3 g. of trinitrobenzene. The complex which separated on standing was recrystallized from ethanol and melted at 105°. The visible spectrum of a solution prepared by decomposition of this fraction (λ_{max} 583, 600, 736 mμ; shoulders at 548, 562, 630, 660, 695 mμ; ϵ_{max} 221, 218, 49; λ_{min} 595; ϵ_{min} 216) indicated that this material consisted largely of the desired azulene, but the bands were less well pronounced than would be expected if it were pure.[10] The mother liquor was concentrated to dryness, rechromatographed and the eluate reconverted to the TNB complex. This was repeated three times in an effort to free the azulene from the less soluble contaminant. The trinitrobenzene complex separating from the last treatment melted at 92–95°, but the visible spectrum indicated no greater degree of purity.

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

The Synthesis of 10-Phenyl-1,2-benzanthracene and the Three Isomeric 10-Monomethylphenyl-1,2-benzanthracenes[1,2]

BY FRANK A. VINGIELLO, ALEXEJ BOŘKOVEC AND JOSEPH SHULMAN

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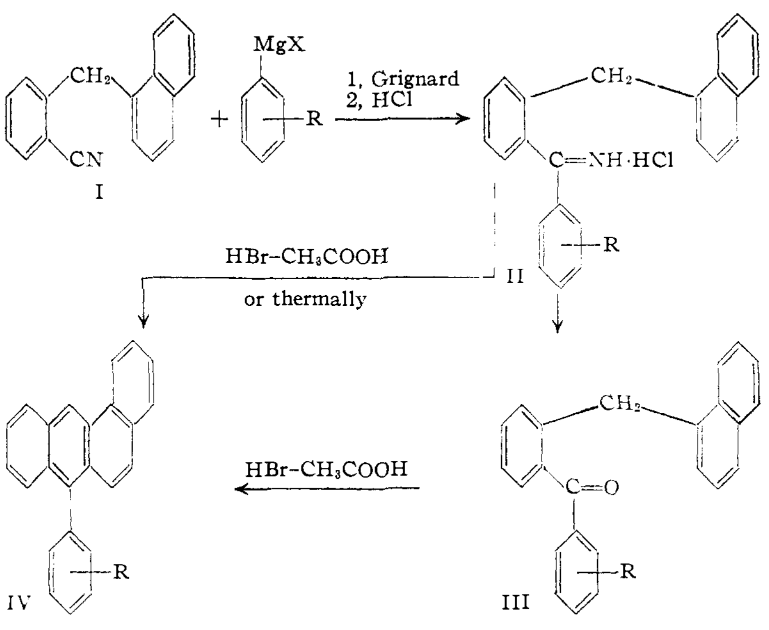
The synthesis of four new ketimine hydrochlorides, four new ketones and four new hydrocarbons has been accomplished. Bradsher's aromatic cyclodehydration reaction[8] has been extended to the 10-phenyl-1,2-benzanthracene system.

In 1940, Bradsher[3] presented a new method for synthesizing aromatic hydrocarbons. In a later publication[4] he extended this aromatic cylodehydration reaction to the preparation of 9-methyl- and 10-methyl -1,2- benzanthracene and suggested that his method might prove useful for the synthesis of other new carcinogenic compounds. We have now extended Bradsher's synthesis to the preparation of hydrocarbons in the 10-aryl-1,2-benzanthracene system.



A new and more convenient method has been found for obtaining the 1-(2-cyanobenzyl)-naphthalene (I) required in the synthesis. Bradsher[4] began with crude 2-chlorophenyl- 1-naphthylcarbinol prepared by the Grignard reaction and reduced this with phosphorus and hydriodic acid to the corresponding *o*-chlorobenzylnaphthalene. Although we were able to isolate the intermediate carbinol,[5] it was found that the reduction step gave variable results. The new method involves the direct condensation of *o*-chlorobenzyl chloride with naphthalene. Previous reports concerning the condensation of naphthalene with benzyl chloride indicate that considerable quantities of di- and tribenzylnaphthalenes are formed concurrently and that the monobenzylnaphthalenes are obtained as a mixture of isomers almost impossible to separate.

We have found that losses due to dibenzylation can be suppressed by adding the high-boiling products to subsequent runs along with the recovered naphthalenes. In this way over-all yields of 79% of monobenzyl derivative (based on the halide) were obtained.

Using zinc dust as a catalyst we were able to produce a mixture of isomers which was 70% 1-(2-chlorobenzyl)-naphthalene.[6] This mixture 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 1-(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.[7] 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 established procedure for this last reaction

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(1) Presented before the Division of Organic Chemistry at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

(2) This paper has been abstracted from the Masters' theses presented to the Virginia Polytechnic Institute by Joseph Shulman in 1950 and by Alexej Bořkovec in 1953.

(3) C. K. Bradsher, THIS JOURNAL, **62**, 486 (1940).

(4) C. K. Bradsher, *ibid.*, **62**, 1077 (1940).

(5) F. A. Vingiello, *ibid.*, **73**, 1887 (1951).

(6) In a future communication we will describe a modified experiment which leads to predominantly the 2-isomer.

(7) Higher yields of the ketones were obtained if the ketimine hydrochlorides, which hydrolyze easily, were not isolated but hydrolyzed directly.

failed to give a satisfactory yield[8] in the case of 2-(1-naphthylmethyl)-2′-methylbenzophenone, where the methyl group is *ortho* to the carbonyl group. In order to cyclodehydrate this ketone in satisfactory yield it was necessary to heat it with the acid mixture in a sealed Carius tube at 180° for 18 hours. It was found that under essentially the same experimental conditions the imine hydrochlorides II could be converted directly to the hydrocarbons IV.

The cyclization of an imine salt had been accomplished earlier by Bradsher and Smith,[9] who considered the possibility that direct cyclization might be involved, but evidently thought it more probable that cyclization occurred *via* the ketone. We now have been able to demonstrate that direct cyclization of an imine salt II can be accomplished under conditions which preclude the possibility of the formation of a ketone III intermediate. When the anhydrous ketimine hydrochloride II was heated in a sealed tube in the absence of other reagents, cyclization to the expected hydrocarbon IV occurred.

The ultraviolet spectra of the new hydrocarbons were taken and the maxima are recorded after Table III. It is interesting to note that these spectra imply that the 10-phenyl group is not coplanar with the 1,2-benzanthracene group. With this in mind it is noteworthy that our attempts to isolate crystalline picrates of these hydrocarbons failed although the benzene solutions of the hydrocarbons did turn red when the picric acid solution was added. In this regard it seems that Ferguson's[10] remarks that the donor molecule should be planar in order to form a strong addition complex are pertinent.

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

Experimental[11,12]

1- and 2-(2-Chlorobenzyl)-naphthalene.—A mixture of 128 g. (1 mole) of naphthalene and 80.5 g. (0.5 mole) of *o*-chlorobenzyl chloride was heated in a 1000-ml. beaker to 100° and 8.2 g. (0.1 mole) of zinc dust was added cautiously. After the evolution of hydrogen chloride had ceased, the hot mixture was filtered through glass wool, washed thrice with water and dried over calcium chloride. The product was then fractionated under reduced pressure and the fraction distilling between 185–195° (1 mm.) was collected.[13] The other two fractions, one boiling below 180° and the other above 200°, were combined and mixed again with 1 mole of naphthalene and 0.5 mole of *o*-chlorobenzyl chloride and the whole reaction was repeated. The entire process was repeated twice more. The total amounts of materials used were: naphthalene 512 g. (4 moles), *o*-chlorobenzyl chloride 322 g. (2 moles) and zinc 33 g. (0.5 mole). The yield of 1- and 2-(2-chlorobenzyl)-naphthalene was 400 g. (79%).

1-(2-Cyanobenzyl)-naphthalene (I).—A mixture of 63 g. of the isomeric chloro compounds prepared above, 28.4 g. of cuprous cyanide, 20 g. of pyridine and 0.1 g. of anhydrous cupric sulfate was heated in a metal-bath maintained at 250° for 40 hours, with an air-cooled condenser to allow the slow evaporation of the pyridine. The reaction mixture was then cooled and subjected to a crude distillation in a von Braun flask (1 mm.). The distillate was poured into about 300 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 225–227° (1.5 mm.) weighed 43 g. (71%). This fraction was dissolved in hot 90% ethanol, treated with charcoal, allowed to cool to room temperature and seeded with a pure crystal of the desired compound. After the solution stood at room temperature for 3 days, colorless prisms formed which were filtered: 11 g., m.p. 59.5–60.0°, lit.[4] 59–60°. The filtrate was concentrated and the crystallization process repeated a total of four times yielding a total of 34 g. (57%) of I.

2-(1-Naphthylmethyl)-3′-methyldiphenylketimine Hydrochloride (II, R = 3′-CH_3).—A Grignard reagent was prepared from 12.9 g. (0.075 mole) of *m*-bromotoluene and 1.8 g. (0.075 mole) of magnesium in 200 ml. of dry ether.[14] Most of the ether was distilled and a solution of 12.2 g. (0.050 mole) of 1-(2-cyanobenzyl)-naphthalene in 150 ml. of dry toluene was added. The mixture was heated under reflux with stirring for 5 hours. It was then cooled and decomposed with the equivalent amount of cold 20% ammonium chloride solution. The toluene layer was poured off and the residue was extracted with benzene. The toluene and benzene solutions were combined and concd. hydrochloric acid was added to precipitate the ketimine hydrochloride. This gave 16 g. (86%) 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 lemon-yellow prisms whose m.p. was 186° dec.

Anal. Calcd. for $C_{25}H_{22}NCl$: C, 80.73; H, 5.98. Found: C, 80.20; H, 6.03.

The other ketimine hydrochlorides were prepared in a similar way.

TABLE I

NEW KETIMINE HYDROCHLORIDES (II)

R	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
H	69	182 dec.	3.92	3.86
2′-CH_3	93	178 dec.	3.76	3.91
3′-CH_3	86	186 dec.	[a]	
4′-CH_3	73	203 dec.	3.76	3.75

[a] See analysis above.

10-(3′-Methylphenyl)-1,2-benzanthracene (IV, R = 3′-CH_3).—A mixture of 3 g. of the above ketimine hydrochloride (II, R = 3′-CH_3), 15 ml. of 48% hydrobrominc acid and 30 ml. of glacial acetic acid was sealed in a Carius tube. The tube was then placed in a Carius furnace and heated for 2 hours at 180°. The tube was cooled, opened, the contents diluted with water and extracted with three portions of benzene. The combined benzene extracts were washed with water and dried over calcium chloride. The benzene was distilled away and replaced with a mixture of 20% diethyl ether and 80% petroleum ether (60–90°). This solution was then chromatographed on a column of alumina using the same ether–petroleum ether mixture as the eluant. When the percolate was evaporated to dryness there remained 2.3 g. (88%) of white crystals. After being recrystallized three times from petroleum ether (60–90°) the white crystals melted at 110–111°.

Anal. Calcd. for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.49; H, 5.73.

2-(1-Naphthylmethyl)-2′-methylbenzophenone (III, R = 2′-CH_3).—A Grignard reagent was prepared in anhydrous ether from 21.1 g. of *o*-bromotoluene and 2.9 g. of magnesium. Most of the ether was distilled and a solution of 10 g. of 1-(2-cyanobenzyl)-naphthalene in 150 ml. of dry toluene was added dropwise with constant stirring. The solution was heated under reflux and stirred for 18 hours and then

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(8) F. A. Vingiello and J. G. VanOot, THIS JOURNAL, **73**, 5070 (1951).

(9) C. K. Bradsher and E. S. Smith, *ibid.*, **65**, 1643 (1943).

(10) L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice–Hall, Inc., New York, N. Y., 1952, p. 49.

(11) All melting points are corrected.

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

(13) A sample taken from the fraction boiling at 256–265° (1 mm.) gave colorless prisms on crystallization from acetone; m.p. 162–164°. This substance is apparently a mixture of di-*o*-chlorobenzylnaphthalenes and could serve as very interesting material for future syntheses of angular polycyclic hydrocarbons which would be difficult to obtain by any other method. *Anal.* Calcd. for $C_{24}H_{18}Cl_2$: C, 76.39; H, 4.81; Cl, 18.79. Found: C, 76.30; H, 5.15; Cl, 19.00.

(14) Our first experiments involved the use of a 3 or 4 molar excess of Grignard reagent over nitrile; however, later experiments gave equally good yields using only a 50% excess of Grignard reagent.

cooled and decomposed with 32 ml. of cold 25% sulfuric acid. Upon addition of the acid the imine salt crystallized out in small yellow flakes. The solid was heated under reflux with 200 ml. of 8 *N* sulfuric acid for 48 hours, at which time all the solid had gone into solution. The solution was cooled to room temperature and washed twice with water. The toluene layer was separated, dried over Drierite, concentrated and the residue fractionated under reduced pressure. The viscous yellow oil obtained weighed 11.7 g., b.p. 240–243 (1.5 mm.) (81%). The oil was crystallized from a water–ethanol mixture yielding 11 g. of white crystals melting at 83–84°.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.25; H, 5.98. Found: C, 89.13; H, 6.06.

The other ketones were prepared in a similar way.

TABLE II

NEW KETONES (III)

R	Yield, %	M.p., °C.	B.p., °C.	Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	80	103–104	248–251	1	89.79	89.40	5.43	5.78
2′-CH_3	81	83–84	240–243	1.5	89.25	89.13	5.98	6.06
3′-CH_3	80	114–115			89.25	89.11	5.98	6.21
4′-CH_3	84	77–78	248–251	3	89.25	89.19	5.98	6.17

10-Phenyl-1,2-benzanthracene (IV, R = H).—A solution of 0.50 g. of 2-(1-naphthylmethyl)-benzophenone (III, R = H) in 24 ml. of glacial acetic acid and 6 ml. of 48% hydrobromic acid was heated under reflux for 2.5 hours, during which time the product had crystallized. The mixture was cooled and the solid filtered, washed thrice with water and dried *in vacuo* yielding 0.48 g. (98%) of crystals, m.p. 182–184°. Two recrystallizations from an ethanol-benzene mixture gave 0.45 g. of white crystals, m.p. 183–184°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.70; H, 5.29. Found: C, 94.84; H, 5.24.

Two of the analogs IV, R = 2′-CH_3, and IV, R = 4′-CH_3, also were prepared by the acid cyclization of the corresponding ketone.

TABLE III

NEW HYDROCARBONS[a] (IV)

R	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H[b]	98	183–184	94.70	94.84	5.30	5.24
2′-CH_3	74	132.5–133	94.30	94.57	5.70	5.60
3′-CH_3	88	110–111	94.30	94.49	5.70	5.73
4′-CH_3	80	121–122	94.30	94.02	5.70	5.78

[a] 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 maxima for all four hydrocarbons appear at the same wave lengths. The optical density values at these wave length maxima are listed for the hydrocarbons in the same order as the hydrocarbons appear in Table III: λ 222 mμ (1.47, 1.34, 1.51, 1.54); λ 259 mμ (1.08, 0.98, 0.97, 0.98); λ 271 mμ (1.33, 1.16, 1.23, 1.20); λ 281 mμ (2.25, 2.05, 1.99, 1.89); λ 291 mμ (2.76, 2.32, 2.38, 2.31); λ 335 mμ (0.24, 0.23, 0.23, 0.22); λ 351 mμ (0.31, 0.30, 0.29, 0.28); λ 366 mμ (0.23, 0.22, 0.22, 0.22). [b] Prepared in 35% yield by cyclizing the corresponding ketimine hydrochloride thermally.

BLACKSBURG, VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF TORONTO AND IOWA STATE COLLEGE]

Base-catalyzed Elimination Reactions of Triphenylsilanecarboxylic Acid and its Derivatives

BY A. G. BROOK AND HENRY GILMAN

RECEIVED JUNE 7, 1954

The preparations of triphenylsilanecarboxylic acid and its methyl ester are described. It is shown that these compounds are subject to base-catalyzed elimination of carbon monoxide by a variety of nucleophilic reagents. Methyl triphenylsilanecarboxylate is readily reduced to triphenylhydroxymethylsilane by lithium aluminum hydride. Triphenylmethoxysilane has been prepared.

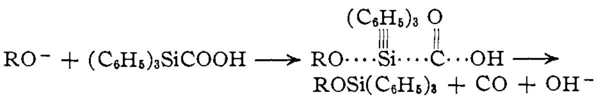
Triphenylsilanecarboxylic acid (I), originally reported by Benkeser and Severson,[1] has been prepared in good yield, free from other products, by the carbonation of triphenylsilylpotassium.[2]

$$(C_6H_5)_3Si{-}Si(C_6H_5)_3 \xrightarrow{Na/K} (C_6H_5)_3SiK \xrightarrow{CO_2}$$

$$\underset{I}{(C_6H_5)_3SiCOOH} \xrightarrow{CH_2N_2} \underset{II}{(C_6H_5)_3SiCOOMe} \xrightarrow{LiAlH_4} \underset{III}{(C_6H_5)_3SiCH_2OH}$$

The yields of acid from this reaction were reproducible only with difficulty, due to a base-catalyzed decomposition which the acid undergoes with great facility, in which triphenylsilanol and carbon monoxide are produced. When this decomposition was avoided by working rapidly in the cold, reproducible yields in excess of 80% were obtained.

While crude triphenylsilanecarboxylic acid is relatively unstable, decomposing in warm absolute ethanol with the evolution of carbon monoxide,[1] purified samples are relatively stable and fail to decompose in absolute ethanol or in ethanol–pyridine solutions. Complete decomposition of the pure acid, with evolution of carbon monoxide occurs rapidly by treatment of the acid with only catalytic amounts of aqueous sodium hydroxide or sodium ethoxide in absolute ethanol, and more slowly with sodium methoxide in absolute methanol, or with aqueous pyridine. In each case the only products isolated from the reaction are carbon monoxide, liberated quantitatively, and triphenylsilanol. These reactions are summarized in the equations



$$RO^- + (C_6H_5)_3SiCOOH \longrightarrow RO\cdots\overset{(C_6H_5)_3}{\overset{|||}{Si}}\cdots\overset{O}{\overset{\|}{C}}\cdots OH \longrightarrow ROSi(C_6H_5)_3 + CO + OH^-$$

$$OH^- + ROSi(C_6H_5)_3 \longrightarrow (C_6H_5)_3SiOH + RO^-$$

R = H, CH_3, C_2H_5

It appears probable that a nucleophilic attack by the base on the acid occurs, and that triphenylalkoxysilane, carbon monoxide and hydroxyl ion are initially formed. This latter species then competes with the alkoxyl ion for the remaining acid and, further, causes hydrolysis of the triphenylalkoxy-

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(1) R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

(2) Henry Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).