[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

Acid-Polymerized Dipinene. I. Dehydrogenation[1]

BY JOHN J. RITTER AND JACOB G. SHAREFKIN[2]

Dipinene, $C_{20}H_{32}$, resulting from the action of acids on alpha- or beta-pinene has been studied by various investigators since its discovery a century ago by Deville,[3] who obtained the substance from turpentine oil and sulfuric acid.[4]

The delayed revival of active interest in the diterpene group is probably due in part to the fact that the diterpenes are comparatively few and their acids quite common, while the converse is true of the sesquiterpenes. Recent workers have made use of sulfur dehydrogenation with inconclusive results in most instances, particularly with the acid-polymerized diterpenes. Up to the present no definite facts bearing upon their structure have appeared. Of the naturally occurring diterpenes alpha-camphorene, distilled from camphor oil[5] and also resulting from myrcene by polymerization,[6] dehydrogenated with sulfur to a product which failed to yield a picrate. Careful fractionation of the unsaponifiable portion of rosin oil[7] gave colophene and diterpenes which were believed to be identical with those prepared by heat and acid polymerization of monoterpenes. Although retene was obtained in the Vesterberg reaction from the colophene fraction, the diterpenes were reported unchanged after this treatment. Neither Aitken[8] nor Blackie[9] obtained an aromatic on sulfur dehydrogenation of the solid diterpene dacrene. The first instance of successful dehydrogenation of a naturally occurring diterpene is Beath's[10] isolation of isoretene from a diterpene which he considered identical with rimunene.

Among the synthetic diterpenes the only reported dehydrogenation resulting in an isolable aromatic is that of dipinene by Dulou,[4] after Kondakow and Saprikin[11] found no aromatic on sulfur dehydrogenation of this substance. Carter, Smith and Read[12] were unable to isolate an aromatic after sulfur dehydrogenation of the closely similar acid-polymerized di-alpha-phellandrene. Dulou's picrate melted at 132° and the hydrocarbon at 64–65°. The latter he stated to be di-isopropyldiphenyl although this compound does not appear in the literature and no proof of structure is given by the author.

We have now reinvestigated the dehydrogenation of dipinene with the immediate view to isolation and identification of a pure aromatic and ultimately arriving at significant facts bearing upon the nature of the carbon skeleton of dipinene. The conditions for most satisfactory dehydrogenation were studied first. High temperature (280°) resulted in complete carbonization while lower temperature (150°) gave no aromatic isolable as picrate. Slow sulfur addition to dipinene at intermediate temperatures (200°) proved most effective in minimizing carbonization; however, the yield of pure aromatic even under the most favorable conditions was of the order of 1.0%. Dilimonene, practically identical with dipinene in physical characteristics, dehydrogenated under the same conditions to the same product. The same product, in yields of the same order, was obtained by the use of diphenyl ether as solvent in the dehydrogenation as well as by slow selenium addition[13] and by the pressure-tube procedure of Ruzicka.[14]

All of the picrates prepared melted at 169.5–170° and showed no depression in mixed melts. From these a solid hydrocarbon was obtained melting at a higher temperature (78.2–78.4°) than that reported by Dulou. This hydrocarbon is not reported in the literature; its analysis and general characteristics indicated a phenanthrene of molecular formula $C_{17}H_{16}$, and its synthesis by an independent method[15] proves it to be 2,6,9-trimethylphenanthrene.

Experimental

Dipinene.—alpha-Pinene was purified by repeated distillation through a 20-cm. column: b. p. 155–156°;

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(3) Deville, *Ann. chim. phys.*, [2] **75**, 66 (1840); *Ann. Chir.*, **37**, 192 (1840).

(4) See Dulou, *Chimie et Industrie*, **27**, (Spec. No.) 651 (1932), for a review of the literature of synthetic dipinenes.

(5) Semmler and Rosenberg, *Ber.*, **46**, 771 (1913).

(6) Semmler and Jonas, *ibid.*, **46**, 1566 (1913).

(7) Knecht and Maurice, *J. Soc. Dyers Colorists*, **41**, 356 (1925).

(8) Aitken, *J. Soc. Chem. Ind.*, **47**, 223T (1928).

(9) Blackie, *ibid.*, **49**, 26T (1930).

(10) Beath, *ibid.*, **52**, 338T (1933).

(11) Kondakow and Saprikin, *Bull. soc. chim.*, **37**, 918, 1415 (1925).

(12) Carter, Smith and Read, *J. Soc. Chem. Ind.*, **44**, 543T (1925).

(13) Diels and Karstens, *Ber.*, **60B**, 2323 (1927).

(14) Ruzicka, *et al.*, *Helv. Chim. Acta*, **16**, 216, 812 (1933); **17**, 200 (1934); **18**, 676 (1935); **19**, 424 (1934).

(15) See the succeeding paper, THIS JOURNAL, **62**, 1509 (1940).

d^{20}_{20} 0.8613; n^{23}_{D} 1.4682; $[\alpha]^{25}_{D}$ +28.12°. Limonene prepared in the same manner gave the constants: b. p. 175.5–175.8°; d^{25}_{25} 0.8395; n^{23}_{D} 1.4710. Phosphoric acid (85%, 500 cc.) is placed in a three-neck flask fitted with a mechanical stirrer, dropping funnel and thermometer; an equal volume of monoterpene is added dropwise with rapid stirring during eight hours while the temperature is held below 30°. After the addition is completed the stirring is continued at room temperature for one hundred and twenty hours. The mixture is then allowed to stand until the layers separate, and the upper layer neutralized with potassium carbonate solution, dried over anhydrous potassium carbonate and distilled. Dipinene, a colorless viscous liquid, is obtained in 71% yield: b. p. 127–128° (1 mm.); d^{25}_{25} 0.9316; n^{25}_{D} 1.5149; $[\alpha]^{25}_{D}$ ±0. *Anal.* Calcd. for $C_{20}H_{32}$: C, 88.15; H, 11.85. Found: C, 87.44; H, 11.71. Dilimonene, prepared in the same way, gave the constants: b. p. 128° (1 mm.); d^{25}_{25} 0.9313; n^{25}_{D} 1.5170; $[\alpha]^{25}_{D}$ ±0. The procedure is that of Carter, Smith and Read[12]; the yields and constants of our products are in agreement with theirs.

Dehydrogenation.—Sulfur (80 g., 2.5 moles) is added to dipinene (136 g., 0.5 mole) in 2–3 g. portions at uniform intervals over a ten-day period, the temperature remaining close to 200° throughout. The resulting black tarry mass is distilled with superheated steam to yield an oil which is extracted from the distillate with ether and distilled at 1 mm. after drying the extract with anhydrous potassium carbonate and removing the ether on the steam-bath. Three fractions are cut: to 140°, 3.7 g.; 140–160°, 36.3 g.; 160° until no further distillation, 32.2 g. Addition of hot saturated alcoholic picric acid to these fractions shows picrate formation only with the latter two.

By the same procedure, 1760 g. of dipinene gave 980 g. of steam-distilled oil which yielded for the three fractions 60, 390, and 375 g., respectively. Redistillation of these through a 20-cm. column at 1 mm. resulted in a fraction of 472 g. at 160–185° which yielded a solid picrate. The crude picrate melted at 137°; after three recrystallizations from alcohol 19.7 g. of pure product, m. p. 169.5–170°, was obtained. *Anal.* Calcd. for $C_{23}H_{19}N_3O_7$: N, 9.35. Found: N, 9.25. The picrate from dilimonene dehydrogenation, m. p. 169–170°, showed no depression in a mixed melting point with that from dipinene. *Anal.* Calcd. for $C_{23}H_{19}N_3O_7$: N, 9.35. Found: N, 9.29. Attempts to increase the yield of the picrate-producing hydrocarbon by re-treatment of the low-boiling fraction from the dehydrogenation with sulfur resulted in failure.

Hydrocarbon $C_{17}H_{16}$.—The picrate from the previous section (23.5 g.) was decomposed in a Soxhlet thimble by refluxing with water for fifteen hours; the 10.5 g. of yellowish solid remaining in the thimble after drying at 40° was extracted with benzene in the Soxhlet apparatus. The extract on evaporation left a solid residue, m. p. 75–75.5°; after three recrystallizations from 95% alcohol colorless tablets, m. p. 78.2–78.4°, were obtained. *Anal.* Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.61; H, 7.53.

Summary

A modified Vesterberg reaction was found most suitable for dipinene dehydrogenation.

All dehydrogenation methods tested with dipinene and dilimonene yielded the same hydrocarbon, which has a higher melting point than that previously reported.

Analysis of the hydrocarbon and its picrate rules out the proposed di-isopropyldiphenyl structure of Dulou.

The hydrocarbon has the composition and general characteristics of a phenanthrene.

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Acid-Polymerized Dipinene. II. Identification of the Dehydrogenate

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In the preceding paper the isolation of a pure crystalline aromatic hydrocarbon $C_{17}H_{16}$ from the sulfur dehydrogenation of acid-polymerized dipinene $C_{20}H_{32}$ is reported. While the limited amount of this substance at hand curtailed rather severely any extended studies of structure by oxidative or other means, its general characteristics indicated the structure of a phenanthrene. Our inability on repeated attempts to isolate a phenanthraquinone on oxidation was ascribed to the presence of a methyl group on carbon atom 9 or 10. Consideration of antecedent literature dealing with dipinene and the action of acids on alpha-pinene led us to the postulation of a carbon skeleton for the dimer which pointed specifically to 2,6,9-trimethylphenanthrene as the most probable substance resulting from its dehydrogenation. This has now been verified by synthesis and the demonstrated identity of the synthetic product with the dehydrogenate.

We proceeded from *l*-menthone (1) which was condensed with *p*-tolylmagnesium bromide to 3-*p*-tolylmenthol (2); the latter was dehydrated to 3-*p*-tolylmenthene-3 (3), which was dehydrogenated with sulfur to $3,4^1$-dimethyl-6-isopropyl-

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