The yields and purity of the crude disulfides were determined by weight and analytical methods.[6,7] Their disulfide and thiol contents were determined and the results are shown in Table I, along with melting points of the crude and purified disulfides.

Oxidation of Benzenethiol.—Two-tenths of a mole of benzenethiol was dissolved in 100 ml. of dimethyl sulfoxide and the solution was maintained at 85 ± 1°. Samples were removed at various intervals and analyzed for thiol and disulfide content.[6,7] The following conversions of thiol to disulfide were found: 85% after 30 min., 92.4% after 1 hr., 96.7% after 2 hr., 98.3% after 4 hr., and 98.9% after 6 hr.

Oxidation of Benzenethiol in the Absence of Air.—A 250-ml. three-necked flask was equipped with a magnetic stirrer, thermometer, a nitrogen gas inlet tube, and an outlet to a trap cooled in Dry Ice. The flask was charged with 11 g. (0.1 mole) of benzenethiol and 50 ml. of dimethyl sulfoxide under a blanket of nitrogen and the solution was heated with stirring at 80° for 18 hr. with a continuous flow of nitrogen through the system. The disulfide isolated in almost theoretical yield by procedure A weighed 10.8 g. and melted at 61–62°.

The liquid condensed in the Dry Ice trap separated in two layers. The upper one proved to be the expected dimethyl sulfide by infrared spectrum and boiling point; the lower layer was mainly water.

Similar results were obtained when the experiment was carried out with α-toluenethiol with the by-products being identified as dimethyl sulfide and water. The disulfide was obtained in 88% yield with m.p. 71–72°.

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The Jacobsen Rearrangement of 6-Methyl-7-propyltetralin[1]

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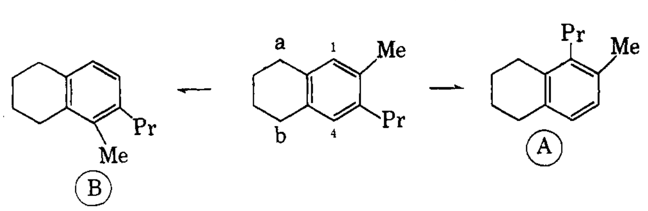
Received May 28, 1963

The Jacobsen rearrangement of 6-methyl-7-propyltetralin was initially investigated by Smith and Lo[2] who reported that a low yield (25%) of 6-methyl-5-propyltetralin was obtained. This result quite apparently was a surprise to the authors since they commented at some length on the mode of formation of this product. Clearly this is a result of considerable mechanistic implication. The starting material contains four alkyl substituents on the benzene ring which are *effectively all nonequivalent*. However, the differences among these four groups are quite subtle, particularly with respect to the *a priori* migratory aptitudes of the two alicyclic groups a and b. If A alone is the product either the propyl group migrates to C-1 or a migrates to C-4 or both occur. Since the product obtained is not the thermodynamically most stable one, it is appropriate to ask that the mechanism explain why the propyl group and/or a can migrate while the methyl and/or b cannot. This entirely unexpected migratory specificity prompted our interest in this case.



We have prepared a sample of 6-methyl-7-propyltetralin according to the procedure of Smith and Lo.[2] The hydrocarbon obtained in this way is impure and careful fractionation showed that it contained at least four other hydrocarbons. A sample of the purified 6-methyl-7-propyltetralin which was homogeneous as shown by gas partition chromatography analysis was subjected to the Jacobsen rearrangement. The hydrocarbon product was isolated in 28–30% yield and was shown to contain at least eleven substances. We have identified by comparison g.p.c. analysis five of these as 6-methyltetralin, 6-propyltetralin, starting material, 6-methyl-5-propyltetralin, and 5-methyl-6-propyltetralin. These latter two make up the major portion of the hydrocarbon product isolated, and are present in equivalent amounts. Thus, whatever the combination of migrating groups may be, it is now clear that we can derive no information about migratory preference from this experiment.

In the course of the synthesis of the starting material and of comparison samples of 6-methyl-5-propyl- and 5-methyl-6-propyltetralins we have had occasion to examine the products of partial reduction of several naphthalenes substituted in one ring. The reduction of β-methylnaphthalene gave 80% 6-methyltetralin, 10% of 2-methyltetralin, and 10% of methyldecalins. Similarly the reduction of 1-methyl-2-propylnaphthalene and of 1-propyl-2-methylnaphthalene gave about 70% of the product with the hydrogen added to the nonsubstituted ring. These results are in good accord with the findings of Hipsher and Wise,[3] though they used copper chromite while we employed Raney nickel.

Experimental

6-Methyltetralin.—2-Methylnaphthalene was reduced over Raney nickel according to the procedure of Fieser and Jones.[4] The product, b.p. 226–227°, $n^{20}\mathrm{D}$ 1.5350, was obtained in 70% yield. G.p.c. at 200° on a 6-ft. Carbowax 1500 column showed this to be a mixture containing an 8:1:1 ratio of two tetralins and isomeric decalins, respectively. Fractional distillation on a 30-in. Podbielniak Heli-Grid semimicro column gave a product, b.p. 130° (48 mm.), $n^{19}\mathrm{D}$ 1.5341, $\bar{\nu}$ 800, 825 cm.$^{-1}$, 97% pure by g.p.c.

6-Methyl-7-propionyltetralin.—Samples of 6-methyltetralin (prepared as described above or by Clemmensen reduction of 7-methyl-1-tetralone[5]) were acylated according to the procedure of Smith and Lo.[2] The ketone was obtained as a clear oil, b.p. 150° (1.25 mm.), $n^{23}\mathrm{D}$ 1.5490–1.5510, in 70–84% yield, showing on g.p.c. analysis a broad peak partially separated into two peaks, but not sufficiently resolved to permit estimation of amounts of the components.

6-Methyl-7-propyltetralin.—Clemmensen reduction of 6-methyl-7-propionyltetralin as described by Smith and Lo[2] gave in 85–92% yield an oil, b.p. 94–99° (0.8 mm.), $n^{20}\mathrm{D}$ 1.5188–1.5284. This material showed two nearly resolved peaks using g.p.c., showing approximately a 5:1 ratio. The hydrocarbon was carefully fractionated on a Podbielniak Mini-Cal column to give 16 fractions. Fractions 11–16, b.p. 124° (6 mm.), $n^{20}\mathrm{D}$ 1.5294–1.5295, $\bar{\nu}$ 865 cm.$^{-1}$ (m), were uniform as indicated by g.p.c.

Rearrangement of 6-Methyl-7-propyltetralin.—A 21.0-g. (0.11 mole) sample of the pure hydrocarbon was mixed with 125 ml. of concentrated sulfuric acid and rearranged as described by Smith and Lo.[2] Hydrolysis of the product with superheated steam at

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[1] Grateful acknowledgment is made to the Atomic Energy Commission (AEC AT (45-1) 352) and the general research grants of Oregon State University for partial financial support of this work. David Lini is indebted to the National Science Foundation for support as an NSF Undergraduate Research Participant during the summer of 1960.

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155° gave 6.7 g. (32%) of a light oil, b.p. 60–66° (0.2 mm.), n^{20}D 1.5443. Analysis by g.p.c. showed 11 peaks. Two peaks, retention times 52.5 and 61.0 min., respectively, made up 90–95% of the total. These were identified by internal comparison as 6-methyl-5-propyltetralin and 5-methyl-6-propyltetralin, respectively.

6-Methyl-5-propyltetralin.—A sample (2.0 g.) of 2-methyl-1-propylnaphthalene[6] was hydrogenated at 1100 p.s.i. and 130° in absolute ethanol over Raney nickel. After 12 hr. the hydrogen uptake had virtually ceased. The product was found to consist of two major components and eight minor components by g.p.c. analysis. The largest component, retention time 54.0 min., was purified by g.p.c. and the infrared spectrum showed strong absorption bands at 1600, 1500, and 810 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 89.02; H, 10.62.

6-Propyltetralin.—Tetralin was converted to 6-propionyltetralin and the ketone reduced according to the procedure of Smith and Lo.[2] The 6-propyltetralin, b.p. 61–63° (0.3 mm.), was obtained in 54% yield over-all, and gave a single peak on g.p.c. analysis.

2-Propylnaphthalene.—A mixture of 15.5 g. of 6-propyltetralin and 0.8 g. of 5% palladium on charcoal was heated for 5 hr. at 300° while a slow stream of nitrogen was passed over the reaction mixture. The product isolated by distillation, b.p. 62° (0.1 mm.), was obtained in 80% yield. A boiling point of 130° (12 mm.) is reported.[7] The substance gave a single peak on g.p.c. analysis.

1-Chloromethyl-2-propylnaphthalene.—A mixture of 12 g. (0.07 mole) of 2-propylnaphthalene, 6.5 g. of paraformaldehyde, 18 g. of glacial acetic acid, 12 g. of 85% phosphoric acid, and 65 g. of concentrated hydrochloric acid was stirred vigorously while being heated for 5 hr. on a steam bath. The reaction mixture was diluted with water and extracted with ether. The product boiled at 98–100° (0.025 mm.), n^{21}D 1.6053, 9.3 g. (60%).

Anal. Calcd. for $C_{14}H_{15}Cl$: C, 76.88; H, 6.91. Found: C, 77.17; H, 7.14.

1-Methyl-2-propylnaphthalene.—Nine grams (0.041 mole) of the previous chloromethylation product was treated with hydrogen at 34-p.s.i. initial pressure and 0.6 g. of palladium on charcoal in acetone. The product was isolated by distillation, b.p. 78° (0.3 mm.), n^{25}D 1.5915, in 55–60% yield; lit.[8] n^{25}D 1.5928.

5-Methyl-6-propyltetralin.—A solution containing 1.56 g. of 1-methyl-2-propylnaphthalene in 15 ml. of absolute ethanol was hydrogenated at 130° and 1050 p.s.i. over W-4 Raney nickel.[9] The product was isolated in the normal manner and g.p.c. analysis showed 10 peaks, the major one constituting about 66% of the total. The material responsible for this peak was isolated by repetitive g.p.c., and showed $\bar{\nu}$ 810 cm.$^{-1}$. The amount isolated was insufficient for analysis.

Gas Chromatography.—All the hydrocarbons were analyzed on a Model 154C Perkin-Elmer vapor fractometer using a 6 ft. × 0.25 in. 5% Ucon Polar on Chromosorb column at 200° with helium as carrier gas. The following retention times are representative though the actual times varied about ± 3% in various runs: 6-methyl-7-propyltetralin, 46 min.; 5-methyl-6-propyltetralin, 60 min.; 6-methyl-5-propyltetralin, 54 min.; 1-methyl-2-propylnaphthalene, 102 min. The 6-methyl-7-propionyltetralin was analyzed on an 8 ft. × 0.25 in. 5% Ucon Polar column at 220°.

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An Extention of the Gomberg–Bachmann Pinacol Synthesis

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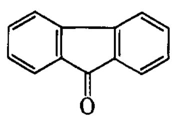
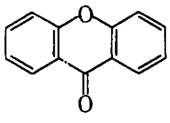
Received June 28, 1963

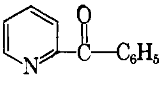
In 1927, Gomberg and Bachmann described the use of a magnesium–magnesium iodide mixture to reduce aromatic ketones to the corresponding pinacols.[2] This technique provided nearly quantitative yields, even in cases such as the reduction of fluorenone (I) and xanthone (II), where the corresponding pinacols had not been obtainable by alternative methods. An apparent limitation of this reaction was noted, however, by Kegelman and Brown, who found that phenyl 2-, 3-, and 4-pyridyl ketones formed insoluble complexes with the magnesium halide.[3] These complexes gave only unchanged starting materials upon hydrolysis. In the case of phenyl 2-pyridyl ketone (III), a 14% yield of the desired pinacol, IV, was obtained by the use of sodium amalgam in aqueous alcohol. We wish to report the successful conversion of III to IV in better than twice this yield by a simple modification of the original Gomberg–Bachmann technique.



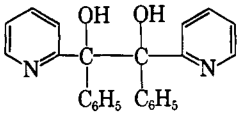
I



II



III



IV

In our initial investigations of this reduction, we obtained negative results similar to those of Kegelman and Brown. A yellow insoluble complex was formed which on hydrolysis yielded the original ketone. With an increased ratio of magnesium iodide to phenyl 2-pyridyl ketone, however, the yellow complex changed to a green precipitate which, on hydrolysis, gave a 38% yield of the pinacol IV.

The need for double the usual amount of magnesium iodide may be explained by assuming that the first half-mole serves to coordinate with the nitrogen of the pyridyl ketone, and that a second half-mole then serves to bring about the actual reduction.

Although we have not studied other examples of this reduction, it would appear that this simple expedient will allow the magnesium–magnesium iodide reductive dimerization to be applied to a wide variety of nitrogen-containing heterocyclic ketones.

Experimental[4]

α,α-Di-2-pyridylhydrobenzoin (IV).—To 5 g. of powdered magnesium (0.21 g.-atom) in 35 ml. of ether and 50 ml. of benzene was added with shaking 14 g. (0.055 mole) of iodine in portions to keep the solution boiling. After complete addition, the mixture was shaken until the liquid was practically colorless. To this mixture was added 18.3 g. (0.1 mole) of phenyl 2-pyridyl ketone dissolved in 30 ml. of benzene. A green precipitate separated which on shaking slowly turned to a yellow solid. The mixture was shaken and heated on a water bath for 1 hr., but no visible change occurred. A small portion of the mixture was withdrawn and hydrolyzed with water. The benzene–ether layer was dried and then evaporated to dryness to give a pale yellow solid, m.p.

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[4] Melting points are corrected.