

against the concentration. For long chains the slope of this line depends on  $\mu_1$ , but not on the chain length of the solute molecules.

3. The quantitative relationships derived for flexible chain molecules should also be applicable to flexible network molecules. For values of  $\mu_1$  greater than a critical value, the theoretical activity-composition curve indicates separation into two phases. One consists of the nearly pure small-molecule component. The other is usually a gel; its composition depends primarily on the value of  $\mu_1$ . From experimental values of equilibrium com-

positions for polystyrene-alkyl laurate gels at different temperatures,  $\mu_1$  is a rectilinear function of  $V_1/T$ , the ratio of the molal volume of the small-molecule component to the absolute temperature.

4. An equation for the solubility of a solid chain compound in a small-molecule liquid is derived and found to be in agreement with measurements at various temperatures of the solubilities of  $n\text{-C}_{34}\text{H}_{70}$  and  $n\text{-C}_{60}\text{H}_{122}$  in decalin. Simplified solubility equations, applicable to long-chain polymers, are deduced.

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## Studies in Dehydrogenation.<sup>1</sup> II. Spirocyclopentane-1,1'-tetralin

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The investigation of the rearrangement and dehydrogenation of spirocyclohexane-1,1'-indane<sup>1</sup> over a palladium on charcoal catalyst showed the importance of cautious postulation of structure based on the products obtained by dehydrogenation. Thus, a compound thought to be a hydrophenanthrene must be carefully examined if the only proof of its structure is dehydrogenation to phenanthrene, especially if its synthesis can theoretically yield isomeric spiranes.

When passed over Pd-C at 370-375°, spirocyclohexane-1,1'-indane was rearranged and dehydrogenated to phenanthrene while at 400-420° the main product was anthracene. This formation of both phenanthrene and anthracene from a tricyclic spirane has since been applied to the detection of spiranes.<sup>3</sup> It therefore appears important to study the action of other spiranes under similar dehydrogenation conditions. The closest isomer to the spirane previously studied is spirocyclopentane-1,1'-tetralin. This compound was therefore passed over the Pd-C catalyst in the vapor phase in a new apparatus especially designed to allow this repeated exposure of the hydrocarbon to the catalyst without the necessity of removing it from one end of the apparatus and reintroducing it at the other.

The heating element (A) was a brass tube 16 mm. in diameter and 75 cm. long, wound with

nichrome wire. The closely fitting Pyrex dehydrogenation tube (B), inserted in the heating element, was closed at one end and had a stopcock sealed on the other end for the removal of samples during the dehydrogenation. The temperature inside this tube was checked beforehand with the temperature inside the thermometer well (C) enclosed by the heating coil. T-Tubes (D and D') were sealed on the dehydrogenation tube 7 cm. from each end of the brass tube. Two 3-way stopcocks (E and E') were connected to these T-tubes in such a way that either end of the dehydrogenation tube could be opened to the mercury trap (F) and a bubble counter (G), while the other end was opened to tube (H) leading to the supply of nitrogen or hydrogen. The palladium catalyst was prepared according to the method of Linstead and Thomas.<sup>4</sup> It was thoroughly mixed with twice its weight of asbestos and packed into the dehydrogenation tube with a space of 8 cm. left at each end as a preheating zone for the compound. The catalyst was changed for each run.

In operation the compound was pipetted into the dehydrogenation tube through (D) while the apparatus was tilted to prevent contact with the catalyst. Washed and dried nitrogen was passed into the apparatus through (H) to displace the air while the temperature was raised to the desired point. During this time stopcock (E) was open to (H) while stopcock (E') led to the mercury trap.

(1) For the first paper in this series see Levitz, Perlman, and Bogert, *J. Org. Chem.*, **6**, 105 (1941).

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(3) Marvel and Walton, *J. Org. Chem.*, **7**, 88 (1942).

(4) Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).

The flow of nitrogen was then stopped and washed and dried hydrogen was admitted to displace the nitrogen. Stopcock (E) was then closed. The tube was tilted to allow the compound to flow slowly into the heated zone. After passing through, the compound condensed and collected in the cool portion. Stopcock (D') was then closed and stopcock (D) was opened to the mercury trap. Any solid which had collected was melted by means of the radiant heat from an electric cigar lighter. The tube was tilted in the opposite direction and the compound was again passed over the catalyst. The process was repeated until dehydrogenation was complete.

The first run was made at 355–375° for six hours. The spirane was rearranged and dehydrogenated to phenanthrene. Another run was made at 420–430° to see whether anthracene would be produced as in the case of the spirocyclohexane-1,1'-indane. Phenanthrene was the only aromatic compound found in the product of this present dehydrogenation.

### Experimental

Spirocyclopentane-1,1'-tetralin was prepared according to the method of Perlman, Davidson and Bogert.<sup>5</sup> Phenylpropyl bromide from phenylpropyl alcohol and phosphorus tribromide was put through a Grignard reaction with cyclopentanone. The resulting carbinol was cyclodehydrated by means of 85% sulfuric acid to the hydrocarbon; yield 32%, b. p. 135–137° (10 mm.),  $n_D^{25}$  1.5539; previously reported<sup>5</sup>: yield 30%, b. p. 137–138° (10 mm.),  $n_D^{25}$  1.5533.

**Dehydrogenation at 355–375°.**—The apparatus was charged with 8 g. of spirocyclopentane-1,1'-tetralin and the temperature was raised to 355°. Dehydrogenation started as soon as the hydrocarbon was passed over the catalyst, as evidenced by the rapid flow of hydrogen through the bubble counter. In twenty minutes all of the compound had passed completely over the catalyst and had condensed in the cool part of the tube. A considerable amount solidified as a low melting white solid. After one and one-half hours of continuous recirculation the rate of flow of hydrogen decreased materially. The temperature was raised to 365° and dehydrogenation was continued for three and one-half hours and finally at 375° for one hour, at the end of which time only solid collected. This was melted and removed from the apparatus. It weighed 6.5 g. and solidified at about 60°. It was crystallized by dissolving in petroleum ether (Skellysolve B) and chilling in a dry-ice-acetone bath. Recrystallization from ethyl alcohol produced phenanthrene melting at 98–99°, not

depressed by an authentic sample. A picrate made with a saturated alcoholic solution of picric acid melted at 144–145°, not depressed by an authentic sample. No other aromatic compound could be isolated.

The catalyst was thoroughly washed with hot benzene. The highly fluorescent solution obtained yielded 0.6 g. of solid material when the benzene was evaporated. Purification produced only phenanthrene.

**Dehydrogenation at 420–430°.**—Six grams of spirocyclopentane-1,1'-tetralin was passed over the catalyst at 420–425° for ten hours. There was evidence that decomposition was taking place at this temperature. The product obtained showed a deep yellow-green fluorescence when liquid. Most of the product solidified at about 40° but 1 g. collected in the apparatus as a liquid. The liquid and solid were removed separately. Refluxing the liquid fraction with an alcoholic solution of picric acid yielded a picrate melting at 140–141° after recrystallization from hot ethyl alcohol. The melting point was not depressed by an authentic sample of phenanthrene picrate.

The solid, which weighed 3.7 g., was dissolved in petroleum ether and chilled in an ice-salt-bath. Filtration yielded 1.5 g. of solid melting at 90°. Recrystallization from ethyl alcohol gave phenanthrene, m. p. 98–99°, not depressed by an authentic sample of phenanthrene. The petroleum ether filtrate was chilled in a dry-ice-acetone bath and filtered. The 0.8 g. of solid melted at 94–95° and recrystallization from ethyl alcohol raised the melting point to 97–98°, not depressed by an authentic sample of phenanthrene.

The petroleum ether filtrate was still highly fluorescent. It was passed through an aluminum oxide adsorption column and developed with 4:1 petroleum ether-benzene. The non-fluorescent fraction which came through first was chilled in a dry-ice-acetone bath. White crystals of m. p. 93–94°, not depressed by an authentic sample of phenanthrene, were obtained. The fluorescent fraction turned out to be quite small when the solvent was evaporated. Refluxing with an alcoholic solution of picric acid gave no picrate on chilling. Picrates made from the phenanthrenes obtained above melted at 143–144°, not depressed by an authentic sample of phenanthrene picrate.

The catalyst was thoroughly digested with hot benzene. Evaporation of the benzene gave only dark carbonaceous material (0.4 g.), evidently the result of decomposition at the elevated temperature.

### Summary

1. Spirocyclopentane-1,1'-tetralin was rearranged and dehydrogenated to phenanthrene when passed over palladium on charcoal at 355–375°.
2. Phenanthrene was the only aromatic compound produced when the reaction was carried out at 420–430°.

(5) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 300 (1936).