

Anal. Calcd. for  $C_{21}H_{26}S_2O_3$ : C, 57.5; H, 6.0; S, 14.6. Found: C, 57.5; H, 6.0; S, 14.8.

Evaporation of the mother liquors from crystallization of the ditosylate from hot ethanol gave an oil, acid to litmus, which after washing well with alkali reacted with 50% of the quantity of bromine required to brominate the unsaturated monotosylate of III.

The aqueous mother liquors from the preparation of the ditosylate (IV) yielded an oil (54 g., 18% on the glycol) which boiled at 143–144°/760 mm.;  $n_D^{20}$  1.4570. This was 2-oxabicyclo[3.3.0]octane for which Hückel and Gelmroth<sup>11</sup> give m.p. 144–145°/760 mm.

Anal. Calcd. for  $C_7H_{12}O$ : C, 75.0; H, 10.8. Found: C, 73.0; H, 10.3.

A freezing point determination indicated the presence of two crystalline modifications, m.p.  $-107^\circ$  and  $-100^\circ$  and although it appeared probable from the cooling curve that the sample was essentially one isomer no purity could be estimated.

*trans*-2-Thiabiacyclo[3.3.0]octane (V). A solution of sodium sulfide nonahydrate (373 g.) in water (0.2 l.) and ethanol (5.6 l.) was stirred at 50° and the crude ditosylate (IV) (688 g.) was added portionwise to it concurrently with a solution of sodium sulfide nonahydrate (373 g. in water 0.2 l.) (4.6 hr.). Stirring at 50° was continued for a further 12 hr. after which the mixture was steam distilled. The steam-distillate was diluted with water (20 l.), treated with caustic soda (160 g.) and extracted with *n*-pentane; after removal of the solvent, distillation gave an oil (17 g., 8.5%) boiling below 44°/0.5 mm. which was mainly the required sulfide. The residue and that from steam distillation, on distillation gave the following fractions (1) b.p. 130–140°/0.8 mm.; 86 g.; (2) 140–230°/0.8 mm.; 16 g.; (3) 230–240°/0.8 mm.; 37 g., and a residue 12 g.

Anal. Calcd. for  $C_{14}H_{22}S$ : C, 75.6; H, 10.0; S, 14.4. Found: C, 73.5; H, 9.9; S, 15.1 for Fraction 1.

Anal. Calcd. for  $C_{23}H_{36}S_3$ : C, 70.2; H, 9.7; S, 20.1. Found: C, 70.9; H, 9.5; S, 19.5 for Fraction 3.

The crude *trans*-2-thiabiacyclo[3.3.0]octane (V) was purified by crystallization of its mercuric chloride complex from ethanol, and the sulfide regenerated by adding the complex suspended in Carbitol,<sup>24</sup> to a refluxing solution of aqueous sodium sulfide nonahydrate solution (50% w./w. in water) and collecting the sulfide in an oil water separator. After thorough water washing and drying the sulfide distilled at 86.5°/20 mm.; m.p.  $-8^\circ$ ;  $n_D^{20}$  1.52845.

Anal. Calcd. for  $C_7H_{12}S$ : C, 65.6; H, 9.4; S, 25.0. Found: C, 65.6; H, 9.4; S, 25.0.

The sulfide proved to be susceptible to oxidation by air. Distillation of a sample which had been stored for several months in a glass-stoppered container in diffuse light gave, in addition to a distillate of the almost pure *trans*-sulfide, a residue (0.31 g.) which by titration contained 25% of sulfoxide, estimated as  $C_7H_{12}OS$ . This residue in ether was reduced with lithium aluminum hydride (0.15 g.), the product was separated into a neutral portion (0.23 g.) (mainly *trans*-sulfide) and an evil-smelling acidic portion which gave a positive doctor test reaction and infrared examination confirmed the presence of a hydroxyl grouping. There was insufficient of this material left for characterization.

*Acknowledgement.* The authors wish to thank the Chairman and Directors of The British Petroleum Company Limited for permission to publish these results and Mr. J. C. Stalley for the determination of the physical constants.

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(24) Carbide and Carbon Chemical Corp. trade name; Carbitol is the monoethyl ether of diethylene glycol.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

## Dehydrogenation of 1-Isopropylindan and 1-Isopropylhydrindan

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Received December 6, 1957

The dehydrogenation of the hydrocarbons in the title has afforded 2,2-dimethyltetralin,  $\beta$ -methylnaphthalene, and a  $C_{20}H_{16}$  hydrocarbon of unknown constitution. The significance of these results with regard to the structure of  $\alpha$ -amyrin is discussed.

Spring and his co-workers<sup>3</sup> have recently proposed for the triterpene,  $\alpha$ -amyrin, a new structure (I) that differs from the generally accepted one (II)<sup>4</sup> by having an isopropyl group attached to the five-membered ring E. Among the reasons for preferring structure I, Spring has suggested<sup>5</sup> that it

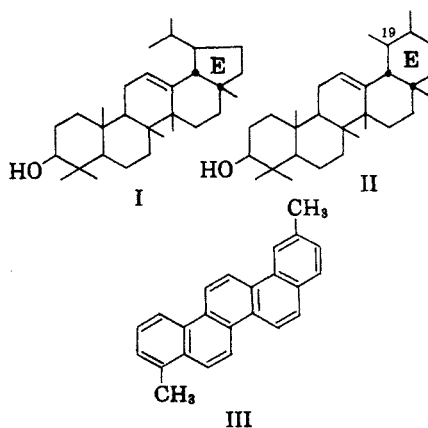
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(2) Alfred P. Sloan Predoctoral Fellow in Chemistry, 1956–1957.

(3) J. M. Beaton, F. S. Spring, R. Stevenson, and W. S. Strachan, *J. Chem. Soc.*, 2610 (1955).

(4) A. Meisels, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1075 (1949); A. Meisels, R. Rügge, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **38**, 1298 (1955); A. Melera, D. Arigoni, A. Eschenmoser, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **39**, 441 (1956).

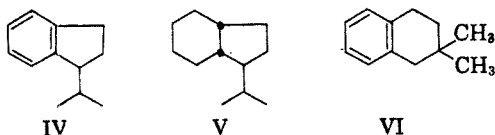
(5) F. S. Spring, private communication.



more satisfactorily explains the formation of 2,9-dimethylpicene (III) on selenium dehydrogenation

of  $\alpha$ -amyrin since expansions of five-membered rings under these circumstances are well known.<sup>6</sup> Conversely, the loss during dehydrogenation of the *non-quaternary* C<sub>13</sub> methyl in structure II has but few analogies in the literature and some of these are not well authenticated.<sup>7</sup>

We decided to test the validity of Spring's suggestion by investigating the dehydrogenation of 1-isopropylindan (IV) and its perhydro derivative (V). The latter compound approximates very closely the geometry and environment of rings D and E of  $\alpha$ -amyrin and was therefore of particular interest in connection with this structural problem. However, since V was first converted to IV during dehydrogenation (as expected), most of our experiments



were performed on the more readily available indan (IV).

Both hydrocarbons (IV and V) were relatively stable to selenium at temperatures below 350° but were dehydrogenated when heated to 380–390° with an equal weight of the catalyst. The rather complex mixture that resulted was best purified by chromatography on alumina followed by fractional distillation of the more volatile components. In this way it was possible to isolate as the main product (*ca.* 40% yield) from IV a hydrocarbon which was originally thought to be unreacted isopropylindan. Various physical properties were significantly different, however, and further investigation showed that the hydrocarbon was in reality the *expanded* product, 2,2-dimethyltetralin (VI) (see Figs. 1 and 2). Although no isopropylindan (IV) was recovered from the reaction mixture *per se*, its presence in small amounts (<7%) was inferred by the isolation of 1-indanone from the distillation residues. Since a fine stream of air had been bubbled through the flask during this distillation, the indan (IV) had apparently been completely oxidized to indanone and isopropyl alcohol, although the latter was not isolated.

In a somewhat smaller yield (4%) we were able to isolate and characterize  $\beta$ -methylnaphthalene, the product of subsequent dehydrogenation of VI. The low yields were not unexpected in view of the reported stability of VI to dehydrogenation.<sup>8</sup> The formation of both VI and  $\beta$ -methylnaphthalene

from IV (and V) is significant in that it establishes a precedent for the dehydrogenation of I to III although the high temperatures involved obviously reduce the reliability of the results for structural purposes.

In addition to the compounds mentioned above, there was isolated a very small amount of a crystalline hydrocarbon, m.p. 146–148°, whose ultraviolet absorption spectrum and analysis indicated that it was tetracyclic in nature. The low yield of this product has made complete structural studies impractical to date although we have tentatively assigned to the hydrocarbon a dimethylchrysene structure. The compound is obviously a result of rather deep-seated rearrangements and recombinations of the starting material and its formation emphasizes the caution that must be observed in the interpretation of dehydrogenation data in structural studies.

#### EXPERIMENTAL<sup>9</sup>

*1-Isopropylideneindan.* To the Grignard reagent prepared from 25.8 g. (0.21 mole) of isopropyl bromide and 7.2 g. (0.22 mole) of magnesium in 50 ml. of anhydrous ether was added, over a period of one hour at 5°, a solution of 27.7 g. (0.21 mole) of 1-indanone in 50 ml. of benzene. The reaction mixture was heated under reflux for two hours and worked up in the usual fashion to afford 25.0 g. (73%) of 1-isopropylideneindan as a pale yellow oil, b.p. 99–100° (2 mm.),  $n_D^{20}$  1.5533. Lit.<sup>10</sup> b.p. 133–135° (17 mm.).

*1-Isopropylindan (IV).* A solution of 25.0 g. (0.16 mole) of 1-isopropylideneindan in 250 ml. of 95% ethanol was hydrogenated at 3-atm. pressure in the presence of 0.72 g. of platinum oxide catalyst to afford 22.4 g. (89%) of 1-isopropylindan as a colorless mobile oil, b.p. 92–94° (9 mm.),  $n_D^{20}$  1.5205,  $d_4^{20}$  1.9480. Lit.<sup>11</sup> b.p. 98–110° (17 mm.).

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>: C, 89.93; H, 10.07. Found: C, 90.18; H, 10.16.

*1-Isopropylhydrindan (V).* A solution of 25.0 g. (0.16 mole) of 1-isopropylideneindan in 200 ml. of glacial acetic acid containing 1.6 g. of platinum oxide catalyst was hydrogenated at 4 atm. of pressure. The usual work-up gave 20.3 g. (78%) of *cis* 1-isopropylhydrindan (V) as a colorless mobile oil, b.p. 84–85° (5 mm.),  $n_D^{20}$  1.4740,  $d_4^{20}$  1.8746; M<sub>R</sub>D (calcd.) 53.72, M<sub>R</sub>D (obs.) 53.44.

*Anal.* Calcd. for C<sub>12</sub>H<sub>22</sub>: C, 86.66; H, 13.34. Found: C, 86.38; H, 13.36.

*Dehydrogenations. a. 1-Isopropylindan (IV).* A mixture of 14.1 g. (0.088 mole) of the indan (IV) and 14.0 g. of finely powdered selenium was heated in a sealed tube for 42 hr. at 385–400°. The contents were taken up in 30 ml. of hexane and chromatographed on 200 g. of acid-washed alumina (pH 3.3). After 400 ml. of hexane had been collected there was obtained on evaporation 7.2 g. of a colorless mobile liquid,  $n_D^{25}$  1.5198. This material was fractionally distilled to afford 0.35 g. of a forerun, b.p. 95–100° (12.5 mm.), 4.60 g. of the main fraction, b.p. 101.5–103° (12.5 mm.),  $n_D^{27}$  1.5183 and 0.93 g. of residue,  $n_D^{27}$  1.5384. The main fraction was shown by independent synthesis to be 2,2-dimethyl-

(6) L. Ruzicka and E. Peyer, *Helv. Chim. Acta*, **18**, 676 (1935); N. D. Zelinsky, *Ber.*, **58**, 2755 (1925); N. D. Zelinsky, I. Titz, and L. Fatejeu, *Ber.*, **59**, 2580 (1926); C. D. Nenitzescu and E. Cioranescu, *Ber.*, **69**, 1040 (1936).

(7) The few examples are discussed by W. Cocker, B. E. Cross, and J. McCormick, *J. Chem. Soc.*, 72 (1952).

(8) G. R. Clemo and H. G. Dickenson, *J. Chem. Soc.*, 255 (1937).

(9) Melting points and boiling points are both uncorrected. Ultraviolet absorption spectra were measured on a Beckman model DK automatic recording spectrophotometer. Analyses are by Schwarzkopf Labs., Woodside 77, N. Y.

(10) C. Courtot, *Ann. chim.*, 61 (1916).

(11) Ref. 10, p. 84.

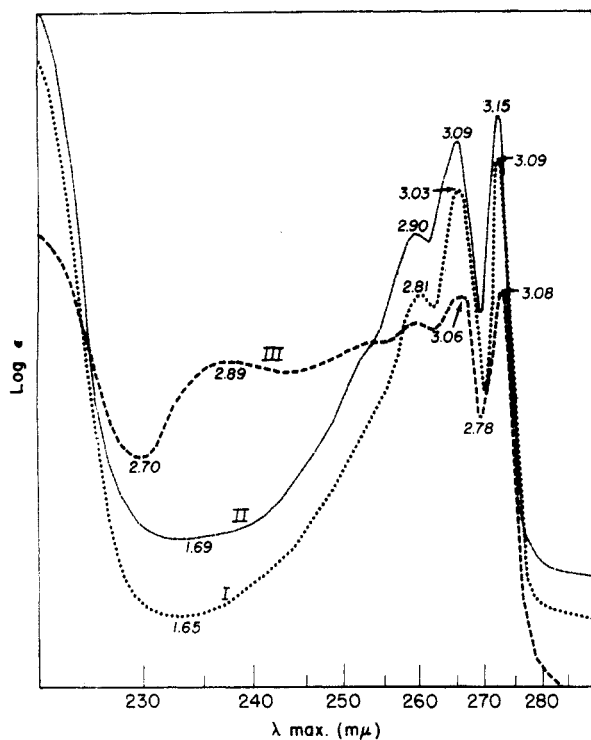


Fig. 1. Curve I: 2,2-Dimethyltetralin (VI) from the dehydrogenation of 1-isopropylindan (IV). Curve II: Synthetic 2,2-dimethyltetralin (VI).<sup>12</sup> Curve III: 1-Isopropylindan (IV). (The numbers refer to the log  $\epsilon$  values as the log  $\epsilon$  scale is arbitrary)

tetralin (VI).<sup>12</sup> The residue from the distillation possessed very strong infrared absorption in the aromatic carbonyl region and was identified as 1-indanone by formation of its

(12) Prepared according to the method of Clemo and Dickenson, ref. 8, who record b.p. 104° (12 mm.). S. C. Sengupta, *J. Prakt. Chem.*, **151**, 82 (1938), reports b.p. 123° (34 mm.) and  $n_D^{25}$  1.5185. Our synthetic material had b.p. 101.5–102.5° (12 mm.) and  $n_D^{25}$  1.5190.

*Anal.* Calcd. for  $C_{12}H_{16}$ : C, 89.93; H, 10.07. Found: C, 89.98; H, 10.10.

Although these values are very similar to those for isopropylindan (IV), the ultraviolet (Fig. 1) and the infrared (Fig. 2) absorption spectra of the two compounds are significantly different (note especially the presence of peaks at 10.30 and 13.85  $\mu$  in IV (curve III, Fig. 2) that are missing in curves I and II).

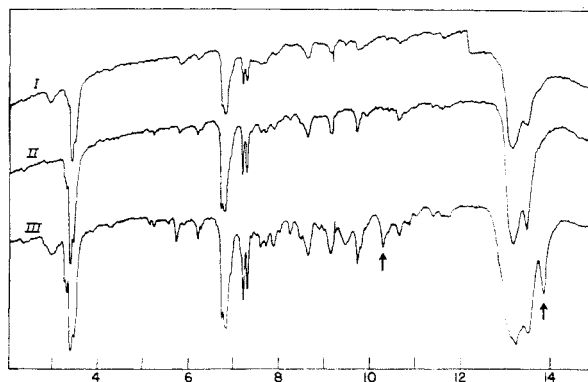


Fig. 2. Curve I: 2,2-Dimethyltetralin (VI) from the dehydrogenation of 1-isopropylindan (IV). Curve II: Synthetic 2,2-dimethyltetralin (VI).<sup>12</sup> Curve III: 1-Isopropylindan (IV)

characteristic red 2,4-dinitrophenylhydrazone, m.p. 263–264°.

The addition of 30% benzene to the hexane eluent afforded 0.51 g. of a colorless, viscous liquid,  $n_D^{20}$  1.6062. The ultraviolet absorption spectrum of this material was superimposable on that of  $\beta$ -methylnaphthalene, and positive identification was made through the *picrate*, m.p. 114–115°, undepressed on admixture with an authentic sample, m.p. 115–116°.

Pure benzene eluted 0.32 g. of a yellow semisolid that was rechromatographed on 10 g. of acid-washed alumina to afford 0.25 g. of a pale yellow oil. On trituration with hexane, this oil deposited 0.13 g. of a hydrocarbon as pale yellow needles, m.p. 135–137°. Two recrystallizations from alcohol afforded 30 mg. of the unknown as colorless needles, m.p. 146–148°.

*Anal.* Calcd. for  $C_{20}H_{16}$ : C, 93.71; H, 6.29. Found: C, 93.67; H, 6.26.

The ultraviolet absorption spectrum in 95% alcohol was reminiscent of chrysene:  $\lambda_{max}$  (log  $\epsilon$ ): 267 m $\mu$  (4.9), 294 (3.8), 307 (2.9), and 321 (2.7) but lacked the fine structure between 280 and 320 m $\mu$  usually associated with this ring system.

The addition of ether to the eluting solvent afforded 1.3 g. of a yellow viscous oil, the properties of which have not been investigated.

*b. 1-Isopropylhydrindan (V).* When the perhydrogenated indan (V) was dehydrogenated as described above, the results were essentially the same as those reported for the indan (IV). In the temperature range 330–360°, however, V was dehydrogenated in good yield to isopropylindan (IV) but subsequent reactions did not occur until the temperature was raised to 390–400°.

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