d^{20}_{20} 0.8613; $n^{23}\mathrm{D}$ 1.4682; $[\alpha]^{25}\mathrm{D}$ +28.12°. Limonene prepared in the same manner gave the constants: b. p. 175.5–175.8°; d^{25}_{25} 0.8395; $n^{23}\mathrm{D}$ 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; $n^{25}\mathrm{D}$ 1.5149; $[\alpha]^{25}\mathrm{D}$ ±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; $n^{25}\mathrm{D}$ 1.5170; $[\alpha]^{25}\mathrm{D}$ ±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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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NEW YORK UNIVERSITY]

Acid-Polymerized Dipinene. II. Identification of the Dehydrogenate

BY JOHN J. RITTER AND VIRGIL BOGERT[1]

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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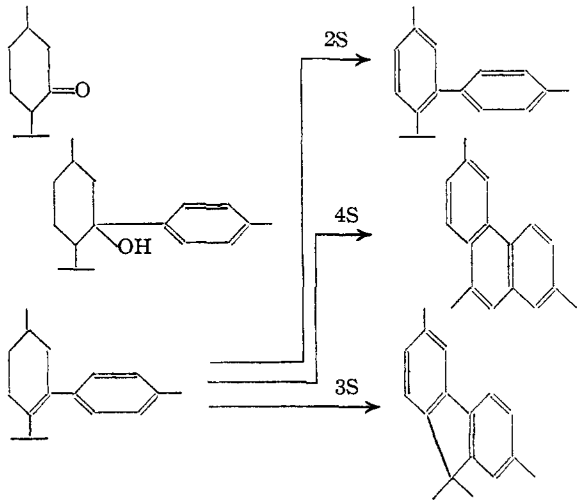
[1] Based upon a portion of the dissertation submitted by Virgil Bogert to the Graduate Faculty of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1940.

diphenyl (4) and also to 2,6,9-trimethylphenanthrene (5). The yield of the phenanthrene was low, the major portion of the product consisting of a liquid aromatic $C_{17}H_{18}$ which appears to be tetramethylfluorene (6). We hope to furnish unequivocal proof of the structure of the latter in a later publication. The tentative assignment of structure to (6) gains added confirmation from the fact that it, like fluorenes generally, forms no crystalline picrate.

The facts here presented serve not only to establish the structure of the dipinene dehydrogenate but seem also to offer an explanation of the principal difficulty of structure determination by dehydrogenation in the acid-polymerized diterpene group, *i. e.*, the formation, principally, of a non-picrating fluorene along with very small quantities of the more easily recognizable phenanthrene. The synthetic trimethylphenanthrene is formed ultimately by dehydrogenative ring-closure of an *o*-isopropyldiphenyl; in spite of the homogeneity of the latter the yield of phenanthrene is of the same order as that resulting from dipinene dehydrogenation under the same conditions. Previous investigators[2] have uniformly disregarded the non-picrating liquid fractions from dipinene dehydrogenation.



We are at present engaged in further studies of the partial and complete dehydrogenation of dipinene with a view to isolation of diphenyls or fluorenes, as well as the more general problem of dehydrogenative ring-closure of *o*-alkyl diphenyls with sulfur. The results of these investigations will appear shortly in THIS JOURNAL.

Experimental

3-*p*-Tolylmenthol.—*p*-Bromotoluene (129 g., 0.75 mole) is added slowly with mechanical stirring to magnesium (18 g., 0.75 mole) and 400 cc. of absolute ether after the reaction has been started with only 50 cc. of ether. After completion of the reaction on the water-bath the mixture is cooled in an ice-bath; ordinary (1) menthone (80 g., 0.52 mole) in 100 cc. of absolute ether is added slowly with continuous stirring. The reaction product is allowed to stand overnight at room temperature, heated on the water-bath for one hour, and then hydrolyzed with 25% aqueous ammonium chloride solution. The ether layer is separated, dried over sodium sulfate, and the ether removed. Distillation of the residue at 2 mm. yields 28–37 g. of menthone and 64–71 g. of the carbinol: b. p. 127–128° (2 mm.); 140–142° (4 mm.); m. p. 39.5°; d^{25}_4 0.9745; n^{25}_D 1.5150; $[\alpha]^{25}_D$ −14.49°. *Anal.* Calcd. for $C_{17}H_{26}O$: C, 82.93; H, 10.57. Found: C, 82.81; H, 10.26.

3-*p*-Tolylmenthene-3.—3-*p*-Tolylmenthol-3 (50 g.) is mixed with twice its weight of anhydrous oxalic acid and the mixture heated in an oil-bath at 150° for six to eight hours. Water is added to dissolve the oxalic acid and the upper layer of hydrocarbon separated. Distillation of the product yields 37–40 g. (80–87%) of 3-*p*-tolylmenthene: b. p. 118–120° (2 mm.); 145–147° (10–11 mm.); d^{25}_4 0.9269; n^{25}_D 1.5218; $[\alpha]^{25}_D$ +49.45. *Anal.* Calcd. for $C_{17}H_{24}$: C, 89.47; H, 10.53. Found: C, 89.59; H, 10.26.

3,4^1-Dimethyl-6-isopropyldiphenyl.—3-*p*-Tolylmenthene-3 (22.8 g., 0.1 mole) is placed in a 50-cc. round-bottom flask sealed to an air-cooled reflux condenser which is in turn connected with a potassium hydroxide trap to collect the evolved hydrogen sulfide. Sulfur (6.4 g.. 0.2 mole) is added in portions of 1–2 g. over a twelve-hour period at 220–230°. The heating is continued for an additional sixty hours or until 6.3–6.7 g. of hydrogen sulfide (93–99% of calcd.) has been collected in the trap: yield, 19 g. (85%); b. p. 108–110° (2 mm.); 130–132° (4–5 mm.); d^{25}_4 0.9619; n^{25}_D 1.5579. *Anal.* Calcd. for $C_{17}H_{20}$: C, 91.07; H, 8.93. Found: C, 91.11; H, 9.09.

Trinitro Derivative.—3,4^1-Dimethyl-6-isopropyldiphenyl is heated for one-half hour on the steam-bath with concentrated nitric–sulfuric acid mixture: m. p. (from alcohol) 164–165°. *Anal.* Calcd. for $C_{17}H_{17}N_3O_6$: N, 11.70. Found: N, 11.76.

Total Dehydrogenation of 3-*p*-Tolylmenthene-3 with Sulfur.—3-*p*-Tolylmenthene-3 (22.8 g., 0.1 mole) is dehydrogenated as in the preceding paragraph with sulfur (12.8 g., 0.4 mole) added in portions of 1–2 g. over a twenty-four hour period. After addition of one-half of the sulfur the temperature is raised from 220–230° to 280–300° and finally to 320–340°, where it is held for thirty-six hours. The total time of dehydrogenation is ninety-six hours, and the weight of hydrogen sulfide collected 12.2 g. Distillation at 2 mm. yields: dimethylisopropyldiphenyl, b. p. 110°, 1.3 g.; 2,6,9,9-tetramethylfluorene, b. p. 123–125°, 5 g.; high-boiling fraction, 130–210°, 1.4 g. The latter yields the picrate of 2,6,9-trimethylphenanthrene; a further quantity of picrate is obtained by alcohol extraction

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[2] Dulou, *Chim. & Ind.*, **27**, 651 (Spec. No.) March (1932); Kondakow and Saprikin, *Bull. soc. chim.*, **37**, 918, 1415 (1925).

of the distillation residue and treatment of the extract with alcoholic picric acid. The total yield of picrate is 0.3 g. (0.66%).

Total Dehydrogenation with Selenium.—3-*p*-Tolylmenthene-3 (22.8 g., 0.1 mole) is dehydrogenated with 32 g. of selenium added over thirty-six hours. Heating for an additional seventy-two hours with gradual increase of the temperature from 290 to 360° gives a product which on ether extraction and distillation yields: 3,4^1-dimethyl-6-isopropyldiphenyl, 3.0 g.; 2,6,9,9-tetramethylfluorene, 4.0 g.; fraction 130–210°, 1.5 g. From the latter and also the distillation residue 0.9 g. of picrate, m. p. 169–170°, is obtained (yield, 2%).

2,6,9-Trimethylphenanthrene.—The hydrocarbon is obtained from its picrate by the method described in the previous paper: yield, 1.4% of calculated from 3-*p*-tolylmenthene-3; m. p. 78.5°. Both the picrate and the hydrocarbon show no depression in mixed melts with the corresponding products from dipinene dehydrogenation.

2,6,9,9-Tetramethylfluorene.—B. p. 123–125° (2 mm.); d^{25}_4 0.9893; n^{25}_D 1.5811; mol. wt. (Rast, camphor) 225, calcd. 222. *Anal.* Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.80; H, 8.20. Monobromo derivative, m. p. 94.5°. *Anal.* Calcd. for $C_{17}H_{17}Br$: C, 67.77; H, 5.64. Found: C, 67.75; H, 5.15. Dinitro derivative (mixed acid at room temperature), m. p. 218° (from alcohol). *Anal.* Calcd. for $C_{17}H_{16}N_2O_4$: N, 8.97. Found: N, 9.15.

Summary

2,6,9-Trimethylphenanthrene has been synthesized, characterized, and shown to be identical with the product of dipinene dehydrogenation.

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Mono- and Di-α-furfuryl Glycines

BY J. E. ZANETTI AND J. T. BASHOUR

We have shown the pronounced reactivity of furfuryl bromide in ether solution on the amino group[1] and it appeared of interest to investigate whether the neighboring presence of a carbethoxy group would influence the reaction. Accordingly we have studied its action on the amino group of α-aminoacetic ethyl ester and found it to proceed quite satisfactorily. The free α-furfurylamino acid can be obtained readily from the ester by hydrolysis. We have found that excess of the ethyl aminoacetate to liberate the furfuryl addition compound from its hydro bromide gave better results than the use of sodium or potassium hydroxides for similar purposes. The reaction may then be written as

$$C_4H_3OCH_2Br + 2NH_2CH_2COOC_2H_5 \longrightarrow$$
$$C_4H_3OCH_2NHCH_2COOC_2H_5 + NH_2HBrCH_2COOC_2H_5$$

The glycine ester hydrobromide precipitates out of the ether, leaving in solution the furfuryl glycine ethyl ester.

As explained in the experimental part, both the mono- and di-α-furfurylglycines can be obtained in one operation by using varying ratios of α-furfuryl bromide to the amino acetate, a procedure which we found unsatisfactory when working with free amines.

Experimental

The general procedure was similar to that already described for the preparation of furfurylalkyl amines.[1] The hydrobromide precipitated and was filtered off in the usual manner. It was also found that the difurfurylaminoacetic ester could be obtained in one operation by slightly increasing the ratio of furfuryl bromide to amine. Two and one-half cc. of ethyl aminoacetate per cc. of furfuryl alcohol used in the bromide synthesis, gives a product consisting of 80% monofurfuryl derivative and 20% difurfuryl derivative. Two cc. of amine per cc. of furfuryl alcohol resulted in approximately equivalent quantities of secondary and tertiary products. Yields were over 80% on the basis of 70% yield of furfuryl bromide.

Ethyl aminoacetate was prepared from glycine through the ester hydrochloride by the methods of Curtius[2] and Fischer.[3] Over-all yields of 65% were readily obtained.

Ethyl Furfurylaminoacetate.—In contrast to glycine ester, this product is quite stable, long standing causing only a slight yellowing with very slight decomposition as determined by redistillation. No diketopiperazine formation was observed. It is soluble in most organic solvents: b. p. 99–101° at 3 mm.; n^{25}_D 1.4735; d^{25}_{20} 1.096. The hydrochloride melted at 68–70°. It was recrystallized from absolute alcohol by addition of absolute ether to incipient cloudiness.

Anal. Calcd. for $C_9H_{13}O_3N$: N, 7.65. Found: N, 7.70.

Ethyl Benzofurfurylaminoacetate.—Three cc. of ethyl furfurylaminoacetate was dissolved in 4.2 cc. of benzoyl chloride with cooling in an ice-bath. Thirty cc. of 2.5 *N* sodium hydroxide, ice-cold, was added at once and the mixture shaken for twenty minutes. Ether was added and the aqueous layer discarded. The ether layer was washed with dilute hydrochloric acid and water, and dried overnight with sodium sulfate. After removal of the ether, the product was collected at 157–162° at approximately 1 mm.

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[1] Zanetti and Bashour, THIS JOURNAL, **61**, 3133 (1939); **62**, 742 (1940).

[2] Curtius and Goebel, *J. prakt. Chem.*, *N. F.*, **37**, 159 (1888).

[3] Fischer, *Ber.*, **34B**, 436 (1901).