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.

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

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

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

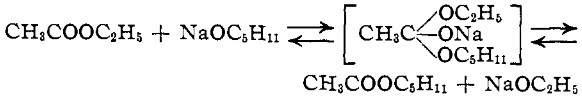
THE B. F. GOODRICH CO.
AKRON, OHIO
RECEIVED MAY 23, 1940

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:



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

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.

(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.

p-Phenylphenacyl α-methyl-γ-phenylbutyrate, m. p. 62–63°. *Anal.* Calcd. for $C_{25}H_{24}O_3$: C, 80.65; H, 6.45. Found: C, 80.74; H, 6.56.

p-Phenylphenacyl β-methyl-δ-phenylvalerate, m. p. 66–67°. *Anal.* Calcd. for $C_{26}H_{26}O_3$: C, 80.83; H, 6.73. Found: C, 80.76; H, 6.79.

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HERBERT E. CARTER

RECEIVED MAY 18, 1940

6-METHYL-5-NITRO-2-NAPHTHOIC ACID

Five grams of 1-nitro-2,6-dimethylnaphthalene[1] (m. p. 67–68°) was refluxed for two days in 50 cc. of water with 45 cc. of nitric acid added in portions. The crude product (5 g.) was collected by filtration and extracted with sodium bicarbonate to give 2 g. of 6-methyl-5-nitro-2-naphthoic acid; the neutral residue was a mixture of dinitrodimethylnaphthalenes. On recrystallization from 95% acetic acid, the acid formed rosets of colorless needles, m. p. 258–259°, neutral equivalent 230 (calcd. 231).

Anal. Calcd. for $C_{12}H_9O_4N$: C, 62.31; H, 3.94. Found: C, 62.61; H, 4.08.

The isomeric 6-methyl-1-nitro-2-naphthoic acid was prepared according to Meyer and Alken[1] in 3% yield, m. p. 238–239°.

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(1) Meyer and Alken, *Ber.*, **55**, 2280 (1922).

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UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
CHARLES C. PRICE

RECEIVED JUNE 27, 1940

DERIVATIVES OF METHACROLEIN

The sample of methacrolein used for the preparation of the derivatives had the following physical constants: b. p. 73.5°; $n^{20}D$ 1.4191; d^{20}_4 0.830; *M*D calcd., 21.37; *M*D found, 21.31. The usual methods were used for the preparation of the derivatives.[1]

Semicarbazone of Methacrolein.—Colorless plates from 25% ethanol, m. p. 197.5–198°.

Anal. Calcd. for $C_5H_9ON_3$: N, 33.06. Found: N, 33.09.

p-Nitrophenylhydrazone of Methacrolein.—Orange crystals from xylene, m. p. 161–163°.

Anal. Calcd. for $C_{10}H_{11}O_2N_3$: N, 20.48. Found: N, 19.99.

2,4-Dinitrophenylhydrazone of Methacrolein.—Orange crystals from xylene, m. p. 206–206.5°

Anal. Calcd. for $C_{10}H_{10}O_4N_4$: N, 22.30. Found: N, 22.05.

1-Phenyl-4-methyl-Δ²-pyrazoline.—Phenylhydrazine reacted with methacrolein to produce the pyrazoline and not the phenylhydrazone. It was recrystallized from petroleum ether, m. p. 73–74°.

Anal. Calcd. for $C_{10}H_{12}N_2$: N, 17.49. Found: N, 17.24.

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(1) Shriner and Fuson, "Systematic Identification of Organic Compounds," 2nd Edition, John Wiley and Sons, N. Y., 1940.

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URBANA, ILLINOIS
R. L. SHRINER
A. G. SHARP

RECEIVED JUNE 28, 1940

COMMUNICATIONS TO THE EDITOR

CONVERSION OF CANNABIDIOL TO A PRODUCT WITH MARIHUANA ACTIVITY. A TYPE REACTION FOR SYNTHESIS OF ANALOGOUS SUBSTANCES. CONVERSION OF CANNABIDIOL TO CANNABINOL

Sir:

Cannabidiol, which has been shown in previous papers to have structure I with doubt merely as to the position of the double bond in the left-hand ring, isomerizes in the presence of pyridine hydrochloride, ethanolic hydrogen chloride, hydrogen chloride in ether, sulfamic acid, ethanolic phosphoric acid or zinc chloride to give tetrahydrocannabinol (II). Undoubtedly other reagents of a similar character will be found to be equally effective for the isomerization. The tetrahydrocannabinol (II) is a colorless highly viscous oil (b. p. 188–190° (2.5 mm.), found: C, 79.90; H, 9.52). It has a constant boiling point regardless of the method of synthesis, but its rotation varies depending on the conditions used; under specified conditions two products of constant rotation are produced, $[\alpha]^{27}D$ −160° and $[\alpha]^{32}D$ −240°. Apparently the reagents sometimes cause a shift in the double bond or an interchange of diastereoisomers. The structure of compound II was demonstrated by dehydrogenation to cannabinol (m. p. 75–76.5°) (III) which has been proved by synthesis to have that formula,