[Contribution from the Department of Chemistry, University of Rochester]

A STUDY OF THE METHYLATION AND TAUTOMERISM OF 8-METHYLPERINAPHTHENE

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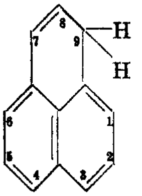
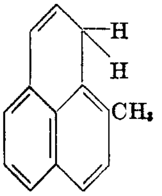
In previous publications (1, 2) general methods were described for the synthesis of perinaphthene and some simple alkyl derivatives. One of the conclusions reached in our previous study was that the perinaphthene nucleus (I) behaves as a unit, making it exceedingly difficult to determine in the case of the substituted perinaphthenes which ring should properly be designated as the *peri* ring. For example, when syntheses designed to give a series of monomethylperinaphthenes having the methyl group located at the 1-, 3-, 7-, and 9-positions, respectively, were carried out, it was discovered that all of these preparations led to the same hydrocarbon which, from its behavior on catalytic reduction, was assigned structure II. Quite evidently, in the case of the simple perinaphthene derivatives, the "extra" hydrogen tautomerizes so readily that only the most stable of the various possible tautomers is isolated.



I



II

Another example of the ease with which tautomerism occurs in these molecules is provided by the alkylation studies on perinaphthene (1). Alkylation of perinaphthene in the cold with phenyllithium and methyl iodide gave a hydrocarbon identical with II, even though in this case the initial product must, of necessity, be 9-methylperinaphthene. In view of this result it appeared to us that the alkylation reaction would be an interesting and useful tool for further defining the nature and ease of tautomerism in simple perinaphthene systems. Successive alkylations of perinaphthene should be possible until a *gem*-dialkyl grouping was formed. In the optimum case, if all of the active hydrogens were replaced, this would mean the introduction of seven alkyl groups.

In the present paper we are reporting the results of such a study using 8-methylperinaphthene (III) as the starting compound. The 8-methyl derivative was chosen in order that the positions taken by incoming groups could be related to a substituent position on the perinaphthene ring. As indicated in the

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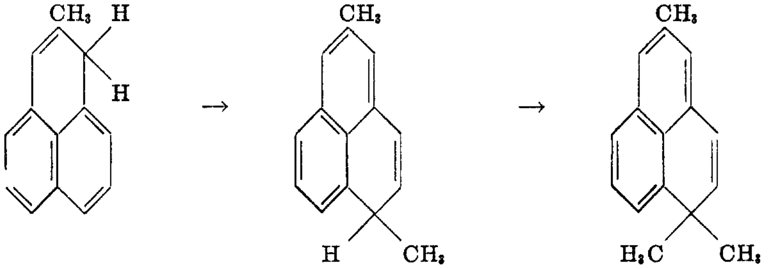
[1] Beaunit Mills Predoctoral Fellow, 1951–1952.

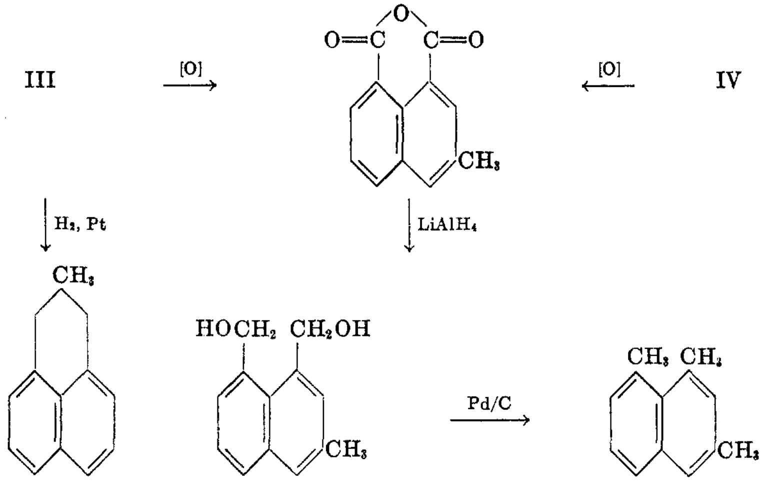
previous discussion, tautomerism of perinaphthenes occurs with such ease that it is not possible to state with certainty the absolute arrangement of double bonds in any of the perinaphthenes isolated. Therefore the desirability of a substituent as a reference point is apparent. Although, for convenience, in the following discussion some perinaphthenes will be named as though the individual arrangement of double bonds were known, it should be recognized that such assignments are tentative.

When 8-methylperinaphthene (III), obtained by the dehydration of 8-methylperinaphthanol-7, was treated with phenyllithium and methyl iodide, there was formed in good yield a dimethylperinaphthene (IV). Likewise, when this product was treated in a similar manner, a second methylation occurred to give a trimethylperinaphthene (V). Attempts to effect a third methylation were unsuccessful and the trimethylperinaphthene (V) was recovered. Since V does not react with phenyllithium to give the deep red color typical of the perinaphthenyl anion, it can be concluded that the second methylation resulted in a *gem*-dimethyl grouping.



III IV V

Although it was clear that a *gem*-dimethyl grouping was formed, the location of the incoming methyl groups remained to be settled. Attempts to decide this question were first directed toward degradation of the substituted perinaphthenes. Since most of the possible trimethylnaphthalenes are known and have been well-described from the work of Ruzicka (3) and Heilbron (4), methods were investigated for degrading IV to a trimethylnaphthalene derivative. In model experiments, it was readily shown that the perinaphthene ring could be degraded to leave two methyl groups at the 1,8-position of the naphthalene ring. Oxidation of perinaphthene with permanganate gave naphthalic anhydride which on reduction with lithium aluminum hydride gave 1,8-bis-(hydroxymethyl)naphthalene. Hydrogenolysis of this over a palladium-on-charcoal catalyst gave 1,8-dimethylnaphthalene. When this reaction sequence was repeated with 8-methylperinaphthene (III), the oxidation product was not the expected naphthalic anhydride but, instead, was 3-methylnaphthalic anhydride, whose structure was established by its ultimate reduction to the known 1,3,8-trimethylnaphthalene. This unexpected result emphasizes again the ease of tautomerization in these systems. The assignment of structure III to the hydrocarbon referred to as 8-methylperinaphthene was based on previous observations that this hydrocarbon is catalytically reduced to 8-methylperinaphthane (VI). It is thus apparent that, in the case of hydrocarbon III, oxidation and reduction preferentially attack different tautomers.

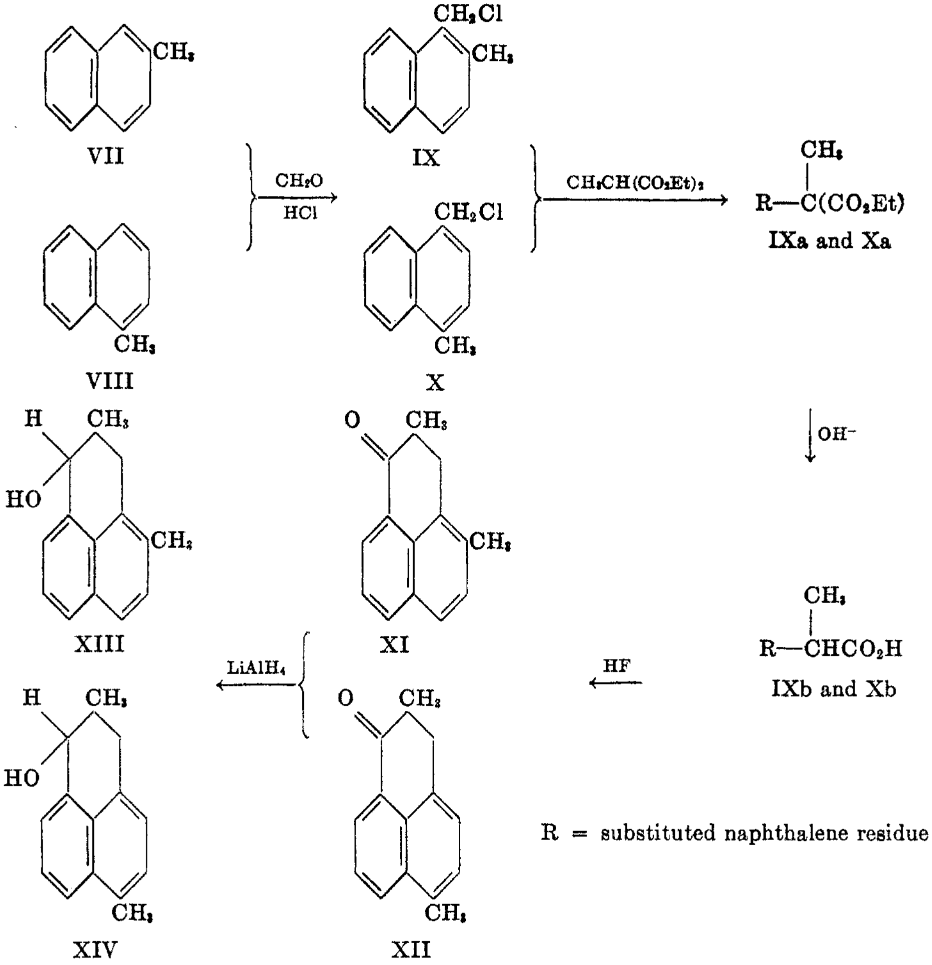


VI

In a similar manner the hydrocarbon IV, obtained by methylation of III, was carried through the same reaction sequence and found to yield 1,3,8-trimethylnaphthalene. From this it is apparent that the oxidation of IV involved the ring holding the newly introduced methyl group and this group must be present at either position 1 or 3 with respect to 8-methylperinaphthene. Unfortunately, this method of degradation does not allow a decision between these two possibilities and so possible methods of synthesizing 1,8- and 1,3-dimethylperinaphthenes were next investigated.

As illustrated, the reaction schemes employed followed closely those used previously for the monomethylperinaphthenes (1, 2). Starting with 2-methylnaphthalene, we were able to obtain 1,8-dimethylperinaphthanone-7 (XI) in an over-all yield of 31% for the four steps. Similarly, 1-methylnaphthalene was converted to 3,8-dimethylperinaphthanone-7 (XII) in an over-all yield of 37%.

The reduction of the perinaphthanones in each instance gave both of the possible racemates of the corresponding perinaphthanols, XIII and XIV. These racemates were carefully separated by fractional crystallization and were separately subjected to dehydration using ethanolic hydrogen chloride. The two racemates corresponding to structure XIII gave the same crystalline dimethylperinaphthene (XV) which was readily shown to be different from the hydrocarbon IV obtained by methylation of 8-methylperinaphthene. On the other hand, dehydration of the two racemates corresponding to XIV gave dimethylperinaphthenes whose *sym*-trinitrobenzene derivatives were identical, both with each other and with the *sym*-trinitrobenzene derivative of IV. Their identity is based on the melting point behavior of these derivatives and a comparison of their infrared spectra.[2] This establishes the fact that methylation of 8-methylperinaphthene occurred at the 3-position.



When the dimethylperinaphthene (XVI), obtained by dehydration of XIV, was reduced catalytically it gave a dihydro derivative (XVII) which was characterized as its trinitrobenzene derivative. When 3,8-dimethylperinaphthanol-7 was subjected to hydrogenolysis, it was found that the resulting 3,8-dimethylperinaphthane (XVIII) had rather different properties from those of XVII. Actually, the properties found for XVII are in good agreement with those reported by Buu-Hoï and Cagniant (5) for 1,5-dimethylperinaphthane and structure XVII has been assigned on the assumption that these two hydro-

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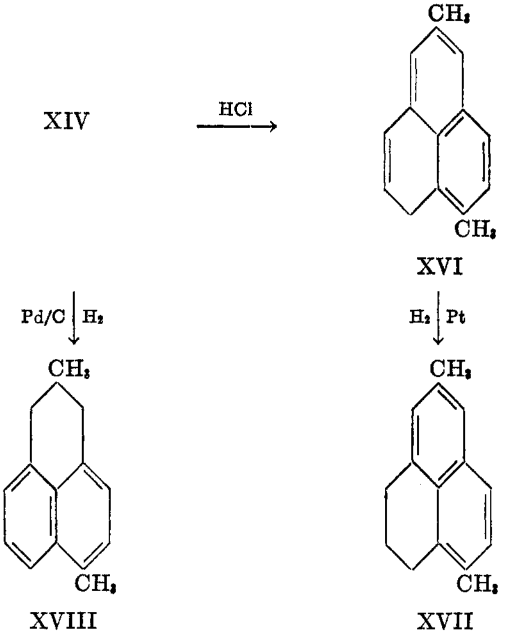
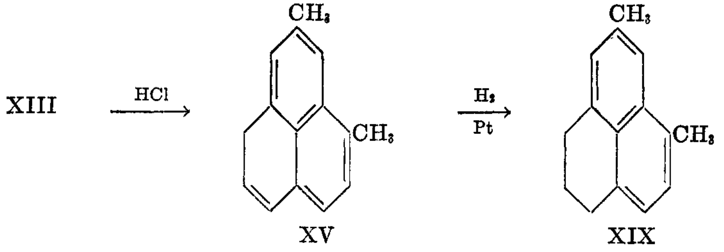
[2] The comparison of these perinaphthenes has been made on the trinitrobenzene derivatives rather than the hydrocarbons themselves, since these were isolated either as oils or as low-melting solids having a wide melting point range.

carbons are identical. It is of interest that in this case also the dimethylperinaphthene behaves as a mixture of tautomers of which structure XVI reacts preferentially on catalytic reduction and structure IV reacts preferentially under the conditions of methylation.



For completeness, the dimethylperinaphthene (XV), obtained from the dehydration of 1,8-dimethylperinaphthanol-7, was likewise reduced catalytically to the corresponding perinaphthane derivative. The properties of this hydrocarbon are not in accord with those of 1,8-dimethylperinaphthane or any of the other known dimethylperinaphthane derivatives. By analogy with the previous series, this dimethylperinaphthane has been tentatively assigned structure XIX and the intermediate dimethylperinaphthene has been given structure XV. The 1,8-dimethylperinaphthane used for comparison was prepared by the Wolff-Kishner reduction of 1,8-dimethylperinaphthanone-7 (XI) and its properties were in agreement with those previously recorded for this compound by Buu-Hoï and Cagniant (6).



EXPERIMENTAL[3]

Methylation of 8-methylperinaphthene (III). To a solution of 1.2 g. of 8-methylperinaphthene (2) in 25 ml. of ether there was added dropwise with stirring 8 ml. of a 0.95 *M* ethereal solution of phenyllithium. The mixture became blood-red in color, and when a solution of 1.0 g. of methyl iodide in 20 ml. of ether was added dropwise with stirring, the color was discharged. The ether solution was then washed with water, dried, and concentrated. The residual oil decomposed on attempted distillation and so it was purified by chromatography over alumina using pentane as solvent. Concentration of the pentane eluate gave 1.11 g. (87%) of a colorless oil, n_D^{22} 1.6525.

Anal. Calc'd for $C_{15}H_{14}$: C, 92.74; H, 7.26.
Found: C, 92.38; H, 7.09.

This compound rapidly decomposed on exposure to the atmosphere and could not be stored, even under nitrogen, for more than a few hours. On treatment with a solution of *sym*-trinitrobenzene in ethanol it gave dull red needles, m.p. 122° dec. The melting point behavior of this derivative was very characteristic in that sharply at 122° the material decomposed explosively. In common with past experience in this field, the T.N.B. derivative underwent dissociation to some extent on recyrstallization from ethanol and was not readily obtainable analytically pure.

Anal. Calc'd for $C_{21}H_{17}N_3O_6$: C, 61.91; H, 4.21.
Found: C, 62.88; H, 4.44.

Dimethylation of 8-methylperinaphthene (III). A solution of 2.0 g. of perinaphthene in 50 ml. of ether was treated with 13 ml. of a 0.95 *M* ethereal solution of phenyllithium. After the addition of 1.65 g. of methyl iodide in 20 ml. of ether, the blood-red color of the solution was discharged. A second addition of 13 ml. of a 0.95 *M* ethereal solution of phenyllithium caused the blood-red color to be regenerated, and this was again discharged by adding a solution of 1.65 g. of methyl iodide in 20 ml. of ether. As before, the ethereal solution was then washed with water, dried and concentrated. The residual oil was purified by dissolving it in pentane and passing it over alumina. Concentration of the pentane eluate gave 2.2 g. (95%) of a pale yellow oil, n_D^{22} 1.6478.

Anal. Calc'd for $C_{16}H_{16}$: C, 92.26; H, 7.74.
Found: C, 91.99; H, 7.74.

This product is considered to be 5,9,9-trimethylperinaphthene (V). Since no satisfactory derivative could be prepared directly from the hydrocarbon, it was characterized by reducing it to the corresponding perinaphthane. A mixture containing 1.9 g. of 5,9,9-trimethylperinaphthene in 25 ml. of ethanol and 200 mg. of Adams catalyst was subjected to hydrogenation at room temperature and atmospheric pressure. One mole of hydrogen was readily absorbed. After removal of the catalyst and solvent, the residual oil was taken up in pentane and purified by chromatography over alumina. This gave 1.85 g. (95%) of a colorless oil, n_D^{22} 1.6098. This product is considered to be 2,7,7-trimethylperinaphthane.

Anal. Calc'd for $C_{16}H_{18}$: C, 91.37; H, 8.63.
Found: C, 91.47; H, 8.71.

The *2,4,7-trinitrofluorenone* derivative of 2,7,7-trimethylperinaphthane readily formed and was obtained, after recrystallization from an ethanol-acetone mixture, as deep maroon needles, m.p. 156.5–158.5°.

Anal. Calc'd for $C_{29}H_{23}N_3O_7$: C, 66.28; H, 4.38.
Found: C, 66.56; H, 4.49.

Attempted trimethylation of 8-methylperinaphthene (III). When a solution of the dimethylation product (V) in ether was treated with phenyllithium, it no longer developed the blood-red color characteristic of the perinaphthenyl anion. Thus, it was concluded that a *gem*-dimethyl grouping was formed. In order to establish this further, a solution of 8-methylperinaphthene in ether was subjected to successive methylations as described in the preceding experiment. After the second addition of methyl iodide, a third addition

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[3] Analyses by Miss Claire King. All melting points are corrected.

of phenyllithium was made. The mixture developed a faint pink color and, when the ethereal solution containing the third mole of methyl iodide was added, the color was discharged completely after one drop of the solution had been added. The reaction mixture was worked up as before and the product was subjected directly to hydrogenation. Treatment of the reduction product with 2,4,7-trinitrofluorenone in ethanol gave in high yield a crystalline derivative which was shown by a mixture melting-point determination to be identical with the 2,4,7-trinitrofluorenone derivative of 2,7,7-trimethylperinaphthane. There was no evidence of the formation of any more highly methylated material.

Lithium aluminum hydride reduction of naphthalic anhydride. A suspension of 2.00 g. of naphthalic anhydride in 400 ml. of benzene was treated with 140 ml. of a 0.3 *M* ethereal solution of lithium aluminum hydride, and the resulting mixture was boiled under reflux for three hours. The excess reagent was then decomposed by the addition of water and the precipitate of metallic hydroxides was dissolved by addition of concentrated alkali containing Rochelle salts. The organic layer was separated and, on concentration, deposited 1.55 g. (81%) of white needles, m.p. 155–156°. The melting point recorded for 1,8-bis-(hydroxymethyl)naphthalene is 152–154° (7).

Hydrogenolysis of 1,8-bis-(hydroxymethyl)naphthalene. A solution of 250 mg. of 1,8-bis-(hydroxymethyl)naphthalene in 20 ml. of methanol was subjected to hydrogenation at room temperature and atmospheric pressure in the presence of 250 mg. of a freshly prepared 10% palladium-on-charcoal catalyst (8). The expected quantity of hydrogen was absorbed in 28 minutes. After removal of the catalyst, the solution was concentrated and then diluted with water. This caused the separation of 130 mg. (60%) of white plates, m.p. 62.5–64° [the recorded m.p. of 1,8-dimethylnaphthalene is 63° (9a)]. A *picrate* was prepared and obtained from ethanol as orange needles, m.p. 154.5–155.5° [lit. gives 148° (9a) and 156° (9b), as the melting point of the picrate of 1,8-dimethylnaphthalene].

Oxidation of 8-methylperinaphthene (III). To a solution of 100 mg. of 8-methylperinaphthene in acetone there was added dropwise with shaking a solution of 350 mg. of potassium permanganate in acetone. The mixture was warmed for several minutes on a stream-bath until the permanganate color disappeared and then aqueous hydrochloric acid was added to destroy the precipitate of manganese dioxide. The solid remaining after this treatment weighed 70 mg. and melted over a range up to 210°. For purification it was dissolved in alkali, treated with *Norit*, reprecipitated with acid, and finally recrystallized from ethanol. In this way, the oxidation product, 3-methylnaphthalic anhydride, was obtained as white needles, m.p. 239–241°, with softening at 230°. The sample for analysis was further purified by sublimation followed by an additional recrystallization from ethanol and melted at 242.5–243.5°.

Anal. Calc'd for $C_{13}H_8O_3$: C, 73.58; H, 3.80.
Found: C, 73.33; H, 3.55.

In preliminary experiments other methods of oxidation were investigated. When 400 mg. of 8-methylperinaphthene was oxidized using sodium dichromate in glacial acetic acid, following the procedure described previously for converting perinaphthene to perinaphthenone (1), it was possible to isolate 380 mg. of an orange oil. This material had the properties to be expected for 2-methylperinaphthenone in that it was acid-soluble and gave a positive test with 2,4-dinitrophenylhydrazine reagent. Further oxidation of 350 mg. of this oil with potassium permanganate, as described in the preceding experiment, gave 200 mg. of white crystals, m.p. 239°, alone or mixed with the previous sample of 3-methylnaphthalic anhydride.

3-Methyl-1,8-bis-(hydroxymethyl)naphthalene. When 530 mg. of 3-methylnaphthalic anhydride (from the oxidation of 8-methylperinaphthene) was reduced with lithium aluminum hydride in the same manner described previously for naphthalic anhydride, there was obtained 339 mg. (67%) of white crystals, m.p. 138–141°. Recrystallization of a sample from benzene afforded white needles, m.p. 143–144°.

Anal. Calc'd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98.
Found: C, 77.34; H, 6.76.

Hydrogenolysis of 3-methyl-1,8-bis-(hydroxymethyl)naphthalene. A solution of 260 mg. of 3-methyl-1,8-bis-(hydroxymethyl)naphthalene in 20 ml. of methanol containing 260 mg. of a 10% palladium on charcoal catalyst was subjected to hydrogenation at room temperature and atmospheric pressure. After the calculated quantity of hydrogen had been absorbed (22 min.), the catalyst and solvent were removed. The residual oil was divided into two portions, one of which was treated with ethanolic picric acid and the other was treated with ethanolic styphnic acid. The *styphnate* was obtained as deep yellow needles, m.p. 137–138° [lit. (3) gives 138° for the m.p. of 1,3,8-trimethylnaphthalene styphnate]; whereas the *picrate* was obtained as orange needles, m.p. 124–125° [lit. (4) gives 125° for the m.p. of 1,3,8- trimethylnaphthalene picrate]. A sample of the styphnate derivative was dissolved in pentane and passed over alumina. Concentration of the eluate gave white plates which, after recrystallization from methanol, melted at 48.0–48.5° [lit. (4) gives 48° for the m.p. of 1,3,8-trimethylnaphthalene].

Degradation of the methylation product (IV). A 600-mg. sample of hydrocarbon IV, the methylation product from 8-methylperinaphthene, was oxidized with potassium permanganate in acetone following the procedure described for the oxidation of 8-methylperinaphthene. The cream-colored solid so produced weighed 300 mg. and melted over a range up to 210°. Since it is difficult to obtain samples of naphthalic anhydride derivatives that melt sharply and are useful for comparison, the oxidation product was reduced directly with lithium aluminum hydride as previously described. This gave 155 mg. (55%) of white needles, m.p. 135–138°. A sample, after recrystallization from benzene, melted at 142–145° and on admixture of a sample of 3-methyl-1,8-bis-(hydroxymethyl)naphthalene showed no depression of melting point. Also, the infrared spectrum of this sample was identical with that of 3-methyl-1,8-bis-(hydroxymethyl)naphthalene.

1,8-Dimethylperinaphthanone-7 (XI). (*a*) *1-Chloromethyl-2-methylnaphthalene* (IX). This was prepared according to the procedure of Angyal, *et al.* (10) and was obtained as white crystals, m.p. 57–60°, in 65% yield.

(*b*) *Ethyl α-carbethoxy-β-(2-methyl-1-naphthyl)isobutyrate* (IXa). The reaction of 1-chloromethyl-2-methylnaphthalene with diethyl methylmalonate was carried out following the general procedure used by Fieser and Novello (11) for similar alkylations. The diester (IXa) was obtained in 71% yield as a pale yellow oil; b.p. 183–187° at 1.5 mm., n_D^{20} 1.5513. These properties are in agreement with those reported previously by Buu-Hoï and Cagniant (6) for this compound.

(*c*) *β-(2-Methyl-1-naphthyl)isobutyric acid* (IXb). Saponification and decarboxylation of IXa was accomplished by heating it for a long period of time with a solution of potassium hydroxide in aqueous ethanol. Buu-Hoï and Cagniant (6), who prepared this acid previously, described it as a viscous oil. Distillation of our sample gave in 72% yield a glass, b.p. 180° at 1 mm., which, on treatment with hot cyclohexane, crystallized to give white needles, m.p. 81–82°, with liquid crystals clearing at 89–89.5°.

Anal. Calc'd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07.

Found: C, 79.20; H, 7.10.

A sample of IXb was converted to the corresponding amide which, after crystallization from benzene, melted at 168.5–170°. Buu-Hoï and Cagniant (6) give 169° as the m.p. of this amide.

(*d*) *1,8-Dimethylperinaphthanone-7* (XI). A 10.0-g. sample of β-(2-methyl-1-naphthyl)-isobutyric acid was dissolved in 100 ml. of anhydrous hydrogen fluoride and the mixture was left at room temperature for 3 hours before allowing the excess hydrogen fluoride to evaporate. The residual oil was poured onto cracked ice, extracted with ether, washed with base, and dried. Concentration of the ethereal extract gave 8.5 g. (93%) of yellow crystals, m.p. 77–79°. Recrystallization from methanol afforded yellow needles, m.p. 82–83°. A sample of the ketone was converted to the corresponding *semicarbazone* derivative, which was obtained as white plates, m.p. 200–202°. These properties agree with those given by Buu-Hoï and Cagniant (6).

1,8-Dimethylperinaphthanol-7 (XIII). A solution of 6.4 g. of 1,8-dimethylperinaphthanone-7 (XI) in 20 ml. of ether was added dropwise with stirring to 100 ml. of a 0.1 *M* ethereal solution of lithium aluminum hydride. After the mixture had been heated under reflux for a few minutes, the excess reagent was decomposed by the careful addition of water followed by dilute hydrochloric acid. The ether layer was separated, washed, dried and concentrated. Trituration of the residue with cyclohexane gave 4.6 g. of crystals, m.p. 112–120°. A careful and lengthy fractional crystallization of this material from cyclohexane and then from methanol gave two fractions: (a) white crystals, m.p. 127.5–129.0° and (b) a more soluble compound as white crystals, m.p. 113–114°. A mixture melting-point diagram was prepared and clearly showed that the two samples were different compounds. Both compounds were sensitive toward acids, decolorizing charcoals, and exposure to the atmosphere, and are assumed to be the two racemates possible for 1,8-dimethylperinaphthanol-7.

Anal. Calc'd for $C_{15}H_{16}O$: C, 84.86; H, 7.60.
Found (Racemate A, m.p. 127.5–129.5°): C, 84.86; H, 7.40.
Found (Racemate B, m.p. 113–114°): C, 84.99; H, 7.89.

2,4-Dimethylperinaphthene (XV). (*a*) *Dehydration of Racemate A.* To a solution of 500 mg. of 1,8-dimethylperinaphthanol-7 (Racemate A) in 10 ml. of absolute ethanol there was added 3 ml. of a saturated solution of ethanolic hydrogen chloride. The mixture was boiled under reflux for five minutes, then cooled in a Dry-Ice bath and diluted with water. The solid, which separated, was taken up in pentane and purified by chromatography, first over alumina and then over *Florisil.* Concentration of the pentane eluate *in vacuo* gave 285 mg. of white crystals, m.p. 101–102°. These crystals were extremely unstable and were analyzed immediately.

Anal. Calc'd for $C_{15}H_{14}$: C, 92.74; H, 7.26.
Found: C, 92.44; H, 7.38.

(*b*) *Dehydration of Racemate B.* When a 250-mg. sample of 1,8-dimethylperinaphthanol-7 (Racemate B) was subjected to the same dehydration procedure, it gave 228 mg. (96%) of white crystals, m.p. 99–101°. The properties of these crystals were identical with those obtained in (*a*).

Hydrogenation of 2,4-dimethylperinaphthene (XV). A mixture of 738 mg. of 2,4-dimethylperinaphthene (XV) and 200 mg. of Adams catalyst in ethanol was subjected to hydrogenation at room temperature and atmospheric pressure. After removal of the catalyst and solvent, the residual oil was taken up in pentane and purified by chromatography over *Florisil.* Concentration of the eluate gave 668 mg. (90%) of a colorless oil, n_D^{21} 1.6143.

Anal. Calc'd for $C_{15}H_{16}$: C, 91.78; H, 8.22.
Found: C, 91.57; H, 8.32.

The *sym-trinitrobenzene* derivative of 2,4-dimethylperinaphthene (XIX) was obtained from methanol as yellow needles, m.p. 135–137°.

Anal. Calc'd for $C_{21}H_{19}N_3O_6$: C, 61.61; H, 4.68.
Found: C, 61.93; H, 4.73.

Wolff-Kishner reduction of 1,8-dimethylperinaphthanone-7 (XI). Although Buu-Hoï and Cagniant (6) had previously reported the reduction of 1,8-dimethylperinaphthanone-7 to 1,8-dimethylperinaphthane by the Clemmensen procedure, it seemed desirable to repeat this reduction by another method in view of our past experience (2) that Clemmensen reductions are not reliable in the case of perinaphthanones. However, when a sample of 1,8-dimethylperinaphthanone-7 was subjected to the Wolff-Kishner reduction following Huang-Minlon's modification (12), there was obtained an oil which was converted directly to its *sym-trinitrobenzene* derivative. This was obtained from cyclohexane as yellow needles, m.p. 145–146°. This is in agreement with and thus confirms Buu-Hoï and Cagniant's preparation of 1,8-dimethylperinaphthane.

3,8-Dimethylperinaphthanone-7 (XII). (*a*) *1-Chloromethyl-4-methylnaphthalene* (X). Following the procedure of Angyal, *et al.* (10), we were able to obtain 1-chloromethvl-4-methylnaphthalene as white crystals, m.p. 60–63°, in 57% yield.

(*b*) *Ethyl α-carbethoxy-β-(4-methyl-1-naphthyl)isobutyrate* (Xa). The reaction of 1-chloromethyl-4-methylnaphthalene with diethyl methylmalonate was carried out according to the general procedure given by Fieser and Novello (11). The diester (Xa) was obtained in 81% yield as a colorless oil; b.p. 172° at 0.2 mm., n_D^{20} 1.5488.

Anal. Calc'd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37.
Found: C, 73.17; H, 7.42.

(*c*) *β-(4-Methyl-1-naphthyl)isobutyric acid* (Xb). The diester (Xa) was saponified by heating it with a solution of potassium hydroxide in aqueous ethanol and decarboxylation was effected by distillation of the product. The hydrolysis was difficult to complete and, unless the diester (Xa) were heated with alkali for long periods of time, only partial saponification occurred. From 124 g. of Xa there was obtained, after distillation, 65 g. (75%) of a glass which crystallized on trituration with hot cyclohexane. Although these crystals were sufficiently pure for use in the next step, they melted over a range from 77 to 91° and the melting point behavior did not improve on recrystallization. A sample for analysis was prepared by regenerating the acid from its benzylpseudothiuronium salt. This gave white crystals, m.p. 104.5–105.5°, after an additional crystallization from hexane.

Anal. Calc'd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07.
Found: C, 78.54; H, 7.10.

The *benzylpseudothiuronium* salt of Xb was obtained as white crystals, m.p. 146–147°.

Anal. Calc'd for $C_{23}H_{27}N_2O_2$: C, 69.84; H, 6.88.
Found: C, 69.71; H, 6.61.

(*d*) *3,8-Dimethylperinaphthanone-7* (XII). The cyclization of β-(4-methyl-1-naphthyl)-isobutyric acid was carried out using anhydrous hydrogen fluoride in the same manner described previously for 1,8-dimethylperinaphthanone-7. The ketone (XII) was obtained in 93% yield as pale yellow crystals which, after recrystallization from methanol, melted at 109.5–110.5°.

Anal. Calc'd for $C_{15}H_{14}O$: C, 85.68; H, 6.71.
Found: C, 85.39; H, 6.54.

The *2,4-dinitrophenylhydrazone* derivative of XII was obtained after crystallization from a chloroform-ethyl acetate mixture as short red needles, m.p. 273–274° dec.

Anal. Calc'd for $C_{21}H_{18}N_4O_4$: C, 64.61; H, 4.65.
Found: C, 64.75; H, 4.52.

The *oxime* derivative of XII was prepared in aqueous methanol and obtained, after recrystallization, from cyclohexane, as white needles, m.p. 186–188° dec.

Anal. Calc'd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71.
Found: C, 80.27; H, 6.93.

3,8-Dimethylperinaphthanol-7 (XIV). The reduction of 3,8-dimethylperinaphthanone-7 with lithium aluminum hydride was carried out in the same manner as described previously for the preparation of 1,8-dimethylperinaphthanol-7 (XIII). The crude product, obtained in 64% yield, melted over a wide range and so was subjected to a careful fractional crystallization as before. From a mixture of cyclohexane and benzene, two separate fractions were obtained. The higher-melting form (Racemate A) was isolated as white needles, m.p. 153–154.5°. The more soluble form (Racemate B) was isolated as white needles, m.p. 106–108°. Again, a mixture melting-point diagram showed them to be different compounds.

Anal. Calc'd for $C_{15}H_{16}O$: C, 84.86; H, 7.60.
Found (Racemate A): C, 85.04; H, 7.68.
Found (Racemate B): C, 84.69; H, 7.70.

Dehydration of 3,8-dimethylperinaphthanol-7. (*a*) *Dehydration of Racemate A.* When a 450 mg. sample of XIV (Racemate A) was treated with ethanolic hydrogen chloride as described previously, the product, after chromatography over *Florisil*, was obtained from the pentane eluate in 75% yield as white crystals, m.p. 50–67°. Since attempts to obtain a sharper-melting sample by recrystallization or chromatography were unsuccessful, it seems possible that this sample represents a mixture of tautomers related to formula XVI (or IV). As evidenced below, the analytical data indicate that the impurities must be isomeric.

Anal. Calc'd for $C_{15}H_{14}$: C, 92.74; H, 7.26.

Found: C, 92.79; H, 7.40.

The *sym-trinitrobenzene* derivative of XVI formed in high yield from methanol as orange needles, m.p. 122° dec. The melting point behavior was identical with that of the *sym*-trinitrobenzene derivative of IV and a comparison of the infrared spectra of the two samples showed them to be identical. Thus, it would appear that XVI and IV are mixtures of tautomers but that, on treatment with *sym*-trinitrobenzene, both yield the same homogeneous derivative. This is also supported by the experiment on dehydration of Racemate B.

(*b*) *Dehydration of Racemate B.* When a 450-mg. sample of XIV (Racemate B) was subjected to dehydration as previously described, there was obtained, after chromatography over *Florisil*, 328 mg. (79%) of white crystals, m.p. 50–65°, from the pentane eluate. When this was mixed with a sample of the corresponding hydrocarbon from (*a*), there was no change in the melting point behavior. The *sym*-trinitrobenzene derivative was obtained from methanol as orange needles, m.p. 122° dec., and was identical in all respects with that obtained from (*a*).

Hydrogenation of XVI. A sample of 530 mg. of XVI from the preceding experiment was dissolved in methanol and subjected to hydrogenation at room temperature and atmospheric pressure in the presence of 100 mg. of Adams' catalyst. After removal of the catalyst and solvent, the residual oil was taken up in pentane and purified by chromatography over *Florisil*. Concentration of the pentane eluate gave 485 mg. (90%) of a colorless oil, n_D^{21} 1.6149.

Anal. Calc'd for $C_{15}H_{16}$: C, 91.78; H, 8.22.

Found: C, 91.79; H, 8.11.

A *sym*-trinitrobenzene derivative of XVII was obtained from methanol as yellow needles, m.p. 152–153.5°. Buu-Hoï and Cagniant (5) have reported that 1,5-dimethylperinaphthane melts at 43–44° and gives a *sym*-trinitrobenzene derivative, m.p. 153°. Therefore, it can be assumed that XVII is 1,5-dimethylperinaphthane.

Hydrogenolysis of 3,8-dimethylperinaphthanol-7 (XIV). A solution of 450 mg. of 3,8-dimethylperinaphthanol-7 (Racemate A) in methanol was subjected to hydrogenation at room temperature and atmospheric pressure in the presence of 500 mg. of a 10% palladium-on-charcoal catalyst. After removal of the catalyst and solvent, a solid residue remained which was taken up in pentane and chromatographed over *Florisil*. Concentration of the pentane eluate gave 317 mg. (76%) of white crystals, m.p. 49–50°.

Anal. Calc'd for $C_{15}H_{16}$: C, 91.78; H, 8.22.

Found: C, 91.88; H, 8.53.

The *sym-trinitrobenzene* derivative of XVIII was obtained from methanol as yellow needles, m.p. 100–101.5°.

Anal. Calc'd for $C_{21}H_{19}N_3O_6$: C, 61.61; H, 4.68.

Found: C, 61.45; H, 4.77.

SUMMARY

The methylation of 8-methylperinaphthene has been studied and found to proceed to give monomethyl and dimethyl derivatives. Attempts to obtain further methylation failed, presumably due to the formation of a *gem*-dimethyl grouping in the dimethylated derivative. Synthetic and degradative experiments have been carried out which establish that the methylation reaction results in the introduction of a methyl group at the 3- position with respect to the original 8-methylperinaphthene.

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