sorbed. The percentage of gas which dissolved in 82.5% sulfuric acid was 2.1. Methylallene should make up much of this portion. The remainder was discarded.

Summary

1-Hexyne and 1-heptyne were pyrolyzed at temperatures of 500, 550 and 600°. The chief gaseous products were propylene, methane and ethylene but some ethane and hydrogen were formed also. By ozonolysis it was established that the liquid products from 1-hexyne contained 1,2-hexadiene, and that the liquids from 1-heptyne contained 1,2-heptadiene. Except in the experiment at 600°, there was no evidence for the production of 2-alkynes, and then only in traces. Aromatic hydrocarbons or 1,3-alkadienes were not formed. Similarly, in work with 1-butyne at 560°, the absence of 1,3-butadiene was established. The rearrangement of 1-alkynes into 1,2-alkadienes does not proceed at 400°, but requires temperatures which are high enough to cause concurrent breakdown into gaseous products. The significance of this fact is brought out in the reaction mechanism.

EVANSTON, ILLINOIS RECEIVED JULY 6, 1937

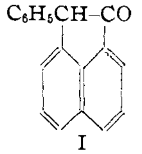
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Action of Aluminum Chloride on Phenyl-α-naphthylacetyl Chloride[1]

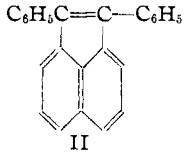
BY C. F. KOELSCH AND H. J. RICHTER

Diphenylacetyl chloride in the presence of aluminum chloride reacts with benzene to give diphenylacetophenone[2] and with naphthalene to give diphenylacetonaphthalene.[3] In attempting to carry out an analogous reaction with phenyl-α-naphthylacetyl chloride, aluminum chloride and benzene, McKenzie and Tattersall[4] obtained not the expected phenyl-α-naphthylacetophenone, but rather a compound, $C_{18}H_{12}O$, formed by the abstraction of hydrogen chloride from the acid chloride. Further than noting that this product did not have the properties of a ketene, these investigators made no suggestions as to its possible structure.

Since α-naphthylacetyl chloride has been shown to yield acenaphthenone on treatment with aluminum chloride in nitrobenzene,[5] it appeared possible that McKenzie and Tattersall's compound was an acenaphthenone derivative. We have found that oxidation of McKenzie and Tattersall's compound yields 8-benzoylnaphthoic acid, indicating that it is to be formulated as 7-phenylacenaphthenone (I) or the enol of this.



I



II

The ketonic formula best represents the behavior of the substance. It is not attacked by bromine, even in boiling acetic acid; it is colorless, while all acenaphthylene derivatives are colored; and, finally, it reacts with phenylmagnesium bromide to give an oily addition product which yields the known orange diphenylacenaphthylene (II) on dehydration. The compound may react in the enolic form, however, for when its solution in pyridine is treated with benzoyl chloride it gives an orange benzoate, whose color indicates that it is an O- rather than a C-derivative. The red color developed when alkali is added to an alcohol solution of the ketone also indicates enolization, but no methyl derivative could be obtained when such a solution was treated alternately with sodium hydroxide and methyl sulfate.

Experimental

7-Phenylacenaphthenone (I).—The following procedure was found to give a considerably better yield than that of McKenzie and Tattersall. A solution of phenyl-α-naphthylacetic acid (25 g.) in 250 ml. of benzene was treated with 20 g. of phosphorus pentachloride and boiled until hydrogen chloride was no longer evolved. Aluminum chloride (14 g.) was then added in portions, the mixture refluxed for one hour, and decomposed with iced hydrochloric acid. The oil left after the benzene had been steam distilled was distilled under reduced pressure, yielding 16 g. of an oil which rapidly solidified. The crude product melted at 106–111°, and, when purified, at 115.5–116.5° in agreement with the reported value.

Oxidation.—A solution of 2 g. of the ketone in 15 ml. of acetic acid was treated with 2 g. of chromic acid, kept at 80° for thirty minutes, and poured into water. From the precipitated organic substances taken up in ether, sodium

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[1] Abstracted from the thesis of H. J. Richter submitted to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the M.S. degree, October, 1935.

[2] Klingeman, *Ann.*, **275**, 83 (1893).

[3] McKenzie and Dennler, *J. Chem. Soc.*, **125**, 2105 (1924).

[4] McKenzie and Tattersall, *ibid.*, **127**, 2522 (1925).

[5] German Patent 230,237, *Chem. Centr.*, **82**, I, 359 (1911).

carbonate removed 1.4 g. of 8-benzoylnaphthoic acid which, in agreement with the literature,[6] melted and decomposed at 110–115°. The ethyl ester of this acid, prepared with thionyl chloride, melted at 164–166° (literature[6] 166–167°).

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.95; H, 5.26. Found: C, 78.7; H, 5.03.

Oxidation of 7-phenylacenaphthenone also may be brought about by oxygen. A suspension of the ketone (1 g.) in 60 ml. of 10% alcoholic potassium hydroxide lost its color after standing exposed to air for twelve hours. The resulting solution, distilled to a small volume and acidified, yielded benzoylnaphthoic acid, identified by conversion into its ethyl ester.

Reaction with Phenylmagnesium Bromide.—A solution of 4 g. of phenylacenaphthenone in benzene (20 ml.) was added to a Grignard reagent prepared from 2.6 g. of bromobenzene. The yellow oil obtained on working up the reaction mixture could not be obtained crystalline, and accordingly was boiled for one hour with 100 ml. of 0.5% sulfuric acid in acetic acid. On cooling, this solution deposited diphenylacenaphthylene (2.7 g.) in the form of orange needles that melted at 164.5–166° (literature,[7] 159.5–161°).

Anal. Calcd. for $C_{24}H_{16}$: C, 94.7; H, 5.26. Found: C, 94.9; H, 5.44.

On treatment with chromic acid in acetic acid, this hydrocarbon gave 1,8-dibenzoylnaphthalene which melted at 186–188° (literature,[8] 189–190°).

Benzoylation.—The benzoate of 7-phenyl-8-hydroxyacenaphthylene was obtained in good yield by adding a slight excess of benzoyl chloride to a solution of phenylacenaphthenone in dry pyridine, adding enough chloroform to dissolve the precipitate formed, and warming the resulting solution to 60° for one hour. It separated from benzene–ligroin in rosets of orange needles that melted at 143–145°.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.2; H, 4.56. Found: C, 86.15; H, 4.6.

Attempted Methylation.—A boiling solution of the ketone (0.5 g.) in methanol (15 ml.) containing methyl sulfate (1 ml.) was treated dropwise with 5% alcoholic potassium hydroxide until the red color was permanent. More methyl sulfate was added, followed by alkali, but although this procedure was repeated several times a point was never reached where the addition of alkali failed to restore the red color. Only unchanged ketone could be isolated.

Summary

When treated with aluminum chloride, phenyl-α-naphthylacetyl chloride yields 7-phenylacenaphthenone, a substance which exists in its ketonic form.

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[6] Mason, *J. Chem. Soc.*, **125**, 2119 (1924).

[7] Wittig, Leo and Wiemer, *Ber.*, **64**, 2405 (1931).

[8] Veschke, *Ann.*, **369**, 201 (1909).

MINNEAPOLIS, MINNESOTA RECEIVED JULY 19, 1937

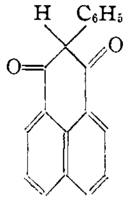
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies in the *peri*-Naphthindene Series. II. The Action of Phenyl-lithium on 8-Phenyl-*peri*-naphthindandione-7,9[1]

BY C. F. KOELSCH AND R. H. ROSENWALD

In continuing the program outlined in paper I of this series[2] it was planned to compare the reactions of 2,3-diphenylindone with those of the unknown 7,8-diphenyl-*peri*-naphthindone. It was hoped that the latter substance could be obtained from 8-phenyl-*peri*-naphthindandione-7,9 (I) and phenyl-lithium, through a reaction similar to that used for the preparation of a number of disubstituted indones[2] (p. 1328).

It was apparent, however, that the product which resulted from this reaction, although having the proper composition, was not the expected hydroxy ketone, since it was soluble in alkali and could not be dehydrated. A further study of the substance has led us to consider it as an enol of 1,8-diphenyl-1,9-α-dihydro-*peri*-naphthindandione-7,9 (II).



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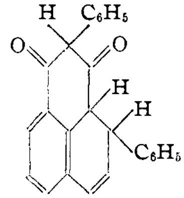

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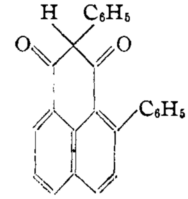

III

The formation of this compound undoubtedly involves the enol of I and in some respects is analogous to the previously observed 1,4-addition of Grignard reagents to benzanthrone. That the primary 1,4-addition product can be isolated in the present instance is of unusual interest, for in all similar reactions so far reported, the addition product has been isolated only after it has become aro-

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[1] Abstracted from the thesis of R. H. Rosenwald, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, December, 1936.

[2] Koelsch, THIS JOURNAL, **58**, 1326 (1936).