The apparent inertness suggests a possible relationship to the steroids of the adrenal cortex [Mason, Myers and Kendall, *J. Biol. Chem.*, **116**, 267 (1936); Reichstein, *Helv. Chim. Acta*, **19**, 1107 (1936)] but so far no additional evidence in support of this attractive hypothesis has been obtained.

The substance was isolated from the neutral total ketonic fraction as the semicarbazone which is strikingly characterized by its practically complete insolubility in boiling organic solvents and water. For analysis the semicarbazone was freed from as many impurities as possible by repeated extractions with hot water, alcohol and acetone. The melting point varied from 300 to 315° (decomp.) with the rate of heating. On hydrolysis with dilute alcoholic sulfuric acid, 103.6 mg. gave 86.0 mg. of the crude ketone; the theoretical yield from a monosemicarbazone of $C_{19}H_{26}O_3$ is 87.1 mg. The product was readily soluble in cold acetone, benzene and chloroform, moderately so in ether and alcohol. The analytical sample was recrystallized four times from alcohol and twice from aqueous acetone. It separated in long white needles melting at 252° (uncorrected) with preliminary softening 3° below this. Nitrogen, halogen and sulfur were absent. *Anal.* (Schoeller) Semicarbazone: calcd. for $C_{20}H_{29}O_3N_3$: C, 66.85; H, 8.08; N, 11.69. Found: C, 67.05, 67.02; H, 7.75, 7.82; N, 10.85, 10.74. Free ketone: calcd. for $C_{19}H_{26}O_3$: C, 75.50; H, 8.61. Found: C, 75.47, 75.50; H, 8.52, 8.45.

The investigation is being continued. Complete experimental details will be published at a later date.

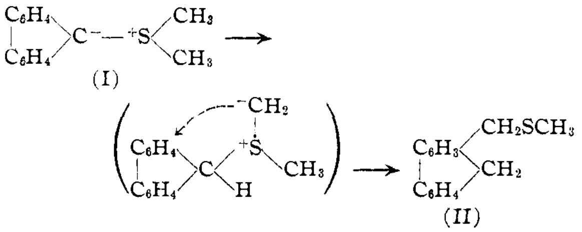
CONNAUGHT LABORATORIES
UNIVERSITY OF TORONTO
TORONTO, ONTARIO, AND
DEPARTMENT OF BIOCHEMISTRY
DALHOUSIE UNIVERSITY
HALIFAX, NOVA SCOTIA
R. D. H. HEARD

RECEIVED JANUARY 18, 1938

REARRANGEMENT OF FLUORYLIDENE DIMETHYL SULFIDE TO FLUORENE-1-DIMETHYL SULFIDE

Sir:

Recent developments [Sommelet, *Compt. rend.*, **205**, 56 (1937); Krollpfeiffer and Schneider, *Ann.*, **530**, 38 (1937)] along lines closely related to those on which we are working have prompted us to record observations dealing with fluorylidene dimethyl sulfide. Our experiments have revealed that fluorylidene dimethyl sulfide (I), which was discovered by Ingold and Jessop [*J. Chem. Soc.*, 713 (1930); see also Hughes and Kuriyan, *ibid.*, 1609 (1935)], rearranges in an alkaline medium such as alcoholic sodium hydroxide or liquid ammonia to fluorene-1-dimethyl sulfide (II).



Evidence favoring the structure assigned to (II) was secured by graded oxidation. By means of hydrogen peroxide (II) is converted to fluorene-1-dimethyl sulfone, whereas with a stronger oxidizing agent such as sodium dichromate in acetic acid, fluorenone-1-dimethyl sulfone and fluorenone-1-carboxylic acid are formed. The last mentioned compound was characterized by comparison with fluorenone-1-carboxylic acid prepared by the oxidation of fluoranthene. As is to be expected, (II) is converted by methyl alcoholic hydrochloric acid to fluorene-1-dimethyl ether and by a solution of hydrogen bromide in acetic acid to fluorene-1-methyl bromide, which with zinc and acetic acid is reduced to 1-methylfluorene.

BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
GUIDO E. HILBERT
LOUIS A. PINCK

RECEIVED NOVEMBER 17, 1937

INTERNAL FREE ROTATION IN HYDROCARBONS

Sir:

In a recent note Kassel[1] puts forward certain arguments which imply that free internal rotation occurs in saturated hydrocarbon molecules at room temperatures. Since we cannot agree with several of the points which he has put forward, we should like to discuss them here and at the same time present a very brief summary of the arguments on the other side of this vexatious question.

Kassel bases his reasoning on a comparison for the reaction *n*-butane ⟷ iso-butane of the entropy change obtained from equilibrium and combustion data (−2.1 e. u.) with that from Third Law measurements by Parks, Shomate, Kennedy and Crawford[2] (−5.8 e. u.). He argues that

---

(1) Kassel, THIS JOURNAL, **59**, 2745 (1937).

(2) Parks, Shomate, Kennedy and Crawford, *J. Chem. Phys.*, **5**, 359 (1937).