Dihydroxystearic Acids.—The lead salts insoluble in hot benzene (Lead Salts, "A") were converted to the free acids in the usual way. From 400 g. of the original oil there resulted 9.3 g. (2.4%) of the crude brownish acids, not quite entirely soluble in hot ether. After repeated crystallizations from ether there was obtained 2.7 g. of a white solid, m. p. 93–93.5°. Further crystallizations from ether or benzene did not change the melting point; neut. equiv., 316.8 (calcd. for a dihydroxystearic acid, 316.3). To avoid complications arising from stereoisomerism of the dihydroxystearic acids, a specimen was oxidized to the corresponding diketostearic acid. From 0.4 g. of the unknown acid there was obtained by oxidation with chromic acid, a pale yellow crystalline diketostearic acid, m. p. 83–84°. A mixed m. p. of this acid with an authentic specimen of 9,10-diketostearic acid, m. p. 83–84° (prepared by a similar oxidation of known 9,10-dihydroxystearic acid, from oleic acid), showed no depression. From these data the acid melting at 93–93.5° is shown to be a mixture of stereoisomeric 9,10-dihydroxystearic acids.

An examination of the mother liquors from the dihydroxystearic acids led to the separation of a small fraction (1.3 g.) which was insoluble in cold petroleum ether. Crystallization from acetone gave four fractions: (a) m. p. 77–80°, (b) 72–75°, (c) 62–74°, (d) 62–72°. The highest fractions may be a mixture of higher saturated fatty acids (C_{20}–C_{24}). The portion which was soluble in cold petroleum ether (5 g.) was deeply colored; attempts to obtain definite information concerning its composition were unsuccessful.

Summary

The fatty acids of lycopodium oil have been found to consist mainly of oleic acid (*ca.* 55–60%) and 9,10-palmitoleic acid (*ca.* 30–35%). The lycopodiumoleic acid of Langer was apparently a mixture of these acids. Palmitic, linoleic and 9,10-dihydroxystearic acids were also identified.

ITHACA, NEW YORK

RECEIVED MARCH 16, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE PHILLIPS PETROLEUM COMPANY]

Thermal Decomposition of Dibutylmercury

BY F. E. FREY AND H. J. HEPP

In 1929 Paneth and Hofeditz[1] reported that the vapors of lead tetramethyl, passed rapidly through a heated tube, acquired the property of removing a lead mirror. The activity was thought to be due to the presence of free methyl radicals. In other investigations[2,3,4,5] additional evidence has been obtained that these active molecules are free alkyl radicals. Rice has proposed a detailed mechanism[6] for the decomposition of paraffins through the intermediate formation of free alkyl radicals. The removal from the paraffin molecule of any one of the hydrogen atoms is

---

(1) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(2) Paneth and Lautsch, *ibid.*, **64**, 2702 (1931).

(3) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

(4) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932). A bibliography of previous work in this field is given.

(5) Meinert, *ibid.*, **55**, 979 (1933).

(6) Rice, *ibid.*, **53**, 1959 (1931).

assumed to take place. The alkyl radical thus formed then undergoes scission of the carbon chain at only those positions which allow of the formation of an olefin molecule and a complementary alkyl radical without migration of hydrogen. Evidence of such radical scission was obtained in experiments to be described.

Experimental Part

Preparation of Mercury Alkyls.—Di-*n*-butylmercury[7] was prepared by the interaction of *n*-butylmagnesium iodide and mercuric chloride. It was distilled at reduced pressure and further purified by fractionation at 24 mm. pressure through a short column; boiling point 121° (24 mm.); d_4^{28} 1.825.

Di-*sec*-butylmercury[8] was prepared and purified in the same way from *sec*-butylmagnesium bromide and mercuric chloride; boiling point 79° (9 mm.); $d_4^{26.5}$ 1.777; Hg found, 63.7; calcd., 63.7. The *n*-butyl iodide and *sec*-butyl bromide were obtained from the Eastman Kodak Company.

Method of Decomposition.—Di-*n*-butylmercury and di-*sec*-butylmercury were decomposed by passing the vapors under a pressure of several millimeters of mercury through a Pyrex tube heated to around 490°. The products were analyzed by a rather elaborate proven method[9] to determine the quantity of each product formed in substantial amount and establish the identity with certainty. A high temperature was used to favor scission reactions. No mercury alkyl was detected in the effluents. From a consideration of experimental decomposition rates at lower temperatures, the several steps of decomposition must have been complete in the inlet portion of the decomposition tube, most of the di-*n*-butylmercury decomposing at 400–450° and the *sec*-butyl at 350–400°. The paraffins and olefins formed could not themselves have been decomposed by the temperature–time conditions used. Moreover, the analyses of the products show that such decomposition was slight.

The mercury alkyl, in a glass bulb, was held at the temperature required to develop a vapor pressure of a few millimeters. The vapors were led by a tube maintained a little above the dew point temperature to a horizontal Pyrex tube of 8 mm. inside diameter heated by an electric tube furnace to effect the decomposition. The decomposition zone was 50 cm. in length. The products were discharged through a trap to retain mercury and heavy products, a length of glass tubing to interpose a flow resistance, and three condensing bulbs cooled by liquid nitrogen. Methane and hydrogen not condensed were removed continuously by a Toepler pump to maintain a constant flow rate. The products were analyzed[9] by fractional distillation in a large column, a small column, and a Shepherd–Porter apparatus, used in conjunction with bromination and sulfuric acid absorption for identifying and estimating olefins. The decomposition train and the analytical train were connected by glass to glass seals throughout.

In starting each experiment, about twice the required amount of fresh mercury alkyl was introduced into the bulb through a small tube. The mercury alkyl was cooled to −30°, the small tube sealed off and the apparatus evacuated. The furnace was then heated to the desired temperature, the mercury alkyl bulb placed in a hot water-bath, at 75 and 60° for the primary and secondary alkyls, respectively, to develop 3 mm. vapor pressure, and flow through the decomposition tube took place. When the desired amount of products had been condensed, the run was terminated by sealing off the exit tube from the furnace and all the products were then analyzed in the closed system. In each run a very slight brown stain was formed in the inlet of the heated tube. In the

---

[7] Gilman and Brown, This Journal, **51**, 929–930 (1929).

[8] Marvel and Calvery, *ibid.*, **45**, 820 (1923).

[9] Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

decomposition of di-*sec*-butylmercury a trace of tarry material (0.02 g.) was formed, and a very little mercury (0.02 g.) separated in the supply bulb. The primary alkyl gave no tar and no decomposition in the bulb. The products collected were closely equivalent to the mercury condensed.

In experiment 4 (Table I) an attempt was made to increase the decomposition temperature by inserting a glass rod coaxially in the inlet of the decomposition tube to decrease the cross-sectional area of the stream. The decomposition was little affected, however.

Discussion

Di-*n*-butylmercury.—The analysis of the decomposition products is shown in Table I, experiment 2. (Experiment 1 was a preliminary run.) The products can be accounted for on the assumption that (1) butyl radicals undergo a characteristic scission and (2) any two radicals unite to

TABLE I

THERMAL DECOMPOSITION OF DIBUTYLMERCURY

Experiment	1	2	3	4
Material decomposed	Di-*n*-butylmercury		Di-*sec*-butylmercury	
Temperature, °C.[b]	490	490	490	515
Pressure, mm.	1	3	3	5
Exposure time, sec.	0.6	0.6	0.4	1.0
Quantity decomposed, g.	1.66	5.48	5.97	7.75
Duration of run, hrs.	7.37	7.17	3.47	7.07
H/C ratio in products[d]		2.26	2.25	2.25
Analysis, mole per cent.				
H_2	0.0	0.0	0.03	0.0
CH_4	0.2	0.27	2.21	2.06
C_2H_4	66.7	56.98	0.11	0.07
C_2H_6	7.3	6.30	0.78	0.76
C_3H_6	1.7	0.18	13.51	12.21
C_3H_8		.44	0.79	0.49
iso-C_4H_8	0	0	0	0
n-C_4H_8	1.4	.98	20.58	22.43
n-C_4H_{10}	22.7[a]	20.54	19.96	20.22
C_5H_{10}		1.34	0.40	0.96
C_5H_{12}			10.72	6.56[c]
C_6H_{12}		0.0	1.38	0.10
C_6H_{14}		10.66		1.12
C_7H_{14}		0.18	0.05	0.02
C_8H_{16}			0.21	0.12
C_7H_{16}		2.13	0.75	0
C_8H_{18}			28.52	32.88
	100.0	100.00	100.00	100.00

[a] The heavier hydrocarbons were not determined because of the small quantity available. [b] Temperatures are average values for heated zone. [c] A little isopentane was lost, and methyl is less than equivalent to propylene. However, the discrepancy is not too large to arise from reactions not discussed, in view of the small extent of the scission reaction. [d] H/C ratio C_4H_9— is 2.250.

form a paraffin molecule. All the important products are accounted for, no absent products are predicted, and the stoichiometric relations indicate that ethyl radical is actually formed.

The decomposition may be represented by the reactions

$$(CH_3CH_2CH_2CH_2)_2Hg \longrightarrow 2CH_3CH_2CH_2CH_2\text{—} + Hg \tag{1}$$

$$CH_3CH_2CH_2CH_2\text{—} \longrightarrow CH_2CH_2 + CH_3CH_2\text{—} \tag{2}$$

$$CH_3CH_2\text{—} + H \longrightarrow CH_3CH_3 \tag{3}$$

$$CH_3CH_2\text{—} + CH_3CH_2\text{—} \longrightarrow CH_3CH_2CH_2CH_3 \tag{4}$$

$$CH_3CH_2CH_2CH_2\text{—} + CH_3CH_2\text{—} \longrightarrow CH_3CH_2CH_2CH_2CH_2CH_3 \tag{5}$$

Nearly all the free *n*-butyl formed by (1) decomposes according to (2). The ethylene survives; the ethyl acquires hydrogen to form ethane (3) to a small extent, but most of it unites with ethyl to form *n*-butane (4) and with butyl to form *n*-hexane (5). The butane and hexane boiled at 0 and 69°, which identifies them as the normal paraffins. A small amount of octane was formed, presumably by union of two butyl radicals. The butene found may have been formed by loss of a hydrogen atom from butyl. Other products are present in only small amounts. The amount of ethyl represented by the above reactions ($6.30 + 20.54 \times 2 + 10.66 = 58.04$) is quite closely equivalent to the ethylene found (56.98). While several paraffins were formed in quantity, ethylene is the only olefin present in substantial amount. The ordinary decomposition of paraffins, on the other hand, yields the greatest proportion of olefins among the products of higher molecular weight.

Di-*sec*-butylmercury.—The decomposition (Table I, experiment 3) may be represented as

$$(CH_3CH_2CHCH_3)_2Hg \longrightarrow 2CH_3CH_2CHCH_3\text{—} + Hg \tag{6}$$

$$CH_3CH_2CHCH_3\text{—} \longrightarrow CH_3CH{=}CH_2 + CH_3\text{—} \tag{7}$$

$$CH_3\text{—} + H \longrightarrow CH_4 \tag{8}$$

$$CH_3\text{—} + CH_3\text{—} \longrightarrow CH_3CH_3 \tag{9}$$

$$CH_3\text{—} + CH_3CH_2CHCH_3\text{—} \longrightarrow CH_3CH_2CH(CH_3)_2 \tag{10}$$

$$2C_4H_9\text{—} \longrightarrow C_4H_8 + C_4H_{10} \tag{11}$$

$$2C_4H_9\text{—} \longrightarrow C_8H_{18} \tag{12}$$

The pentane formed (10) boiled at 28° and was not attacked by bromine, which establishes its identity with isopentane. Very little pentene or *n*-pentane accompanied it. The high yield of isopentane accompanied by little pentene is of particular interest for the reason that no greatly different mechanism for its formation is evident, and the existence of methyl radicals and probably butyl radicals in the free state is strongly indicated. The methyl represented by equations (8), (9) and (10) ($2.21 + 2 \times 0.78 + 10.72 = 14.49$) is nearly equivalent to the propylene (13.51).

By reason perhaps of the lower temperature at which decomposition occurred, or a greater inherent stability of *sec*-butyl radicals, the fracture reaction was less prominent than others. A large amount of *n*-butane accompanied by an equal amount of butene, partly butene-1 but chiefly butene-2, were formed, perhaps by disproportionation. Octane distilling mostly at 117–118° was a major product (12). Di-*sec*-butyl boiling at 116.5°[10] would be expected.

Summary

1. Di-*n*-butylmercury and di-*sec*-butylmercury were thermally decomposed within the range 350–450° under 3 mm. pressure and the products were given a rather complete analysis.

2. In addition to fracture of the carbon–mercury bonds, the carbon chains underwent fracture at a single point characteristic for each alkyl, at the middle carbon–carbon bond for the primary alkyl and at the terminal bond for the secondary alkyl.

[10] "International Critical Tables," McGraw-Hill Book Co., New York, 1926.

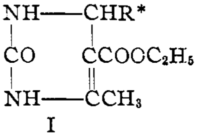
BARTLESVILLE, OKLAHOMA RECEIVED MARCH 16, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

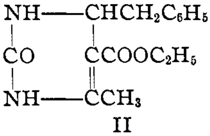
Researches on Pyrimidines. CXXXIV. The Reaction of Phenylacetaldehyde and Acetophenone with Urea

BY KARL FOLKERS[1] AND TREAT B. JOHNSON

In a recent paper from this Laboratory, improved experimental conditions were described for condensing an aldehyde and urea with a β-keto ester to form a tetrahydropyrimidine compound.[2] The various aldehydes investigated, of both the aromatic and aliphatic series, underwent condensation with ethyl acetoacetate and urea, for example, to form 2-keto-4-R-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidines as represented by the general formula I.



I



II

* R = the organic radical attached to the aldehyde group CHO (CH_3CHO, etc.).

In order to complete a series of this type of pyrimidines for pharmacological study, we desired to obtain 2-keto-4-benzyl-5-carbethoxy-6-methyl-1,2,3,4-tetrahydropyrimidine, II. Accordingly, urea, ethyl acetoacetate and phenylacetaldehyde were refluxed together according to the usual technique in ethanol solvent and in the presence of a few drops of hydrochloric acid as catalyst. Only one crystalline product was isolated. This was comparable in solubility, melting point, and also in yield and general properties to the tetrahydropyrimidines formed in our previous experiments with

---

[1] E. R. Squibb & Sons Research Fellow in Organic Chemistry.

[2] Folkers, Harwood and Johnson, THIS JOURNAL, **54**, 3751 (1932).