the zone reached the bottom of the adsorbing material before all of the original solution had passed into the adsorbent. At this stage the entire column of adsorbent was in equilibrium with the solution of concentration c_0, and the zone was coextensive with the column. The situation would ordinarily be different under the normal conditions of chromatography, such as in the separation of two or more substances. Here the length of the zone should be small compared with the length of the column of adsorbent. In such cases the concentration of the emerging liquid might not reach c_0 and, therefore, there would not be a flat portion of the curve. Instead, diffuseness of both the leading and following edges of the zones would be expected, the effect being greater the slower the approach to equilibrium. Examples of such curves will be found in a later paper dealing with the separation of fatty acids by means of adsorption analysis. Experiments of the "liquid chromatogram" type might be useful in the study of rates of adsorption and desorption.

Summary

It has been shown in a simple case that the chromatography of a solution containing a single solute is in reasonable agreement with the theory.

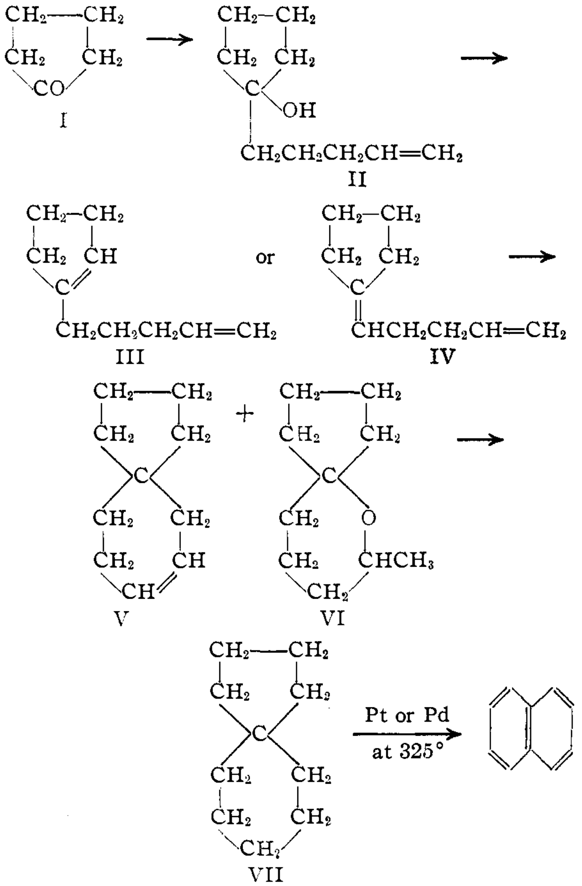
New Haven, Connecticut Received July 11, 1941

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Preparation and Dehydrogenation of Spirodecane and 3-Methylspirodecane[1]

By C. S. Marvel and Lester A. Brooks

The possible formation of spirans as by-products in the cyclization of dienynes and the dehydrogenation of spirocyclohexane-1,1'-indane[2] to give phenanthrene and anthracene has led us to study the preparation and dehydrogenation of some simple spirans. The present work describes a new synthesis of spirodecane and 3-methylspirodecane based on the method which Hibbit and Linstead[3] have devised for the synthesis of 1,1-dimethyl-3-cyclohexene. Some studies of the dehydrogenation of these two spirans with platinum, palladium and selenium also have been made.



Condensation of cyclopentanone (I) with the Grignard reagent from 1-bromo-4-pentene gave the tertiary alcohol (II) which on distillation with a trace of iodine yielded 1-(Δ^1-cyclopentenyl)-4-pentene (III) or its isomer (IV). Cyclization of this diene with sulfuric acid produced spirodecene (V) contaminated with an oxygen containing by-product which was presumably a cyclic ether (VI). The exact position of the double bond in the spirodecene (V) was not determined. Reduction of the mixture of the spirodecene and the ether with hydrogen over Raney nickel[4] gave a mixture of spirodecane (VII) and the ether from which the latter could be removed by washing with concentrated sulfuric acid. The properties of our spirodecane are compared in Table I with its proper-

---

(1) This is the twelfth communication on the cyclization of dienynes. For the previous article see, This Journal, 63, 2218 (1941).

(2) Levitz, Perlman and Bogert, *J. Org. Chem.*, 6, 105 (1941).

(3) Hibbit and Linstead, *J. Chem. Soc.*, 470 (1936).

(4) Covert and Adkins, This Journal, 54, 4116 (1932).

ties as given by Zelinsky and Schuikin[5] and also with *cis*- and *trans*-decalins which are possible products of the cyclization reactions which we used.

TABLE I

PHYSICAL CONSTANTS OF SPIRODECANE AND DECALINS

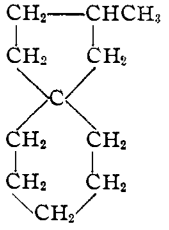
	B. p., °C.	$n^{20}{}_D$	$d^{20}{}_4$	M_D calcd.	M_D found
Spirodecane (M + B)	184–186.5	1.4744	0.8805	43.93	44.14
Spirodecane (Z + S)	185–186	1.4748	.8877	43.93	43.81
cis-Decalin[6]	193	1.4805	.895	..	..
trans-Decalin[6]	185	1.4695	.869	..	..

Zelinsky and Schuikin reported that their hydrocarbon reacted vigorously with bromine to give a tetrabromide. The product which we obtained did not show this behavior. They also have reported experiments on dehydrogenation of their hydrocarbon over palladium and platinum at 300°. The refractive index changed but no naphthalene was identified in their product.

Our spirodecane was dehydrogenated readily when passed over either platinum or palladium on charcoal at 325°. These catalysts gave, respectively, 33 and 35% yields of crystalline naphthalene. Presumably the other products of the reaction were gaseous and escaped from the reaction vessel. Clemo and Ormiston[7] have reported that spirodecane can be dehydrogenated by selenium at 290–300° to give low yields of naphthalene. We heated our spirodecane with selenium at 300–350° for thirty-one hours and recovered the starting material unchanged. Our failure to effect dehydrogenation with selenium has no obvious explanation.

The mixture of spirodecene and cyclic ether was sensitive to air and, if allowed to stand for a few days, formed peroxides. The peroxide-containing mixture reacted with 2,4-dinitrophenylhydrazine but no derivatives could be characterized.

The same general reactions have been used to prepare 3-methylspirodecane (VIII) from 3-methylcyclopentanone.



VIII

This spiran was readily dehydrogenated by platinum at 325° to give a 31% yield of 2-methylnaphthalene. No 1-methylnaphthalene was detected among the dehydrogenation products. No dehydrogenation was achieved by heating this spiran with selenium at 320–330° for thirty-six hours.

Experimental

1-Bromo-4-pentene.—This was obtained in the same yield as described by Gaubert, Linstead and Rydon.[8]

1-(4-Pentenyl)-cyclopentanol (II).—A solution of 52 g. of freshly distilled cyclopentanone in 50 cc. of anhydrous ether was added slowly and with stirring to a solution of the Grignard reagent prepared from 15.6 g. of magnesium and 100 g. of 1-bromo-4-pentene in 300 cc. of anhydrous ether. The mixture was stirred for a half hour after the reagents were mixed and then decomposed by pouring into ice water and ammonium chloride. The ether extract was separated, dried and distilled. The product boiled at 82–83° at 4 mm.; 94–95° at 8 mm. and 209–211° under atmospheric pressure; $n^{20}{}_D$ 1.4705. The yield was 50 g. (53%).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.90; H, 11.70. Found: C, 78.29; H, 11.70

Dehydration of the Alcohol to Diene (III or IV).—To 30 g. of the alcohol was added a crystal of iodine and the mixture was slowly distilled. The product was then dried over calcium chloride and distilled over sodium. The yield was 24 g. (90%) of compound, b. p. 172–175°; $n^{20}{}_D$ 1.4655.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.25; H, 11.75. Found: C, 87.89; H, 12.01.

Cyclization of the Diene.—Fifty grams of the diene was added slowly with stirring to 42 cc. of 84% sulfuric acid which was held at 5–10°. The mixture was stirred for one-half hour after the addition was complete and then poured into ice water. The organic material was collected in low-boiling petroleum ether and washed with 5% sodium carbonate solution. The petroleum ether solution was then dried over magnesium sulfate and distilled. The removal of the solvent went smoothly. When the bath temperature reached 120°, a vigorous reaction took place and considerable sulfur dioxide and water were liberated. After this, the distillation was continued and the crude product boiling at 180–200° was washed with sodium carbonate solution, dried and distilled. After three distillations from metallic sodium, 27 g. of product boiling at 185–191° was collected.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.25; H, 11.75. Found C, 87.74; H, 11.77.

This product was tested for peroxides by the method of Kharasch and Mayo[9] and was found to give a strong positive test which became more pronounced on standing. When freshly prepared, the mixture did not give a positive Zerewitinoff test for active hydrogen or react with 2,4-dinitrophenylhydrazine. After standing in air for thirty days, considerable self-oxidation had occurred and ketonic reagents gave derivatives but no pure compounds were

---

[5] Zelinsky and Schuikin, *Ber.*, **62**, 2180 (1929).

[6] Hückel, *ibid.*, **58**, 1449 (1925).

[7] Clemo and Ormiston, *J. Chem. Soc.*, 352 (1933).

[8] Gaubert, Linstead and Rydon, *ibid.*, 1971 (1937).

[9] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

isolated. The analysis of the portion of the mixture described above after thirty days of standing gave 77.20% C and 10.34% H.

Spirodecane.—An 18-g. sample of the above mixture was hydrogenated with hydrogen over Raney nickel[7] at 175° and 1900 lb. pressure. The catalyst was removed by filtration and the product was washed repeatedly with cold, concentrated sulfuric acid and finally four times with 10 cc. portions of 4:1 concentrated sulfuric acid and 20% oleum mixture. The product was finally washed with water, dried and distilled. The yield was 6 g. of a product, b. p. 184–186.5°; $n^{20}\text{D}$ 1.4744; d^{20}_4 0.8805. This product did not react with bromine.

Anal. Calcd. for $C_{10}H_{18}$: C, 87.00; H, 13.00. Found: C, 87.26; H, 13.32.

3-Methylspirodecane.—3-Methylcyclopentanone, b. p. 140–144°, was obtained in 70% yield from β-methyladipic acid[10] by the procedure described for the preparation of cyclopentanone.[11] Using the same reactions described for the cyclopentanone, 73.5 g. of methylcyclopentanone gave 66 g. (52%) of the tertiary alcohol, b. p. 105–106° at 12 mm.; 214–217° at atmospheric pressure; $n^{20}\text{D}$ 1.4647.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.70; H, 11.90. Found: C, 78.46; H, 12.08.

Dehydration of 50 g. of this alcohol gave 35 g. of diene b. p. 186–189°; $n^{20}\text{D}$ 1.4595.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.90; H, 12.10. Found: C, 87.65; H, 12.46.

Cyclization of this diene gave 14.5 g. of impure methylspirodecene, b. p. 198–203°.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.90; H, 12.10. Found: C, 85.88; H, 11.69.

This analysis shows that the hydrocarbon obviously contained an oxygen derivative as an impurity.

Reduction of 10 g. of the above mixture and subsequent purification as described before for the homolog gave 6 g. of hydrocarbon, b. p. 195–197°; $n^{20}\text{D}$ 1.4660.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.85; H, 13.15. Found: C, 86.59; H, 13.41.

Dehydrogenation of Spirodecane. With Selenium.—A 1.875-g. sample of spirodecane was heated with 5.4 g. of selenium at 300–305° for five hours at 315–320° for twelve hours and then at 350–355° for fourteen hours. There was no apparent evolution of hydrogen selenide during the heating period. The product was isolated from the selenium and redistilled. The recovery was that expected if only mechanical losses had occurred and the product had the same refractive index that it had before the treatment.

With Palladium on Charcoal.—A 2.072-g. sample of spirodecane was refluxed over a palladium on charcoal catalyst[5] held at 320–325° for ten hours. Tests of the effluent gases indicated that dehydrogenation began at 290°. After thirty minutes of the treatment crystals began to appear in the cool parts of the flask in which the sample was being heated. The yield of naphthalene m. p. 79–80° was 0.667 g. (34.7%). This material did not depress the melting point of an authentic sample of naphthalene.

With Platinum on Charcoal.—A 1.653-g. sample of spirodecane was dehydrogenated over a platinum on charcoal catalyst[12] at 320–325° in the same manner as described for the palladium catalyst. The yield of naphthalene was 0.515 g. (33.5%), m. p. 79–80°.

Dehydrogenation of 3-Methylspirodecane. With Selenium.—Heating 1.7 g. of 3-methylspirodecane with 4.5 g. of selenium for thirty-six hours at 320–330° did not cause dehydrogenation and the hydrocarbon had the same properties after the treatment as before.

With Palladium on Charcoal.—A 2.1-g. sample of 3-methylspirodecane was refluxed over a palladium on charcoal catalyst[5] held at 325° for eight hours. This treatment gave 1.51 g. of light brown oil with an odor somewhat like that of naphthalene. From 0.190 g. of the oil 0.153 g. of 2-methylnaphthalene picrate, m. p. 115–116°, was isolated. By way of comparison 0.2 g. of authentic 2-methylnaphthalene similarly treated gave 0.380 g. (70%) of picrate which melted at the same point and did not depress the melting point of the above picrate from the dehydrogenation mixture. Based upon a 70% yield of picrate the dehydrogenation produced 31% of 2-methylnaphthalene. No evidence of the presence of naphthalene or 1-methylnaphthalene was obtained.

Summary

Spirodecane and 3-methylspirodecane have been prepared by new procedures. Spirodecane was readily dehydrogenated to naphthalene by platinum or palladium catalysts at 325° and 3-methylspirodecane was converted to 2-methylnaphthalene by heating with palladium at 325°. Neither spirodecane nor its 3-methyl derivative was dehydrogenated by selenium at 300–350°.

Urbana, Illinois Received July 18, 1941

---

(10) This acid was obtained by the method of Semmler, *Ber.*, **25**, 3513 (1892).

(11) Thorpe and Kon, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 187.

(12) Linstead, Millidge, Thomas and Walpole, *J. Chem. Soc.*, 1146 (1937).