

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 <sup>3</sup> 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,<sup>3</sup> by the passage of acetylene and hydrogen through a hot porcelain tube,<sup>4</sup> from the "stupp" remaining after the distillation of mercury ores,<sup>5</sup> and now by the thermal decomposition<sup>1</sup> of natural gas in the presence of excess hydrogen at a hot brick surface.

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

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

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

THE B. F. GOODRICH CO.  
AKRON, OHIO

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### Note on the "Redistribution Reaction"

BY ROBERT D. STIEHLER AND THOMAS L. GRESHAM

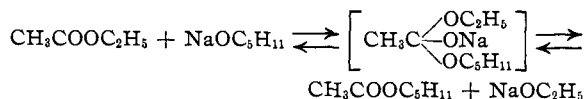
The "Redistribution Reaction" described by Calingaert and co-workers<sup>1</sup> is not a "new, unrecognized and unusual" reaction in organic chemistry. Rather the important contribution of these workers is the discovery of some new catalysts for certain types of chemical reactions. These catalysts establish 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<sup>2</sup> of 1.0. This constant gives the distribution in the "Redistribution Reaction." A similar reaction between ethyl acetate and amyl butyrate has a constant<sup>2</sup> of 1.3 and hence cannot be classified as a "Redistribution Reaction." Does this imply

(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).

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:



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,<sup>1</sup> 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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## NEW COMPOUNDS

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### *p*-PHENYLPHENACYL ESTERS

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

*p*-Phenylphenacyl  $\alpha$ -methyl- $\beta$ -phenylpropionate, m. p. 71-72°. *Anal.* Calcd. for C<sub>24</sub>H<sub>22</sub>O<sub>3</sub>: C, 80.45; H, 6.15. Found: C, 80.33; H, 6.30.