there is a fairly sharp end-point of titration just when one equivalent of oxidizing agent is used up. The drawn-out curve is the one calculated for a univalent oxidation curve (index potential, 28.6 mv.), the circles are experimental points. The potentials corresponding to more than 100% oxidation drift much more than those within the titration curve proper. The normal potential under the conditions prevailing in this experiment was +0.900 volt.

The absorption spectrum of the radical (Fig. 2) was determined with a König–Martens spectrophotometer for a solution of the amine in 80% acetic acid containing 1.5×10^{-4} mole per liter and oxidized with 25% of the equivalent amount of lead tetraacetate. The color is not perfectly stable in time, but the fading is negligible within the period necessary for the readings.

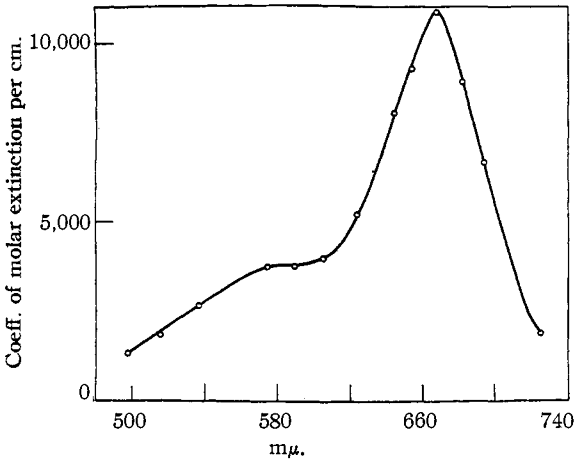

Fig. 2.

Tri-*p*-tolylamine was prepared according to Wieland[1] as a crystalline white powder, m. p. 117°. Lead tetraacetate was prepared according to J. C. Bailar.[4]

(4) "Inorganic Syntheses," Vol. I, 1939.

ROCKEFELLER INSTITUTE FOR
MEDICAL RESEARCH
NEW YORK, N. Y.

RECEIVED MAY 29, 1940

Note on the Grignard Reagent

BY MARTIN KILPATRICK AND EUGENE A. BARR, JR.

In connection with kinetic studies of the reaction of magnesium with alkyl and aryl halides it was noted that the reaction of magnesium[1,2] with bromobenzene gave a black precipitate. This precipitate has been noted in other reactions with magnesium but has not been identified. We assumed the precipitate to be colloidal magnesium, and we have confirmed this assumption by analysis. The black precipitate was washed with ether, weighed, dissolved in hydrochloric acid, precipitated as magnesium ammonium phosphate, and weighed as magnesium pyrophosphate.

Black ppt., mg.	Magnesium found, mg.
4.45	4.35
7.35	7.07

The black precipitate has been obtained with magnesium from various sources including the analyzed samples used by Kilpatrick and Rushton.[3]

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(1) Kilpatrick and Simons, *J. Org. Chem.*, **2**, 459 (1937).

(2) Gzemski and Kilpatrick, *ibid.*, **5**, 264 (1940).

(3) Kilpatrick and Rushton, *J. Phys. Chem.*, **38**, 269 (1934).

DEPARTMENT OF CHEMISTRY
AND CHEMICAL ENGINEERING
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PA.

RECEIVED MAY 16, 1940

The Presence of Indole in "Practical" α-Methylnaphthalene

BY M. S. KHARASCH, STEPHEN S. KANE AND HERBERT C. BROWN

The presence of indole in the coal tar fraction of b. p. 220–260° has been demonstrated by Weissgerber.[1] However, to our knowledge no mention is made anywhere that "Practical" α-methylnaphthalene contains about 1–2% of indole. This product was found by us in a study of the action of oxalyl chloride on commercial α-methylnaphthalene.

Experimental

The practical α-methylnaphthalene obtained from Eastman Kodak Co. is vacuum distilled. The original liquid is dark red with a beautiful blue fluorescence, while the distillate (b. p. 118° (17 mm.)) is light straw yellow but still shows the blue fluorescence. The red color returns on exposure to air. On addition of 2–3 cc. of oxalyl chloride to about 15 cc. of the distilled methylnaphthalene, 0.25 g. of gold yellow precipitate separates and is collected on a filter. The filtrate is distilled and a non-fluorescent, practically colorless methylnaphthalene (b. p. 118° (17 mm.)) is obtained. Exposure to light and air has no effect on the color of pure α-methylnaphthalene, but addition of a trace of indole produced a red color after a short exposure to air.

The yellow precipitate was shown to be the acid chloride of 3-indole glyoxalic acid by comparing its properties and those of its derivatives with the compounds obtained by treatment of pure indole dissolved in pure α-methylnaphthalene or benzene with oxalyl chloride. The same

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(1) Weissgerber, *Ber.*, **43**, 3520 (1910).

TABLE I

MELTING POINT AND NITROGEN VALUES

	$(COCl)_2$ plus crude α-methylnaphthalene A	$(COCl)_2$ plus indole B	M. p. of 90% A and 10% B	Oddo, etc.	Giua
Acid chloride	132d	135–136d	133d		138–139
Acid	214d	215d	213d	215d	224–225d
Amide	249–251	251–252	249–252	248	
Ethyl ester	184–185			186	
Acid chloride, N %	6.88			6.74 calcd.	
Amide, N %	14.78			14.89 calcd.	
Ester, N %	6.49			6.45 calcd.	
Acid, N %	7.10			7.41 calcd.	
Amide, C %	64.33			63.83 calcd.	
Amide, H %	4.47			4.26 calcd.	

compounds were prepared by Oddo and Albanese[2] and Majima and Shigematsu.[3] These authors had prepared the ethyl ester of 3-indole-glyoxalic acid by treatment of ethyl oxalyl chloride with the magnesium derivative of indole. Note, however, that Giua[4] claims that indole dissolved in absolute ether reacts with oxalyl chloride to give 2-indole-glyoxalyl chloride.

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(2) Oddo and Albanese, *Gazz. chim. ital.*, **57**, 827 (1927).

(3) Majima and Shigematsu, *Ber.*, **57B**, 1449 (1924).

(4) Giua, *Gazz. chim. ital.*, **54**, 593 (1924).

JONES CHEMICAL LABORATORY
THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

RECEIVED JUNE 10, 1940

4-Phenylcyclohexene

BY CHARLES C. PRICE AND JOSEPH V. KARABINOS

Since the 3-phenylcyclohexene formed from the dehydration of *trans*-2-phenylcyclohexanol[1] gave no satisfactory degradation products with permanganate or ozone, while dilute nitric acid oxidation gave β-phenyladipic acid, it seemed desirable to ascertain whether it was indeed the 3-isomer by comparison with a sample of the 4-isomer, which might have been formed by a shift in the double bond. The latter compound has already been prepared from styrene and butadiene[2] but its physical properties were not reported.

We have, therefore, repeated this preparation, obtaining 4-phenylcyclohexene in a yield of 8%. (*Anal.* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.32; H, 9.16.) Its physical properties, b. p. (16 mm.) 88–90°, n^{20}_D 1.5420, d^{20}_4 0.9715, differ markedly from those of the 3-isomer.

To confirm its structure, 2.6 g. of the hydrocarbon was oxidized with 5.5 g. of potassium permanganate in 50 cc. of water for twenty-four hours. Filtration, acidification and cooling gave crystals of β-phenyladipic acid, m. p. 147–148°. The neutral equivalent was 114, in agreement with the calculated value of 111.

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(1) Price and Karabinos, THIS JOURNAL, **62**, 1159 (1940).

(2) Alder and Rickert, *Ber.*, **71**, 379 (1938).

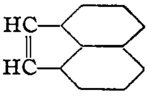
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED MAY 23, 1940

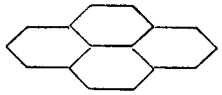
The Isolation and Identification of Fluoranthene from Carbon Black

BY JOHN REHNER, JR.

When carbon black is produced by the thermatomic[1] process a waxy material is observed to deposit from the hydrogen stream during the cracking of the natural gas. It has been shown[2] that this wax consists partly of acenaphthylene and pyrene.

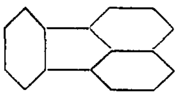


Acenaphthylene



Pyrene

We were interested in this Laboratory in determining whether compounds of similar polycyclic structure exist in the hydrocarbon-soluble fraction of carbon produced by the above process. A 5-kg. sample of thermatomic carbon (of the commercial brand known as "P-33") was saturated overnight at room temperature with 20 liters of benzene and the extract filtered and evaporated to dryness, 14 g. of residue being obtained. This was distilled in the temperature range of 150–230° at 4 mm. pressure and yielded 3.5 g. of orange-colored crystals. These were recrystallized three times from hexane and were identified as fluoranthene by the following analysis: C, 95.08, 95.13; H, 5.02, 5.05 observed; C, 94.97; H, 5.03 calcd.; molecular weight 179 (in benzene), 198 (in 1,4-dioxane); 202, calcd. The hydrocarbon was further purified by con-



Fluoranthene

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(1) Moore, *Ind. Eng. Chem.*, **24**, 21 (1932).

(2) Campbell, Cromwell, and Hager, THIS JOURNAL, **58**, 1051 (1936).