The Physical Constants of Pentanol-3

BY FRANK C. WHITMORE AND J. D. SURMATIS

Pure pentanol-3 was required in large quantity for work in progress in this Laboratory. Since the physical constants for the carbinol reported in the literature[1] show wide disagreement, a study was made on the purity of material synthesized in the laboratory and that obtained from Sharples Solvents Corporation.

Propionaldehyde, b. p. 48.0° at 736 mm., n^{20}_{D} 1.3636, was prepared by dehydrogenation of *n*-propyl alcohol with a copper catalyst. It was treated in four 8-mole lots with ethylmagnesium chloride in anhydrous ethyl ether. The crude product obtained in 67% yield after distillation through a column of approximately 25 theoretical plates, was refractionated through a column, 2 × 260 cm. of the total condensation partial take-off type, having approximately 85 theoretical plates. From this distillation a yield of 90% of constant boiling and constant index material resulted. The boiling point was determined in a laboratory Cottrell apparatus, with a thermometer calibrated against one checked by the Bureau of Standards; the refractive index was determined by a Valentine refractometer: b. p. 114.4° at 740 mm., n^{20}_{D} 1.4104, d^{20}_{4} 0.8218.

Approximately 2800 g. of Sharples pentanol-3 was distilled through a column of approximately 16 theoretical plates, and then refractionated twice through the 85-plate column described above. Of the starting material 27% was obtained with the physical constants: b. p. 114.3–114.5° at 741.5 mm., n^{20}_{D} 1.4102–1.4104, d^{20}_{4} 0.8203.

SCHOOL OF CHEMISTRY AND PHYSICS
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA. RECEIVED DECEMBER 26, 1939

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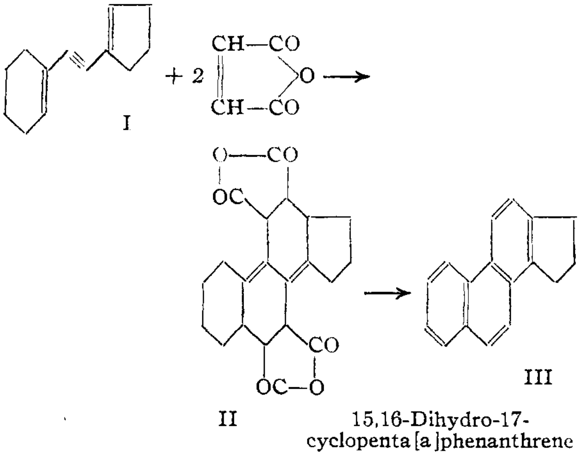
[1] Brunel, THIS JOURNAL, **45**, 1334 (1923); Lucas and Moyse, *ibid.*, **47**, 1460 (1925); Morris and Cortese, *ibid.*, **49**, 2644 (1927); Sherrill Otto and Pickett, *ibid.*, **51**, 3027 (1929); Timmermans and Hennaut-Roland, *J. chim. phys.*, **29**, 529 (1932); Clark and Hallonquist, *Trans. Roy. Soc. Can.*, [3] **24**, 115 (1930); Lauer and Stodola, THIS JOURNAL, **56**, 1216 (1934); Brooks, *ibid.*, **56**, 1998 (1934); Packendorff, *Ber.*, **67**, 905 (1934).

COMMUNICATIONS TO THE EDITOR

THE TOTAL SYNTHESIS OF A NON-BENZENOID STEROID[1]

Sir:



15,16-Dihydro-17-cyclopenta[a]phenanthrene

We reported in the last paper[2] that a derivative of hexahydronaphthalene results from the addition of maleic anhydride to 2,5-dimethyl-1,5-hexadiene-3-yne. It has now been found that an analogous reaction occurs when the hydrocarbon I[3] is heated with one mole of maleic anhydride at 130° without solvent. The crystalline product, from ethyl acetate or benzene, has m. p. 249–251° (cor.) with decomposition, and is converted in low yield to 15,16-dihydro-17-cyclopenta[a]phenanthrene (III), m. p. 132–133° (cor.), by heating with palladium–charcoal. This hydrocarbon did not depress the m. p. of an authentic specimen[4] kindly furnished by Dr. Erich Mosettig. *Anal.*[5] Calcd. for $C_{21}H_{20}O_6$: C, 68.5; H, 5.5. Found: C, 68.7; H, 5.6. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.5; H, 6.5. Structure II is tentatively assigned to the compound $C_{21}H_{20}O_6$ on the basis of analogy with the hexahydronaphthalene previously[2] described and the absorption curve of the solution in ethanol, λ max. 2555 Å., ε 19,000. It is suggested that a compound of this

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[1] This work is supported by Bankhead-Jones funds. (Not subject to copyright.)

[2] Butz, Gaddis, Butz and Davis, *J. Org. Chem.* (recently submitted for publication). The present communication is the fourth paper in the series "Synthesis of Condensed Ring Compounds."

[3] Pinkney, Nesty, Wiley and Marvel, THIS JOURNAL, **58**, 972 (1936).

[4] Burger and Mosettig, *ibid.*, **59**, 1307 (1937).

[5] By Arlington Laboratories, Arlington, Virginia.

structure be called 8(14),9-steradiene-6,7,11,12-tetracarboxylic-6,7,11; 12-dianhydride.

BUREAU OF ANIMAL INDUSTRY LEWIS W. BUTZ
UNITED STATES DEPARTMENT OF ADAM M. GADDIS
AGRICULTURE ELEANORE W. J. BUTZ
BELTSVILLE, MARYLAND RUSSELL E. DAVIS

RECEIVED MARCH 18, 1940

FURTHER COMPOUNDS HAVING ANTI-HEMORRHAGIC ACTIVITY

Sir:

In an investigation involving the synthesis and assay of a number of additional naphthoquinones and derived or related products, considerable data have been accumulated on the problem of correlating vitamin K activity and structure which will be presented after completion of adequate assays on the entire series of compounds synthesized in the two Laboratories. In the meantime we wish to report certain observations from the synthetic work and give some indication of the potencies of the new compounds.

The method developed by one of us for the synthesis of vitamin K_1 [Fieser, THIS JOURNAL, **61**, 2559, 3467 (1939)] has been found capable of wide application. By using 1,4-naphthohydroquinone as one component 2-geranyl, 2-farnesyl, and 2-phytyl-1,4-naphthoquinone have been synthesized in good yield. The phytyl compound [yellow oil, found: C, 82.82; H, 10.31] is the most active member of the series and gives a full response in the chick assay at 50 γ. Similarly the 3-farnesyl derivative of 2-methyl-1,4-naphthoquinone [found: C, 82.97; H, 8.98] is more potent than the 2-geranyl derivative but somewhat less active than vitamin K_1. The synthesis is also applicable in the benzohydroquinone series. 2,3,5-Trimethyl-6-phytyl-1,4-benzoquinone [yellow oil, found: C, 81.04; H, 11.00, hydroquinone diacetate, m. p. 56°] shows no vitamin K activity but it provides a new route to a vitamin E factor. By treatment with stannous chloride in acetic–hydrochloric acid the quinone was converted smoothly into α-tocopherol, identified through the allophanate, m. p. 175–176°, and *p*-nitrophenylurethan, m. p. 130°. Butadiene-toluquinone condenses with phytol under the usual conditions but at the reflux temperature, giving rise to 2 - methyl - 3 - phytyl - 5,8 - dihydro - 1,4 - naphthoquinone [found: C, 82.27; H, 10.86], which is active at a level of 5–6 γ. By hydrogenating synthetic vitamin K_1 and purifying the products in the form of the solid hydroquinones, the β,γ-dihydride (active at 6 γ, hydroquinone diacetate, m. p. 57–58°) and β,γ,5,6,7,8-hexahydride (slight activity, diacetate derivative, m. p. 53°) have been obtained in analytically pure form. Both butadiene-toluquinone and 2-methyl-5,8-dihydro-1,4-naphthohydroquinone show marked activity, the latter at dosages as low as 8 γ.

A by-product of the vitamin K_1 synthesis, characterized as a ketonic substance of the formula $C_{31}H_{48}O_2$ [found: C, 82.38; H, 10.65; maxima at 253 and 300 mμ; 2,4-dinitrophenylhydrazone m. p. 107–108°], shows moderate vitamin K activity (50 γ). The Zerewitinoff determination indicates the presence of one active hydrogen and one carbonyl group. Aluminum isopropylate reduction gives a diol, probably $C_{31}H_{52}O_2$ [found: C, 81.52; H, 11.48], and pyrolysis of the by-product gives rise to small amounts of vitamin K_1. The isomeric naphthotocopherol [found: C, 82.30; H, 10.69; maxima at 246 and 320 mμ; *p*-nitrobenzoate, m. p. 84–85°] is active at a higher level (300 γ); on oxidation it yields a yellow hydroxyquinone [found: C, 79.19; H, 10.17].

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY, CAMBRIDGE, MASS. L. F. FIESER
RESEARCH LABORATORIES, MERCK AND M. TISHLER
CO., INC., AND MERCK INSTITUTE FOR W. L. SAMPSON
THERAPEUTIC RESEARCH
RAHWAY, NEW JERSEY

RECEIVED MARCH 20, 1940

THERMAL DECOMPOSITION OF ACETONE CATALYZED BY IODINE

Sir:

Several investigators[1] have shown that small amounts of iodine sensitize the thermal decomposition of various organic compounds. In the case of acetone, Bairstow and Hinshelwood[1a] have reported that the decomposition was not appreciably affected by the presence of iodine. However, Rice and Weiler[2] observed that the decomposition of acetone containing methyl iodide was appreciably faster than the rate for pure acetone. Moreover it was found that the addition of approximately 1% of ethyl iodide enormously increased the rate of decomposition of acetone at 526°.[3] When a small amount of ethyl iodide was allowed to decompose completely in the reaction vessel first and then the acetone added, a large increase in the rate also was observed. This

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[1] (a) Bairstow and Hinshelwood, *J. Chem. Soc.*, 1147 (1933); (b) P. A. K. Clusius, *ibid.*, 2607 (1930); (c) Faull and Rollefson, THIS JOURNAL, **58**, 1755 (1936); Rollefson and Garrison, *ibid.*, **62**, 588 (1940).

[2] Weiler, Dissertation, Johns Hopkins University, 1930.

[3] Rice and Walters, unpublished results.