[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

THE VON AUWERS REARRANGEMENT IN THE NAPHTHALENE SERIES

REYNOLD C. FUSON AND THOMAS G. MILLER[1]

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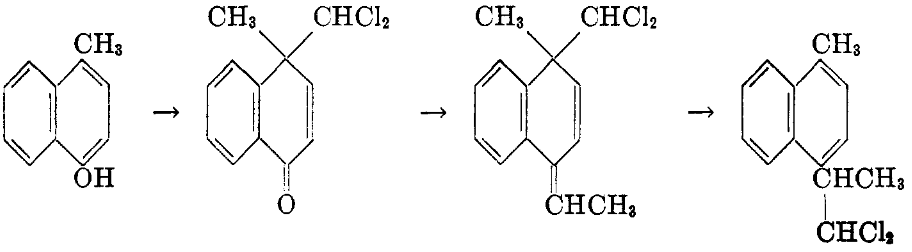
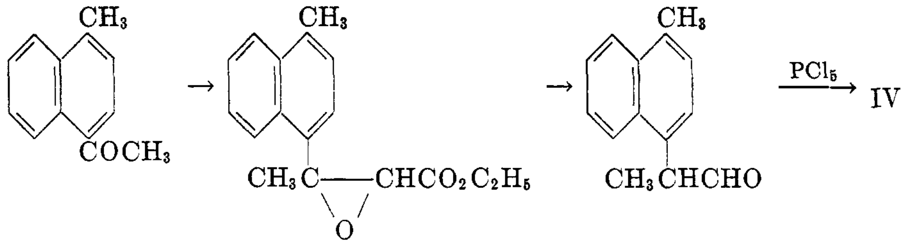
It was discovered by von Auwers that certain alkylidene-4-(dichloromethyl)-4-methylcyclohexadienes undergo thermal, non-catalytic rearrangement involving aromatization of the ring and transfer of the dichloromethyl group to the α-carbon atom of the alkylidene side chain (1). von Auwers and others (2) showed that cyclohexadienone derivatives are formed when suitable *o*- or *p*-alkyl phenols are treated with chloroform and alkali under the conditions of the Reimer-Tiemann aldehyde synthesis and that the cyclohexadienones made from the *para*-substituted phenols can be transformed by the action of Grignard reagents to carbinols, which undergo dehydration to yield the alkylidene derivatives.

In the present work it has been demonstrated that the formation of dichloromethyl derivatives of this type and their rearrangement can likewise be realized in the naphthalene series. 4-Methyl-1-naphthol (I) when treated with chloroform in the presence of sodium hydroxide yields 4-(dichloromethyl)-4-methyl-1(4H)-naphthalenone (II). By use of the ethyl Grignard reagent the naphthalenone was converted to 1-ethylidene-4-(dichloromethyl)-4-methyl-1,4-dihydronaphthalene (III). When heated the ethylidene derivative isomerized to 1,1-dichloro-2-(4-methyl-1-naphthyl) propane (IV).



I II III IV

The identity of the rearrangement product was established by an independent synthesis involving the following steps.



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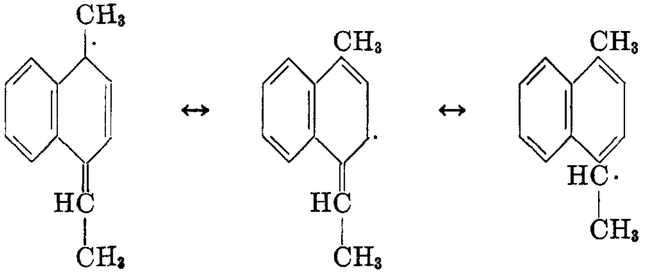
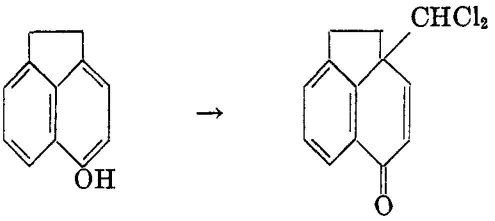
[1] Present address: E. I. du Pont de Nemours and Company, Wilmington, Delaware.

The reason for migration of the dichloromethyl group to the side chain rather than the nucleus becomes apparent when the resonance structures of the other moiety are considered. If it is assumed, for example, that the dichloromethyl group migrates as a radical, the residual radical may be depicted by the following structures. Of these *c* would be favored because it has a completely aromatized naphthalene nucleus. The argument would be of equal force if the dichloromethyl group migrated as an ion.



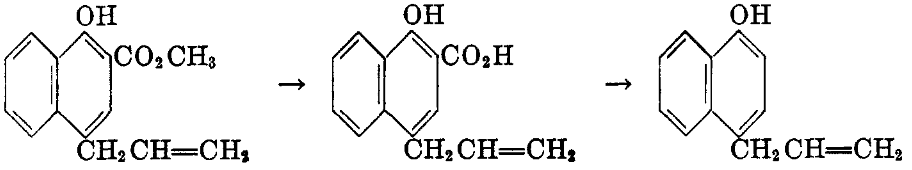
a *b* *c*

A dichloromethyl derivative (VI) of a new type was furnished by 5-acenaphthenol (V), derived from the corresponding amine (3). However, rearrangement of the corresponding ethylidene compound could not be realized; polymerization occurred instead.



V VI

Attempts to prepare naphthalene derivatives holding an allyl radical in a position appropriate for migration were unsuccessful. For example, 4-allyl-1-naphthol (IX), made by the following scheme, failed to yield a dichloromethyl derivative. This result is in contrast with that observed with 1-allyl-2-naphthol and 1-(3-chloro-2-butenyl)-2-naphthol which have been found to give good yields of dichloromethyl ketones under the conditions of the Reimer-Tiemann reaction (4).



VII VIII IX

EXPERIMENTAL

4-(Dichloromethyl)-4-methyl-1-(4H)-naphthalenone (II). 4-Methyl-1-naphthol was prepared in a yield of 42% from potassium 4-methyl-1-naphthalenesulfonate by the method of Elbs and Christ (5). A solution of 10 g. of the naphthol in 200 g. of 10% sodium hydroxide was heated in an oil-bath at 95°, and 24 g. of chloroform was added gradually, with stirring over a period of 3 hours. The heating was continued for 45 minutes and 100 ml. of chloroform was added. The mixture was shaken and the chloroform layer extracted three times with 50-ml. portions of 5% sodium hydroxide. The chloroform solution was washed with water and subjected to distillation. After removal of the solvent under slightly reduced pressure the residue was distilled at 0.5 mm.; b.p. 150–163°. A solution of the distillate in petroleum ether was shaken with Darco, filtered, and chilled. The naphthalenone separated as white needles; m.p. 108–109°; yield 2.2 g. The presence of chlorine was shown by a sodium fusion test.

Anal.[2] Calc'd for $C_{12}H_{10}Cl_2O$: C, 59.77; H, 4.18.
Found: C, 59.66; H, 4.19.

The *2,4-dinitrophenylhydrazone* crystallized from an ethanol-ethyl acetate mixture in tiny red plates melting at 211–212°.

Anal. Calc'd for $C_{18}H_{14}Cl_2N_4O_4$: C, 51.32; H, 3.35; N, 13.30.
Found: C, 51.41; H, 3.43; N, 13.04.

1,1-Dichloro-2-(4-methyl-1-naphthyl)propane (IV). A solution of 1.04 g. of 4-(dichloromethyl)-4-methyl-1(4H)-naphthalenone in 20 ml. of ether was added rapidly, with stirring, to a Grignard reagent prepared from 9.40 g. of ethyl bromide, 2.1 g. of magnesium, and 30 ml. of ether. The reaction mixture was poured into a solution of 5 ml. of glacial acetic acid in 120 ml. of water. The ether layer was shaken with two 25-ml. portions of 5% sodium carbonate and dried over sodium sulfate. The pale yellow liquid, left by evaporation of the ether under slightly reduced pressure, was dissolved in 50 ml. of low-boiling petroleum ether, but the tertiary alcohol could not be induced to crystallize from this solution. The petroleum ether was evaporated and the residue heated in an oil-bath at 120° for one hour. Distillation of the resulting dark oil yielded a few drops of a clear, colorless liquid boiling at 105–110° (0.5 mm.). This compound, presumed to be 1-ethylidene-4-(dichloromethyl)-4-methyl-1,4-dihydronaphthalene, was placed in a test tube heated by an oil-bath. When the oil-bath temperature reached 160° the temperature of the contents, which had lagged about 10° behind that of the oil-bath, rose rapidly to 175°. At the same time a characteristic naphthalene odor developed. When allowed to cool the 1,1-dichloro-2-(4-methyl-1-naphthyl)-propane formed a cream-colored solid, which crystallized from methanol in small white plates; m.p. 70–71°.

Anal. Calc'd for $C_{14}H_{14}Cl_2$: C, 66.42; H, 5.57.
Found: C, 66.33; H, 5.66.

A sodium fusion test showed the presence of chlorine.

In another experiment the rearrangement was realized without any attempt to isolate the intermediates or to dehydrate the tertiary alcohol.

2-(4-Methyl-1-naphthyl)-1-propanone. Sodium ethoxide (5.9 g.) was added in small portions, with stirring, to a mixture of 15.7 g. of 4-methyl-1-acetonaphthone and 10.5 g. of ethyl chloroacetate cooled in an ice-bath. The ice-bath was removed and the stirring continued for 48 hours, during the last 3 of which the temperature was maintained at 80°. A solution of 10 g. of acetic acid in 75 ml. of cold water was added and the mixture extracted with 150 ml. of benzene. The benzene solution was dried over sodium sulfate and the solvent removed by distillation under diminished pressure. The product was distilled from a modified Claisen flask. A fraction boiling at 130–142° (0.5 mm.) (yield 9.5 g.) reacted with 2,4-dinitrophenylhydrazine but not with dilute sodium hydroxide solution. A second fraction believed to be the glycidic ester, boiled at 142–167° (0.5 mm.); yield 3 g.

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[2] The microanalyses were carried out by Miss Emily Davis, Miss Rachel Kopel, and Miss Jean Fortney.

The glycidic ester was heated for 2 hours at 100° with 25 ml. of 10% sodium hydroxide solution. Then 10 ml. of conc'd hydrochloric acid was added and the solution heated on a steam-bath for 2 hours. Extraction of the solution with ether gave a small amount of colorless oil, which gave a positive fuchsin-aldehyde test and was believed to be 2-(4-methyl-1-naphthyl)-1-propanone.

1,1-Dichloro-2-(4-methyl-1-naphthyl)propane (IV). A solution of the crude aldehyde in the minimum amount of ether was allowed to react with a small amount of phosphorus pentachloride. The reaction mixture was stirred occasionally and at the end of 2 hours was treated with a small amount of ice. The product was extracted with 10 ml. of ether. The ether solution was stirred for 8 hours with 57 ml. of 40% sodium bisulfite solution and dried over sodium sulfate. The residue, left by evaporation of the ether, was dissolved in methanol and the methanol solution cooled in a Dry Ice-acetone bath. The gummy precipitate which appeared was removed. The dichloro compound separated from the mother liquor in white plates (yield 150 mg.) which after recrystallization from methanol melted at 70–71°. A mixture melting point with the product of the rearrangement showed no lowering.

5-Acenaphthenol (V). 5-Nitroacenaphthene was prepared by the method of Sachs and Mosebach (6) and reduced to 5-acenaphtheneamine according to directions given by Fleischer and Schranz (3). A solution of 5.7 g. of acenaphtheneamine in 48 ml. of glacial acetic acid was added to an ice-cold solution of 25 ml. of sulfuric acid in 200 ml. of water. To the cold mixture was added drop by drop, with stirring, a solution of 2.7 g. of sodium nitrite in 20 ml. of water, The solution of the diazonium salt was then added drop by drop from an ice-jacketed dropping-funnel into a boiling solution of 48 ml. of sulfuric acid in 200 ml. of water. The mixture was chilled and filtered, and the solid material was heated under reflux for 18 hours with 100 ml. of high-boiling petroleum ether. The petroleum ether solution was separated from the insoluble material. Removal of the solvent left a dark solid which was boiled for a few minutes with 75 ml. of 5% sodium hydroxide solution. The alkaline solution was extracted with 30 ml. of ether, then acidified with hydrochloric acid. The precipitated naphthol was collected and crystallized from high-boiling petroleum ether; yield 1.1 g. (19%).

2a-Dichloromethyl-5-keto-2a,5-dihydroacenaphthene (VI). A solution of 12.5 g. of 5-acenaphthenol in 250 ml. of 10% sodium hydroxide was warmed in a 70° oil-bath. To it was added, with stirring, 30 g. of chloroform over a period of 4 hours. The solution was separated from a tarry solid and was extracted with 100 ml. of ether. This ether solution plus an additional 100 ml. of ether was added to the tarry residue, and the mixture was heated at reflux for one hour. The solution was filtered from some insoluble material, washed three times with 75-ml. portions of water, and dried over sodium sulfate. Removal of the ether by distillation left a semi-solid residue. Vacuum-distillation of the material through a small short-path still at 0.3 mm. gave a small amount of a brown oil. The distillate, by trituration with an equal volume of ether and decantation of the liquid, gave a light solid. The compound crystallized from high-boiling petroleum ether in white prisms melting at 161–162°; yield 1.14 g. (6%). Infrared analysis of the ketone discloses an absorption maximum at 1668 cm.$^{-1}$ which is characteristic of doubly-conjugated carbonyl groups.[3] The compound is soluble in benzene and alcohol, but less soluble in ether.

Anal. Calc'd for $C_{13}H_{10}Cl_2O$: C, 61.68; H, 3.98.

Found: C, 61.53; H, 4.35.

Treatment of the ketone (VI) with ethylmagnesium bromide converted it to a brown oil which failed to crystallize. The oil was dissolved in 6 ml. of high-boiling petroleum ether, and the solution was warmed. No water appeared in the test tube, but a brown solid (polymer?) began to separate from the solution. The solvent was removed under diminished pressure and the residue heated to 200° in an oil-bath; there was no evolution of heat or other sign of rearrangement.

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[3] The infrared absorption spectra were recorded and interpreted by Miss Elizabeth Petersen.

Methyl 4-allyl-1-hydroxy-2-naphthoate (VIII). A mixture of 314 g. of methyl 1-hydroxy-2-naphthoate, 194 g. of allyl bromide, 221 g. of potassium carbonate, and 450 ml. of acetone was heated under reflux, with stirring, for 40 hours and then shaken with 1 l. of water. The water layer was extracted with 400 ml. of ether. The combined organic layers were extracted twice with 400-ml. portions of 5% sodium hydroxide and finally with a solution of 10 ml. of acetic acid in 500 ml. of water. After the solution had been dried over magnesium sulfate, the solvents were removed by distillation. The residual liquid weighed 361 g. Further purification was not attempted. The crude methyl 1-allyloxy-2-naphthoate (23 g.) was heated at 230° for one hour in a stream of carbon dioxide. The heat evolved by the rearrangement was sufficient to raise the temperature to 280°. When cooled, the material solidified to a yellow mass which yielded 14 g. (61%) of white needles after three crystallizations from a one part benzene-two parts ethanol mixture. The compound is insoluble in 5% sodium hydroxide and melts at 74.5–75°. A blue color is produced with ferric chloride in 50% ethanol.

Anal. Calc'd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82.

Found: C, 74.37; H, 5.80.

4-Allyl-1-hydroxy-2-naphthoic acid (VIII). A mixture of 45 g. of methyl 4-allyl-1-hydroxy-2-naphthoate, 29 g. of potassium hydroxide, and 400 ml. of methanol was heated under reflux for 12 hours, then poured into 1.5 l. of water. The precipitate was removed and the filtrate was acidified with concentrated hydrochloric acid. The precipitated acid was collected on a filter and pressed with a rubber dam. After two recrystallizations of the material from benzene and treatment with Darco, the yield was 20 g. (47%) of tiny white needles melting at 186–187°. The acid gives a blue color with ferric chloride in 50% ethanol.

Anal. Calc'd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30.

Found: C, 73.80; H, 5.50.

4-Allyl-1-naphthol (IX). 4-Allyl-1-hydroxy-2-naphthoic acid (21 g.) was heated in a 60-ml. Claisen flask for 20 minutes at a bath temperature of 210°. Water-pump suction was applied during the last 5 minutes. The temperature was allowed to fall to 120°, and the material was distilled at low pressure. The naphthol distilled in the range 117–129° (0.4 mm.). Crystallization of the distillate was effected from low-boiling petroleum ether. The yield was 12.4 g. (73%) of tiny white needles melting at 47.5–48° and soluble in dilute sodium hydroxide. Ferric chloride produces a purple color with the naphthol in 50% ethanol. Infrared analysis indicates a terminal olefinic double bond.

Anal. Calc'd for $C_{13}H_{12}O$: C, 84.75; H, 6.57.

Found: C, 84.54; H, 6.76.

SUMMARY

The von Auwers rearrangement has been extended to the naphthalene series. 4-Methyl-1-naphthol has been found to react with chloroform in the presence of sodium hydroxide to yield 4-(dichloromethyl)-4-methyl-1(4H)-naphthalenone. The naphthalenone has been converted to 1,1-dichloro-2-(4-methyl-1-naphthyl)-propane by a method involving the isomerization of 1-ethylidene-4-(dichloromethyl)-4-methyl-1,4-dihydronaphthalene.

URBANA, ILLINOIS

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