was removed by filtration. On cooling, the *l*-**menthyl ester of** *d*-*cis*-**2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrophenanthrenacetic acid** precipitated. After four recrystallizations it had a melting point of 111–114°, which was not altered by further recrystallizations; $[\alpha]^{27}D$ +77° (in benzene). This product apparently still contained a small amount of the diastereoisomer but purification at this stage did not improve the melting point. Complete removal of the racemic compound was possible at later stages of the synthesis.

Anal. Calcd. for $C_{29}H_{38}O_4$: C, 77.3; H, 8.5. Found: C, 77.4; H, 8.5.

d-**Desoxyisoequilenin.**—A solution of 4 g. of the higher-melting menthyl ester (m.p. 159–160°), and 50 g. of potassium hydroxide in 80 cc. of methanol and 20 cc. of water was heated on a steam-bath for six hours. After removal of the methanol in a current of air, the residue was dissolved in water, the menthol was extracted with benzene and the *l*-*cis*-**2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthreneacetic acid** recovered by acidification of the aqueous solution, m.p. 209–210.5°. Without further purification, this diacid was esterified and half hydrolyzed according to the procedure described for the racemate.[1] Crystallization from 60% methanol yielded *l*-*cis*-**2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrophenanthreneacetic acid,** m.p. 113.5–114.5°, $[\alpha]^{29}D$ −173° (in benzene).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.1; H, 6.4. Found: C, 73.0; H, 6.7.

The Arndt–Eistert reaction was carried out on this acid ester by the method described for the racemate.[1] The resulting **dimethyl ester of** *l*-*cis*-**2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthrenepropionic acid** was crystallized from methanol, m.p. 122–123°. A solution of 1.4 g. of the dimethyl ester in 60 cc. of anhydrous benzene was added to dry sodium methoxide, prepared from 0.228 g. of sodium, and heated for two hours under an atmosphere of nitrogen so that the solvent distilled slowly. The product was worked up, hydrolyzed and decarboxylated according to the described procedure.[1] The *d*-**desoxyisoequilenin** was purified by filtration of a benzene solution through a column of activated alumina, and by recrystallization from 90% aqueous methanol; m.p. 107–108°, $[\alpha]^{26}D$ +159° (in chloroform); yield, 0.85 g. (reported,[4,7] m.p. 107.5–108.5°, $[\alpha]^{27}D$ +168)°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.4; H, 7.2. Found: C, 86.3; H, 7.6.

l-**Desoxyisoequilenin.**—The reactions employed in the synthesis of *l*-desoxyisoequilenin from the lower melting menthyl ester (m.p. 111–114°) were the same as those described in the previous experiment for the synthesis of the enantiomorph. The *d*-*cis*-**2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrophenanthreneacetic acid** had m.p. 112.5–114.5° after several recrystallizations from 60% aqueous methanol.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.1; H, 6.4. Found: C, 73.0; H, 6.5.

The Arndt–Eistert reaction yielded the **dimethyl ester of** *d*-*cis*-**2-methyl-2-carboxy-1,2,3,4-tetrahydrophenanthrenepropionic acid**; m.p. 122–123°.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.1; H, 7.1. Found: C, 74.1; H, 7.1.

The Dieckmann reaction and subsequent hydrolysis and decarboxylation afforded *l*-**desoxyisoequilenin**; m.p. 107–108°; $[\alpha]^{28}D$ −159° (in chloroform).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.4; H, 7.2. Found: C, 86.1; H, 7.4.

A hot solution of equal weights of the *d*- and *l*-isomers of desoxyisoequilenin in 90% aqueous methanol deposited colorless plates of *dl*-desoxyisoequilenin; m.p. 100.5–101.5° alone and when mixed with an authentic specimen.

ANN ARBOR, MICHIGAN RECEIVED NOVEMBER 30, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Polycyclic Compounds. I. The Reimer–Tiemann Reaction with 1-Alkyl-2-naphthols

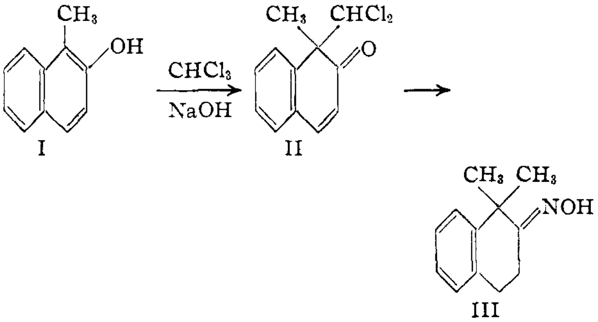
BY R. M. DODSON AND WILLIAM P. WEBB[1]

The Reimer–Tiemann reaction with 1-methyl-2-naphthol, 1-allyl-2-naphthol and 1-(3-chloro-2-butenyl)-2-naphthol produced the corresponding 1-alkyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene in fair yield. All of these bicyclic compounds possess a quaternary carbon atom. An unsuccessful attempt was made to hydrolyze and cyclize the 1-(3-chloro-2-butenyl)-1-dichloromethyl-2-keto-1,2-dihydronaphthalene with 90% sulfuric acid to 2-keto-12-dichloromethyl-2,3,4,12-tetrahydrophenanthrene.

For the past year we have been studying the Reimer–Tiemann reaction with 1-alkyl-2-naphthols in order to develop a method for the synthesis of polycyclic compounds containing a quaternary carbon atom which could be useful in the synthesis of steroids. Recently, the Reimer–Tiemann reaction with 1-methyl-2-naphthol was reported.[2] This prompts us to report our preliminary results with this reaction.

1-Methyl-2-naphthol (I) reacted with chloroform and aqueous sodium hydroxide to form 1-methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (II) in 77% yield. The only other organic material isolated from the reaction proved to be starting material. The structure of II followed from the analysis, from the analogy with the Reimer–Tiemann reaction with alkylphenols,[3] and from its conversion to 1,1-dimethyl-2-tetralone oxime (III).

1-Methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (II) failed to react with hydroxylamine and semicarbazide, but the infrared spectra of a solution of II in carbon tetrachloride indicated the presence of a conjugated carbonyl group (1660 cm.$^{-1}$). No vibrational frequency corresponding to a hydroxyl group (3400–3600 cm.$^{-1}$) was present.[4]



The ultraviolet absorption spectra of II in 95% alcohol has maxima at 239 mμ (ε 11,900) and 314 mμ (ε 9,200). Pyrolysis of II in liquid petrolatum at

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[1] Abstracted, in part, from the Ph.D. thesis of William P. Webb.

[2] Bell and Hunter, *J. Chem. Soc.*, 2903 (1950); received December 1, 1950.

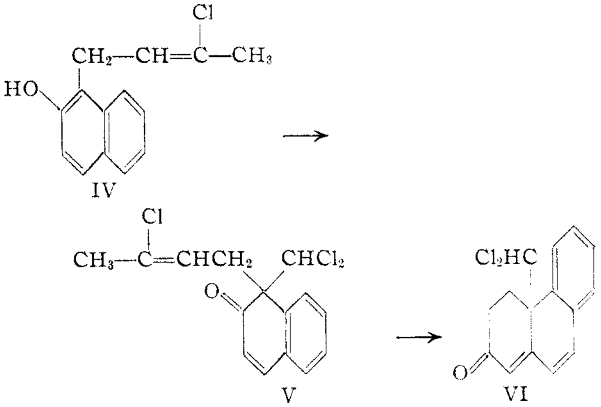
[3] v. Auwers and Winternitz, *Ber.*, **35**, 465 (1902).

[4] We are indebted to Dr. Bryce Crawford and Mr. John Lancaster for the infrared spectra.

300° converted part of it back to 1-methyl-2-naphthol. Unlike the 1-keto-4,4-dialkyl-1,4-dihydronaphthalenes,[5] compound II is relatively stable to sulfuric acid. Thus, when treated under conditions similar to those used previously,[5] the 1-methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene was recovered unchanged. It was also recovered unchanged when heated on a steam-bath in 90% sulfuric acid for ten minutes. 1-Methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (II) was readily hydrolyzed with alcoholic potassium hydroxide to give an acidic material. For this reason ethyl alcohol was omitted from the Reimer–Tiemann reaction. The results of this hydrolysis will be reported later.

The catalytic hydrogenation of 1-methyl-1-dichloromethyl - 2 - keto - 1,2 - dihydronaphthalene proved difficult. Hydrogenation in acidic media was very slow. The hydrogenation of compound II in ethyl alcohol containing sodium acetate using a platinum oxide catalyst stopped after the absorption of slightly more than one molar equivalent of hydrogen. 1-Methyl-1-dichloromethyl-2-tetralone was isolated in 74% yield. Hydrogenation of II using Raney nickel catalyst followed by oxidation of the product and reaction of the resulting ketone with hydroxylamine gave 1,1-dimethyl-2-tetralone oxime (III) in low yield. Because of the instability of II in alcoholic potassium hydroxide, sodium acetate was used as the base in the reduction catalyzed by Raney nickel.

The Reimer–Tiemann reaction was next run with 1-allyl-2-naphthol and 1-(3-chloro-2-butenyl)-2-naphthol (IV). The reactions proceeded as expected to give 1-allyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene and 1-(3-chloro-2-butenyl)-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (V), respectively. The required 1-(3-chloro-2-butenyl)-2-naphthol (IV) was prepared by the C-allylation of 2-naphthol with 1,3-dichloro-2-butene.



Compound V was prepared with the hope that the chlorobutenyl side-chain could be hydrolyzed with 90% sulfuric acid and the resulting 1,5-diketone cyclized[6] at the same time to give VI, which possesses the first three rings of the steroids. However, even though compound II proved stable to 90% sulfuric acid, only polymeric materials were obtained when V was treated in a similar manner. It is possible that compound VI, if formed, would not be stable under the conditions used. It is interesting to note that, with compounds containing a quaternary carbon atom adjacent to the carbonyl group, Prelog, Barman and Zimmerman[6] obtained a bridged ring system rather than the simple polycyclic ring system desired here. Investigations of modifications of these reactions that may lead to a simple synthesis of 2-keto-12-dichloromethyl-2,3,4,12-tetrahydrophenanthrene (VI) are now in progress.

Experimental[7]

1-Methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (II).—A solution of 33.0 g. of 1-methyl-2-naphthol and 66.0 g. of sodium hydroxide in 660 ml. of water was heated to 75°. To it was added 132.0 g. of chloroform over a period of three hours. The resulting mixture was heated for an additional hour. The organic layer was separated from the aqueous layer and the aqueous layer was extracted with 100 ml. of chloroform. The combined chloroform solution was washed first with a dilute sodium hydroxide solution, then with water. It was dried with magnesium sulfate; then the chloroform was removed by distillation. By distillation of the residual yellow oil under vacuum, 38.5 g. (77%) of 1-methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene, b.p. 131–134° (2.5 mm.), was obtained. Most of the material distilled at 131–132° (2.5 mm.). On standing, the yellow distillate slowly crystallized, and after one crystallization from dilute alcohol, the product (34.5 g.) melted at 64–65°. The analytical sample, m.p. 65–65.5°, was prepared by crystallization from petroleum ether and methanol.

Anal. Calcd. for $C_{12}H_{10}Cl_2O$: C, 59.77; H, 4.18. Found: C, 59.55; H, 4.49.

Pyrolysis of 1-Methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene.—1 - Methyl - 1 - dichloromethyl - 2 - keto-1,2-dihydronaphthalene (1.00 g.) in 50 ml. of liquid petrolatum was heated at 300° for one hour. Hydrogen chloride was liberated during this time. The dark solution was cooled and extracted with 50 ml. of 10% sodium hydroxide solution in two portions. Acidification of this alkaline extract gave 0.10 g. (18%) of crude 1-methyl-2-naphthol, m.p. 101–106°. Crystallization of this material from petroleum ether raised the melting point to 108–110°. A mixture of this material with 1-methyl-2-naphthol melted at 108–110°.

1-Methyl-1-dichloromethyl-2-tetralone.—A solution of 9.64 g. (0.04 mole) of 1-methyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene and 2.0 g. of sodium acetate in 100 ml. of ethanol was shaken with 0.50 g. of Adams platinum oxide catalyst at a hydrogen pressure of 50 pounds per square inch. Slightly more than one molar equivalent of hydrogen was absorbed in 30 minutes. The reduction then stopped. The catalyst was removed by filtration; the solution was heated on the steam-bath, then diluted with water until slightly cloudy and cooled. In this way 7.20 g. (74%) of of 1-methyl-1-dichloromethyl-2-tetralone, m.p. 67.5–68.5°, was obtained. Crystallization of the compound from dilute alcohol raised the melting point to 72–73°. The presence of the carbonyl group was confirmed by the infrared spectrum of the compound. (A strong absorption bond was present at 1720 cm.$^{-1}$.)

Anal. Calcd. for $C_{12}H_{12}Cl_2O$: C, 59.28; H, 4.98. Found: C, 59.30; H, 5.35.

1,1-Dimethyl-2-tetralone Oxime (III).—A solution of 9.64 g. (0.04 mole) of 1-methyl-1-dichloromethyl-2-ketone-1,2-dihydronaphthalene (II) and 13.6 g. of sodium acetate in 100 ml. of 95% alcohol was hydrogenated at 25° and 950 lb./sq. inch of hydrogen for one-half hour using 10 g. of a Raney nickel catalyst. The temperature was then raised to 100° for 15 minutes. The drop in pressure was slightly greater than that calculated for the absorption of four molar equivalents of hydrogen, but the error involved in this reading is very great. The catalyst was removed by filtration, and the alcohol was evaporated. Distillation of the residue

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[5] Arnold, Buckley and Dodson, This Journal, **72**, 3153 (1950), and preceding papers in this series.

[6] Wichterle, Prochazka and Hofman, *Collection Czechoslov. Chem. Commun.*, **13**, 300 (1948); *C. A.*, **42**, 8162 (1948); Prelog, Barman and Zimmerman, *Helv. Chim. Acta*, **32**, 1284 (1949).

[7] Microanalyses by William Cummings and Harry Turner.

yielded 6.05 g. of a colorless liquid, b.p. 98–119° (3 mm.), which still contained some chlorine.

A 2.00-g. portion of this distillate was oxidized with 1.20 g. of chromium trioxide in 20 ml. of 90% acetic acid by allowing the solution to stand at room temperature overnight. The excess chromium trioxide was reduced by the addition of methyl alcohol and the organic material was isolated. This material was converted to an oxime by heating it for two hours with a solution of 2.00 g. of hydroxylamine hydrochloride and 8.0 g. of potassium hydroxide in 40 ml. of ethyl alcohol. Most of the alcohol was then removed by evaporation and the suspension was poured into water. The crude oxime (1.00 g.) was separated by filtration. Crystallization from petroleum ether, b.p. 60–68°, containing a little benzene and from dilute methanol produced an analytically pure sample, m.p. 111–111.5°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99. Found: C, 76.11; H, 7.99.

1,1-Dimethyl-2-tetralone was also prepared in 72.8% yield by the methylation of 2-tetralone using methyl iodide and potassium *t*-butoxide in *t*-butyl alcohol. The material so obtained boiled at 142–146° (24 mm.); n^{25}D 1.5406. An oxime prepared from this ketone melted at 109.5–110° and showed no depression of melting point when mixed with the oxime obtained above. After this work was completed, the preparation of 1,1-dimethyl-2-tetralone by the methylation of 2-tetralone using methyl iodide and sodium hydride in benzene was reported.[8]

1-(3-Chloro-2-butenyl)-2-naphthol.—To a solution of 146.1 g. (1.015 moles) of 2-naphthol in 500 ml. of warm toluene under nitrogen was added 23.3 g. (1.012 moles) of sodium wire in small portions with stirring. The resulting paste was thinned by the addition of 300 ml. of toluene. To the rapidly stirred suspension heated at 100–110° was slowly added 142.5 g. (1.14 moles) of 1,3-dichloro-2-butene over a period of one hour. The mixture was then heated under reflux for five hours. The mixture was diluted with water and the unreacted 2-naphthol (24.1 g.) was removed by extraction of the toluene solution with a 5% sodium hydroxide solution. The toluene was removed by distillation. The residual oil was mixed thoroughly with four times its volume of Claisen alkali[9] and the resulting suspension was extracted thoroughly with petroleum ether. The Claisen alkali was acidified with hydrochloric acid; the red oil which separated was extracted with ether; and the ether solution was dried over magnesium sulfate, then distilled. Distillation under vacuum yielded 114.7 g. of 1-(3-chloro-2-butenyl)-2-naphthol, b.p. 165–175° (1.5 mm.). The distillate, which slowly solidified on standing, was crystallized from petroleum ether, b.p. 60–68°, and gave 105.3 g. (45.5%) of product, m.p. 65.5–66°. Further crystallization of this substance raised its melting point to 68–68.5°. The compound slowly turns green on standing in air.

Anal. Calcd. for $C_{14}H_{13}ClO$: C, 72.26; H, 5.63. Found: C, 71.91; H, 5.80.

1-(3-Chloro-2-butenyl)-2-naphthyl benzoate was prepared by treating the naphthol with benzoyl chloride and aqueous sodium hydroxide. After crystallization from methanol it melted at 84–84.5°.

Anal. Calcd. for $C_{21}H_{17}ClO_2$: C, 74.89; H, 5.08. Found: C, 74.84; H, 5.27.

1-(3-Chloro-2-butenyl)-1-dichloromethyl-2-keto-1,2-dihydronaphthalene (V).—A solution of 60.0 g. (0.26 mole) of 1-(3-chloro-2-butenyl)-2-naphthol and 120 g. of sodium hydroxide in 1200 ml. of water was heated to 76° with stirring. To it was added 240 ml. of chloroform over a period of five hours. The resulting mixture was then heated under gentle reflux for an additional three hours. The chloroform solution was then separated from the aqueous layer; the aqueous layer was extracted with two 50-ml. portions of chloroform; and the chloroform solutions were combined. The chloroform was removed by distillation. The residual oil was mixed with four times its volume of Claisen alkali[9] and the resulting mixture was extracted six times with 25-ml. portions of petroleum ether, b.p. 60–68°. These extracts were combined, dried over magnesium sulfate, then concentrated under reduced pressure. During this concentration the product separated as a light tan solid. In this manner 24.3 g. (35%) of 1-(3-chloro-2-butenyl)-1-dichloromethyl-2-keto-1,2-dihydronaphthalene, m.p. 68–70°, was obtained. The compound is readily crystallized from ethanol.

Anal. Calcd. for $C_{15}H_{13}Cl_3O$: C, 57.08; H, 4.15. Found: C, 57.40; H, 4.43.

1-Allyl-1-dichloromethyl-2-keto-1,2-dihydronaphthalene was prepared in 47% yield from 1-allyl-2-naphthol[10] by a procedure similar to that described above. The product distilled at 126–132° at 1.5 mm. The analytical sample was obtained by refractionating this material, b.p. 122° (0.8 mm.); n^{25}D 1.6085.

Anal. Calcd. for $C_{14}H_{12}Cl_2O$: C, 62.94; H, 4.53. Found: C, 63.19; H, 4.69.

Acknowledgment.—The authors are indebted to the Research Corporation for a grant in support of this research.

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[8] Soffer, Stewart, Cavagnol, Gellerson and Bowler, THIS JOURNAL, **72**, 3704 (1950).

[9] Claisen, *Ann.*, **418**, 96 (1919); Claisen, Kremers, Roth and Tietze, *ibid.*, **424**, 210 (1925).

[10] The 1-allyl-2-naphthol used in this preparation was prepared in 40% yield by the direct allylation of 2-naphthol with allyl bromide by a procedure similar to that described for 1-(3-chloro-2-butenyl)-2-naphthol.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 20, 1950

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Cyclic and Linear Nitramines Formed by Nitrolysis of Hexamine[1]

BY W. E. BACHMANN, W. J. HORTON, E. L. JENNER, N. W. MACNAUGHTON AND L. B. SCOTT

The procedure for the preparation of cyclotrimethylenetrinitramine (RDX) by nitrolysis of hexamine in acetic anhydride in the presence of ammonium nitrate has been improved. In the reaction some of the cyclic tetranitramine, a high explosive with an eight-membered ring, is formed. By suitable modification the reaction mixture can be made to yield a linear trinitramine. The use of isotopic ammonium nitrate in the RDX reaction is described.

Recently we described a new process for preparing the high explosive cyclotrimethylenetrinitramine (I, RDX) by the reaction of hexamethylenetramine (hereinafter called hexamine) with nitric acid, acetic anhydride and ammonium nitrate.[2] It was shown that the product of the reaction contained a small amount (0–10%) of a high-melting compound which was called HMX. As a result of hundreds of experiments, conditions have been worked out whereby RDX (with some HMX) can be obtained in yields higher than 80%; the highest yield obtained was 90% (based on the formation of two moles of RDX per mole of hexamine).

On the basis of analysis (identical with that of RDX), high melting point, and molecular weight we suggested (in 1941) that HMX was 1,3,5,7-

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[1] This investigation was carried out under a contract recommended by the NDRC between the OSRD and the Regents of the University of Michigan, 1940–1945. This material has been released by the Security Review Branch of the Department of Defence.

[2] W. E. Bachmann and J. C. Sheehan, THIS JOURNAL, **71**, 1842 (1949).