[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

STUDIES IN DEHYDROGENATION. III. THE DEHYDROGENATION OF A METHYL SPIRAN

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In their recent studies on the inactive perhydrodiphenic acids, Linstead and Doering (1) were confronted with the problem of having available a greater number of isomeric acids than the six called for by classical stereochemical theory. One of these acids, labeled Linstead and Walpole acid, m.p. 203°, was made from the product of the cyclization of *dl*-$\Delta^{1,1'}$-cyclohexenylacetylene with formic acid. This cyclization product was first prepared by Marvel and co-workers (2) and was considered by them to be 9-dodecahydrophenanthrene, since reduction by the Clemmensen method followed by dehydrogenation over platinum-charcoal in the vapor phase yielded phenanthrene (3).

Studies by our laboratories on the compound spirocyclohexane-1,1'-indane (4) isomeric with octahydrophenanthrene led us to suggest that the compound prepared by Marvel and co-workers had a spiran structure rather than a hydophenanthrene structure. This suggestion was based partly on the fact that the spiran studied readily yielded phenanthrene when passed over palladium-charcoal in the vapor phase. Another isomeric spiran, spirocyclopentane-1,1'-tetralin has also been found to yield phenanthrene under the same conditions (5). The proposed spiran skeleton was accepted by Linstead and Doering (1). Consequently they decided that the excess acid, m.p. 203°, was actually dicyclohexyl-1,2'-dicarboxylic acid which would be derived from a spiran structure.

One reaction studied by Marvel and co-workers (6) may still point to a hydrophenanthrene structure. They condensed the supposed 9-dodecahydrophenanthrone (I) with methylmagnesium chloride, dehydrated the carbinol (II), and subjected the hydrocarbon (III) to dehydrogenation over platinum-charcoal at 320° for three hours. They obtained 9-methylphenanthrene (IV). This was offered as evidence for the hydrophenanthrene structure, since they considered it unlikely that an alkyl group would retain its position in the rearrangement of a spiran to a phenanthrene under dehydrogenation conditions.

To test the validity of this conclusion, similar reactions with a typical tricyclic spiran were carried out in these laboratories. Spirocyclopentane-1,1'-tetralin (V) was oxidized to the tetralone (VI) and condensed with methylmagnesium iodide. The carbinol (VII) was dehydrated and the resulting hydrocarbon (VIII) was continuously recirculated over palladium-charcoal in the vapor phase at 330–340° for five hours. The methyl spiran readily rearranged and dehydrogenated to 9-methylphenanthrene. The methyl group retained its position.

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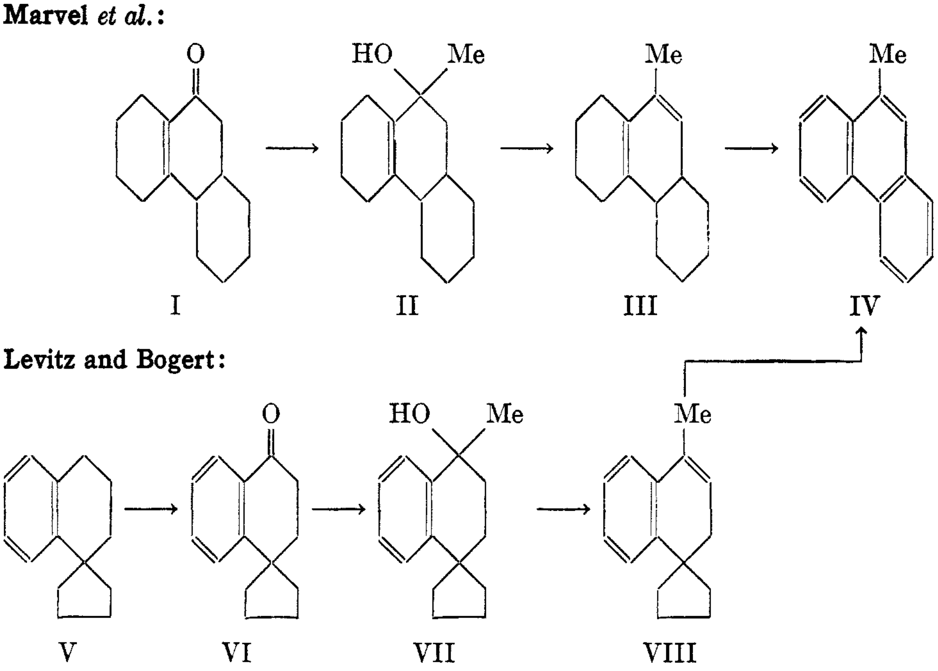
FLOW-SHEET



EXPERIMENTAL

Spirocyclopentane-1,1′-tetralin (V) was prepared according to the method of Perlman, Davidson, and Bogert (7). Thirteen grams dissolved in 75 ml. of glacial acetic acid was oxidized with chromic acid in acetic acid at room temperature as previously described (4). Yield of spirocyclopentane-1,1′-tetralone-4′ (VI), 7.8 g. or 56%; b.p. 140–142°/3 mm.; n_{D}^{25} 1.5716.

The semicarbazone was prepared by refluxing the ketone with semicarbazide hydrochloride and sodium acetate in ethyl alcohol for two hours, and was recrystallized from hot ethyl alcohol, m.p. 204.5–205.5° (corr.).

Anal. Calc'd for $C_{15}H_{19}N_3O$: C, 70.0; H, 7.4.
Found: C, 70.0; H, 7.5.

By the usual procedure, 6.3 g. of the ketone in 10 ml. of ether was brought into reaction with the methylmagnesium iodide made from 2.4 g. of magnesium and 14.2 g. of methyl iodide. The resulting carbinol (VII) was heated for 40 minutes with an equal weight of fused potassium bisulfate under 18 mm. pressure at 150–160°. The hydrocarbon (VIII) was extracted with petroleum ether and distilled. A yield of 4.4 g. or 70% was secured; b.p. 109–110°/2 mm.; n_{D}^{25} 1.5737.

Anal. Calc'd for $C_{15}H_{18}$: C, 90.9; H, 9.2.
Found: C, 90.9; H, 9.2.

Dehydrogenation was carried out in a continuous recirculation apparatus similar to the one previously described (5), but designed for smaller quantities. The heating furnace was 48 cm. long with an internal diameter of 11 mm. The apparatus was charged with 3.7 g. of the methyl spiran (VIII) and the temperature was raised to 330°. Dehydrogenation started as soon as the hydrocarbon was passed over the palladium-charcoal catalyst, as evidenced by the rapid flow of hydrogen through the bubble-counter. The operation was continued for five hours at 330–340°. The solid then removed from the apparatus weighed

3 g. Recrystallization from ethyl alcohol gave 2.4 g. of 9-methylphenanthrene, m.p. 90–91° (corr.). The picrate made by heating with an alcoholic solution of picric acid melted at 156° (corr.). Previously reported for 9-methylphenanthrene, m.p. 91–92° and for the picrate m.p. 154–155° (6).

SUMMARY

Marvel, Pearson, and White (6) have synthesized a ketone which they believe to be a 9-dodecahydrophenanthrone, and in support of this structure cite the preparation therefrom of 9-methylphenanthrene by a series of reactions involving a final dehydrogenation over platinized charcoal for 3 hrs. at 320°. They conclude that their initial ketone (I) could not have been the isomeric spiran (VI) because "it would be unlikely that an alkyl group would retain its position in the rearrangement of a spiran to a phenanthrene under dehydrogenation conditions." The present paper shows that this particular spiran, when carried through a similar series of reactions, does yield 9-methylphenanthrene, without any shift in the initial position of the methyl group.

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