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).

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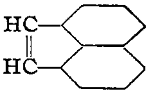
[1] Price and Karabinos, THIS JOURNAL, **62**, 1159 (1940).

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

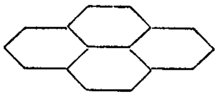
The Isolation and Identification of Fluoranthene from Carbon Black

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.

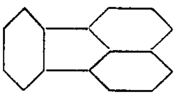


Acenaphthylene



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).

verting it to the picrate, recrystallizing the latter from alcohol, followed by reconversion to the hydrocarbon through the action of ammonium hydroxide. The picrate and dibromide of this product were prepared and the melting points taken.

	Observed m. p. (cor.), °C.	Literature[3] value, °C.
Fluoranthene	107–110	109
Fluoranthene picrate	180–184	182–183
Fluoranthene dibromide	200–204	204–205

The variety of conditions under which the synthesis of fluoranthene occurs is of interest, for it can be prepared by the dry distillation of coal or coal tar,[3] by the passage of acetylene and hydrogen through a hot porcelain tube,[4] from the "stupp" remaining after the distillation of mercury ores,[5] and now by the thermal decomposition[1] of natural gas in the presence of excess hydrogen at a hot brick surface.

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(3) Fittig and Gebhard, *Ann.*, **193**, 142 (1878).

(4) Meyer and Taeger, *Ber.*, **53**, 1261 (1920).

(5) Goldschmiedt, *ibid.*, **10**, 2022 (1877).

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AKRON, OHIO

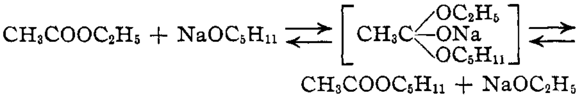
RECEIVED MAY 23, 1940

Note on the "Redistribution Reaction"

BY ROBERT D. STIEHLER AND THOMAS L. GRESHAM

The "Redistribution Reaction" described by Calingaert and co-workers[1] is not a "new, unrecognized and unusual" reaction in organic chemistry. Rather the important contribution of these workers is the discovery of some new catalysts for certain types of chemical reactions. These catalysts establish equilibrium for all reactions that are chemically related, no matter what the equilibrium distribution of the components may be.

According to Calingaert and co-workers, if one of two related reactions has a particular "random" distribution at equilibrium, it is a "new, and unrecognized" reaction while the other reaction is not. These reactions have different equilibrium constants, *i. e.*, different free energies of reaction. This is illustrated by two related ester interchange reactions: the reaction between methyl acetate and ethyl butyrate has an equilibrium constant[2] of 1.0. This constant gives the distribution in the "Redistribution Reaction." A similar reaction between ethyl acetate and amyl butyrate has a constant[2] of 1.3 and hence cannot be classified as a "Redistribution Reaction." Does this imply that the first reaction is "new, unrecognized and unusual" in organic chemistry while the second is not? Ester interchange reactions are well known in organic chemistry. Classically sodium alcoholates are known to cause substitution in esters by the reaction:



$$CH_3COOC_2H_5 + NaOC_5H_{11} \rightleftarrows \left[CH_3C \begin{matrix} \diagup OC_2H_5 \\ -ONa \\ \diagdown OC_5H_{11} \end{matrix} \right] \rightleftarrows CH_3COOC_5H_{11} + NaOC_2H_5$$

In a mixture of esters, sodium alcoholates act as catalysts to establish equilibrium conditions according to the law of mass action.

In the reactions between metalloalkyls,[1] the distribution of the components at equilibrium is likewise determined by the free energy of the reaction. For certain free energy values, the distribution must be the same as in the "Redistribution Reaction." The reactions most likely to have these free energies will be those involving the interchange of alkyl groups closely related, *e. g.*, methyl and ethyl. When the reaction involves the interchange of widely different groups, *e. g.*, methyl and amyl, a "random" distribution is not to be expected. Consequently, similar chemical reactions may or may not be classed as "Redistribution Reactions" depending on their free energies. All interchange reactions between esters, metalloalkyls, etc., are, in the broadest sense, redistribution reactions and have a random distribution of the components at equilibrium. Those reactions which have the particular "random" distribution described by Calingaert and co-workers as "Redistribution Reactions" are merely members of the entire set of chemical equilibria, the totality of which is governed by the various statistical laws embodied in the kinetic theory of reactions.

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(1) THIS JOURNAL, **61**, 2748 (1939); *Science*, **90**, 430 (1939).

(2) Calculation from esterification data of Berthelot and Péan de Saint Gilles, *Ann. chim. phys.*, [3] **68**, 235 (1863).

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NEW COMPOUNDS

p-PHENYLPHENACYL ESTERS

These derivatives were prepared in the usual manner and purified by recrystallization from alcohol:

***p*-Phenylphenacyl α-methyl-β-phenylpropionate,** m. p. 71–72°. *Anal.* Calcd. for $C_{24}H_{22}O_3$: C, 80.45; H, 6.15. Found: C, 80.33; H, 6.30.