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

# Pyrolysis of the 1,4-Addition Products Obtained from 1-Naphthyl Trityl Ketone and Grignard Reagents[1]

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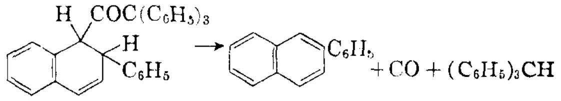
The Grignard reagents obtained from phenyl, *o*-tolyl and *p*-tolyl bromides have been found to condense in the 1,4-manner with 1-naphthyl trityl ketone to yield the corresponding dihydrobenzenoid derivatives. Heating the phenylated compound with palladium-on-charcoal did not produce the aromatized ketone, but instead carbon monoxide, triphenylmethane and 2-phenylnaphthalene. The same type of cleavage occurred when the compound was pyrolyzed in the absence of catalysts. The *o*- and *p*-tolyl derivatives decomposed in a similar way.

1,4-Addition of Grignard reagents to hindered aryl ketones in such a way as to involve an aromatic ring, first observed by Kohler and Nygaard,[2] is facilitated if the ring is naphthyl rather than phenyl.[3] In the present study this idea has been extended to the β-benzopinacolone series. Instead of the pinacolone, which had been studied by Schmidlin and Wohl[4] and by Mosher and Huber,[5] 1-naphthyl trityl ketone was examined. As expected the addition of Grignard reagents occurred much more readily than with β-benzopinacolone.

An important difference in procedure that was discovered is that, with the naphthyl ketone, the condensation must be conducted in the absence of oxygen. The effect of oxygen had been noted when mesityl naphthyl ketone was treated with the phenyl Grignard reagent and the reaction mixture was decomposed in the presence of air.[6] Oxidation of the intermediate enol by air seems probable here since mesitoic acid was obtained along with a compound tentatively identified as 2-phenylnaphthol. A similar enol has actually been isolated and characterized[7]; 9-phenyl-10-phenanthrol was obtained by the condensation of mesityl 9-phenanthryl ketone with the phenyl Grignard reagent in the presence of air.

Another conspicuous difference noted in our study was that in this series only dihydro derivatives could be isolated. In fact, deliberate attempts to aromatize these products failed. The dihydro compound obtained with the phenyl Grignard reagent, for example, was found to survive treatment with chloranil in boiling *m*-xylene. Examination of molecular models indicated that aromatization of such dihydro compounds might be opposed by steric factors.

The most interesting discovery encountered in the investigation concerned the behavior of the dihydro products at high temperatures. Pyrolysis occurred in such a way as to yield triphenylmethane, carbon monoxide and the corresponding β-aryl naphthalene. With the phenylated compound, for example, the reaction was



The carbonyl absorption in the infrared spectra of the addition compounds is shifted to a frequency higher than that of the starting material, the difference being as much as 20 cm.$^{-1}$ with the phenylated product. Aliphatic hydrogen is indicated by a small peak or shoulder just below 3000 cm.$^{-1}$. Strong bands, usually assigned to *o*-substituted phenyl (745 cm.$^{-1}$) and *p*-substituted phenyl (810 cm.$^{-1}$), are found in the spectra of the *o*- and *p*-tolyl compounds, respectively.

Hydrogenation of the phenylated compound was accomplished over platinum in high yield. The infrared spectrum of the reduction product possesses peaks similar to those found in the starting material with a few significant exceptions. A band of medium to strong intensity was found for aliphatic hydrogen (2925 cm.$^{-1}$), for example. More striking, however, was the appearance of only two bands, both strong, in the region from 700 to 900 cm.$^{-1}$. Peaks which can be ascribed to monosubstituted phenyl (700 cm.$^{-1}$) and *o*-substituted phenyl (745 cm.$^{-1}$) are present. The carbonyl frequency is shifted only slightly (from 1712 to 1704 cm.$^{-1}$). When an attempt was made to hydrogenate 1-naphthyl trityl ketone under the conditions employed with the dihydro compound, or even at a hydrogen pressure of 1000 lb. per sq. in., starting material was recovered nearly quantitatively.

Pyrolysis of the ketones produced cleavage. Carbon monoxide was detected by its ability to reduce palladium ion to black palladium.[8] Chromatography was found to give the best separation of the two hydrocarbons. Triphenylmethane was isolated in yields of 92, 86 and 90% from the phenyl, *o*-tolyl and *p*-tolyl addition compounds, respectively. In a similar way the corresponding β-naphthyl derivatives were obtained from the phenyl, *o*-tolyl and *p*-tolyl dihydro compounds in yields of 87, 69 and 85%, respectively. The high yields of the two hydrocarbon products can be accounted for only on the basis of the dihydro structure; they do not, however, exclude the formation of the completely aromatized ketone as an intermediate. 2-Phenyl- and 2-*o*-tolylnaphthalene are known and were identified by their melting points. The 2-*p*-tolylnaphthalene, apparently not previously described, was made by an alternative route.

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[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] E. P. Kohler and E. M. Nygaard, THIS JOURNAL, **52**, 4128 (1930).

[3] R. C. Fuson and Y. F. Shealy, *J. Org. Chem.*, **16**, 643 (1951).

[4] J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

[5] W. A. Mosher and M. L. Huber, THIS JOURNAL, **75**, 4604 (1953).

[6] R. C. Fuson, M. D. Armstrong and S. B. Speck, *J. Org. Chem.*, **7**, 297 (1942).

[7] R. C. Fuson and S. J. Strycker, THIS JOURNAL, **79**, 2633 (1957).

[8] V. J. Altieri, "Gas Analysis," Amer. Gas Assn., Inc., New York, N. Y., 1945, p. 257.

Samples from the pyrolysis and the synthetic path have identical infrared spectra, and a mixture melting point test did not show a depression.

Thermal decomposition of trityl carbonyl compounds appears to have been studied only in a few cases. Triphenylacetaldehyde had been reported to decompose to yield triphenylmethane and carbon monoxide.[9] Also, β-benzopinacolone, when distilled below 465°, had been found to yield triphenylmethane as the chief product.[10] Smaller amounts of *p*-benzoyltriphenylmethane, benzene and benzophenone were isolated. Traces of benzaldehyde and tetraphenylethylene were identified also.

Inspection of molecular models indicates that the rotation of the trityl group in the compounds investigated in our study is greatly restricted. It is postulated that the initial step of the decomposition is the rupture of the trityl carbonyl–carbon bond to form radicals.

## Experimental[11]

**1-Naphthoyl Chloride.**—Both phosphorus pentachloride[12] and thionyl chloride[13] had been employed in this synthesis. An improved procedure, involving thionyl chloride, which affords the chloride in nearly quantitative yields is: A mixture of 57.4 g. (0.33 mole) of 1-naphthoic acid and a large excess of thionyl chloride (100 ml.) was allowed to stand at room temperature for 1 hr., then heated on a steam-bath for 3 hr. and finally allowed to stand at room temperature for 2 hr. The excess thionyl chloride was removed under aspirator pressure, and the residue distilled *in vacuo*. The fraction boiling at 96° (0.3 mm., the boiling point had been reported as 189° at 20 mm.[12]) was collected; weight 55 g. (95%). It was found later that the use of the undistilled 1-naphthoyl chloride did not lower the yield of 1-naphthyl trityl ketone.

**1-Naphthyl Trityl Ketone.**—The procedure was that of Mosher and Huber.[14] The triphenylmethylsodium, prepared from 63 g. (0.226 mole) of trityl chloride,[15] was mixed with 42 g. (0.22 mole) of 1-naphthoyl chloride in 1500 ml. of anhydrous ether, and the mixture warmed gently for 24 hr. The 1-naphthyl trityl ketone, melting at 158–158.5° (recorded m.p. 157–158°[14]), was obtained in a 22% yield. The infrared spectrum[16] exhibits peaks which can be assigned to a conjugated carbonyl group (1692 cm.$^{-1}$), monosubstituted phenyl (700 cm.$^{-1}$) and the vicinally trisubstituted aromatic nucleus (740, 785, 810 cm.$^{-1}$).

**Condensation of the Phenyl Grignard Reagent with 1-Naphthyl Trityl Ketone.**—The entire procedure, including decomposition and the evaporation of solvents, was conducted under nitrogen. When the reaction was attempted without the nitrogen blanket, the residual oil (chromatographed on alumina) gave triphenylmethane, starting material and an intractable oil. Nitrogen was also used in the experiments with the *o*-tolyl and *p*-tolyl Grignard reagents.

The phenyl Grignard reagent was prepared from 4.15 g. (0.17 g. atom) of freshly ground magnesium, 27.4 g. (0.17 mole) of bromobenzene and 70 ml. of sodium-dried ether. Filtering to remove the slight amount of magnesium, before the addition of the ketone, was found to have no effect on the yield of the product. To the dark-colored Grignard reagent was added a solution of 7.0 g. (0.17 mole) of 1-naphthyl trityl ketone in 60 ml. of sodium-dried benzene. The resulting green-colored mixture was heated under reflux for 24 hr. and chilled by placing the flask in an ice-bath. Decomposition was effected by the addition of 150 ml. of saturated aqueous ammonium chloride. The mixture was then heated under gentle reflux, with stirring, for 18 hr. The organic layer and three 100-ml. ether extracts of the aqueous phase were dried over sodium sulfate and concentrated on a hot plate under nitrogen. Trituration of the residual oil with alcohol produced a solid which, after recrystallization from alcohol or acetic acid, gave white crystals melting at 178–179°, yield 7.8 g. or 93% (based on a monophenylated product). The infrared spectrum of this compound has peaks corresponding to aliphatic hydrogen (broad hump at 2925 cm.$^{-1}$) and a non-conjugated carbonyl group (1713 cm.$^{-1}$). Several bands in the range 700–775 cm.$^{-1}$ can be assigned to monosubstituted phenyl and *o*-substituted phenyl.

*Anal.*[17] Calcd. for $C_{36}H_{28}O$: C, 90.72; H, 5.92. Found: C, 90.67; H, 6.09.

**Condensation of the *o*-Tolyl Grignard Reagent with 1-Naphthyl Trityl Ketone.**—The action of the *o*-tolyl Grignard reagent, prepared from 2.4 g. (0.10 g. atom) of ground magnesium, 16.5 g. (0.10 mole) of *o*-bromotoluene and 50 ml. of anhydrous ether, on 4.0 g. (0.01 mole) of 1-naphthyl trityl ketone under the conditions described for the phenyl reagent, produced 1-(1,2-dihydro-2-*o*-tolyl)-naphthyl trityl ketone which melted at 163.5–164.5° after recrystallization from acetic acid. The yield of the dihydro compound was 1.21 g. (24.6%). The infrared spectrum of this compound contains bands assignable to aliphatic hydrogen (2925, 2975 cm.$^{-1}$), a non-conjugated ketone function (1710 cm.$^{-1}$) and monosubstituted phenyl (700 cm.$^{-1}$). Peaks at 725, 737 and 740 cm.$^{-1}$ can be ascribed to the dihydro naphthaene nucleus.

*Anal.* Calcd. for $C_{37}H_{30}O$: C, 90.57; H, 6.16. Found: C, 90.17; H, 6.33.

Concentration of the mother liquor produced 2.5 g. (62.5%) of starting material.

**Condensation of the *p*-Tolyl Grignard Reagent with 1-Naphthyl Trityl Ketone.**—The *p*-tolyl Grignard reagent, prepared from 2.4 g. (0.10 g. atom) of ground magnesium, 17.1 g. (0.10 mole) of *p*-bromotoluene and 45 ml. of anhydrous ether, reacted with 4.0 g. (0.01 mole) of 1-naphthyl trityl ketone to give 1-(1,2-dihydro-2-*p*-tolyl)naphthyl trityl ketone which melted at 183.5–185° after recrystallization from alcohol. The yield was 2.0 g. (40.8%). The infrared spectrum possesses peaks which can be assigned to aliphatic hydrogen (2915 cm.$^{-1}$), a non-conjugated ketone group (1705 cm.$^{-1}$), monosubstituted phenyl (700 cm.$^{-1}$) and *p*-substituted phenyl (812 cm.$^{-1}$). Other bands (740, 750, 762 cm.$^{-1}$) can be ascribed to the dihydro naphthalene nucleus.

*Anal.* Calcd. for $C_{37}H_{30}O$: C, 90.57; H, 6.16. Found: C, 90.11; H, 6.34.

**Pyrolysis of the Phenylated Compound.**—Attempts to dehydrogenate the phenylated compound with chloranil in *m*-xylene failed: with palladium-on-charcoal pyrolytic cleavage was observed. Pyrolysis in the absence of catalysts was carried out in such a way that the carbon monoxide produced was conducted into an aqueous solution of palladium chloride.[8] After the ketone (0.50 g., 0.001 mole) had been heated for 10 min. at 235°, a black deposit of palladium could be seen in the receiver. At the end of 4 hr. the contents of the flask were allowed to cool and then extracted with an ether–benzene mixture. Evaporation of the solvents left an oil which was chromatographed on 30 g. of alumina. Triphenylmethane and 2-phenylnaphthalene were isolated in yields of 92% (0.215 g.) and 87% (0.180 g.) respectively. Both compounds were identified by mixture melting point determination and infrared analysis. The leaflets of 2-phenylnaphthalene melted at 101–102.5° (recorded[18] m.p. 101–102°).

**Pyrolysis of the *o*-Tolyl Addition Compound.**—The ketone (0.49 g., 0.001 mole) was heated at 230–240° for 4.5 hr. in the manner described for the phenyl adduct, and the resulting oil was chromatographed on 50 g. of alumina. Triphenylmethane was isolated in a yield of 86%. *o*-Tolylnaphthalene was obtained as an oil which solidified when

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(9) A. Orekhoff and M. Tiffeneau, *Compt. rend.*, **182**, 67 (1926).

(10) M. Delacre, *Bull. soc. chim.*, [4] **5**, 1144 (1909).

(11) All melting points are corrected. All boiling points are uncorrected.

(12) P. Chovin and J. Gunthart, *Bull. soc. chim.*, [5] **12**, 105 (1945).

(13) W. H. Linnell and I. M. Roushdi, *Quart. J. Pharm. and Pharmacol.*, **14**, 270 (1941).

(14) W. A. Mosher and M. L. Huber, THIS JOURNAL, **73**, 795 (1951).

(15) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(16) The infrared spectra were recorded by Mr. James Brader, Mr. Paul McMahon and Miss Mary DeMott.

(17) Microanalyses were performed by Mr. Josef Nemeth, Miss Claire Higham and Mrs. Frederick Ju.

(18) N. Campbell and D. Kidd, *J. Chem. Soc.*, 2154 (1954)

chilled, m.p. 42–45° (recorded[19] m.p. 45–46°), yield 69.5%. The 1,3,5-trinitrobenzene derivative melted at 100.5–101.5° (recorded m.p. 101.2–102.5°[19]). The carbon monoxide test was again positive.

**Pyrolysis of the *p*-Tolyl Addition Compound.**—From this ketone (0.5 g., 0.001 mole), heated at 235–245° for 4.5 hr., was obtained an oil. When chromatographed on 50 g. of alumina, it gave triphenylmethane (90% yield) and 2-*p*-tolylnaphthalene, m.p. 96–97° (85% yield). The infrared spectrum of this compound has peaks which can be assigned to aliphatic hydrogen (2910 cm.$^{-1}$) and *p*-substituted phenyl (810 cm.$^{-1}$); three bands (850, 890, 945 cm.$^{-1}$) of medium to strong intensity are also present. Likewise these three bands are found in the spectra of 2-phenyl- and 2-*o*-tolylnaphthalene. The test for carbon monoxide was found to be positive for this reaction also. The tolylnaphthalene was analyzed.

*Anal.* Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.83; H, 6.27.

**Synthesis of 2-*p*-Tolylnaphthalene.**—The procedure employed here is similar to that used by Friedel, Orchin and Reggel in the preparation of 2-*o*-tolylnaphthalene.[19] The lithium reagent from 2-bromonaphthalene was prepared by heating a mixture of 1.90 g. (0.27 g. atom) of freshly-cut lithium pieces and 20.0 g. (0.096 mole) of 2-bromonaphthalene in a solvent system consisting of 95 ml. of anhydrous ether and 25 ml. of sodium-dried benzene. After the mixture had been boiled for 2 hr., much of the lithium had disappeared. To this red-colored mixture was added a solution of 11.9 g. (0.106 mole) of freshly distilled *p*-methylcyclohexanone in 45 ml. of anhydrous ether. The mixture became orange in color within a few minutes. After being heated under reflux for 6.5 hr., it was decomposed by cautious addition of 100 ml. of ice-water. The organic layer was concentrated to an oil, the spectrum of which possessed an intense, broad band at 3500 cm.$^{-1}$. Twenty grams of freshly fused, powdered potassium bisulfate was added to the crude oil, and the mixture was heated at 160–170° for 2.5 hr. The flask was cooled, and its contents were extracted with benzene. Removal of the organic solvent left an oil which was partially fractionated. All fractions boiling at or below 110° at 5 mm. pressure were discarded. To the crude, residual, fluorescent material was added 1.2 g. of 10% palladium-on-charcoal, and this mixture was heated for 2.5 hr. at 310–325°. After the flask had cooled, its contents were leached with benzene. Removal of the organic solvent left an oil which deposited impure crystals of 2,2-binaphthyl. This hydrocarbon was purified and identified by a mixture melting point determination with an authentic sample. The remaining oil was chromatographed on 320 g. of alumina. A white, crystalline compound melting at 95–96.5° was isolated, yield 4.52 g. (20% yield, based on the 2-bromonaphthalene converted). A mixture melting point determination and an infrared analysis showed the synthetic compound to be identical to the 2-*p*-tolylnaphthalene obtained from the pyrolysis.

**Hydrogenation of the Phenylated Compound.**—The hydrogenation was accomplished in a microhydrogenation apparatus by use of sodium-dried, thiophene-free benzene. The benzene was necessary since the ketone was very sparingly soluble in the solvents normally employed for such reductions. When 0.026 g. of platinum oxide had been reduced, a solution of 0.30 g. (0.0006 mole) of the ketone in 18 ml. of dry, thiophene-free benzene was added. The hydrogenation was completed within 1 hr. Removal of the catalyst and evaporation of the benzene left an oil which, when triturated with alcohol, became a solid. Recrystallization from acetic acid gave white crystals melting at 163–164.5°, identified tentatively as 1-(1,2,3,4-tetrahydro-2-phenyl)-naphthyl trityl ketone. The yield was practically quantitative. The infrared spectrum of this compound has peaks for aromatic hydrogen (3050, 3080 cm.$^{-1}$), aliphatic hydrogen (2925 cm.$^{-1}$), a non-conjugated ketone group (1704 cm.$^{-1}$), monosubstituted phenyl (700 cm.$^{-1}$) and *o*-substituted phenyl (745 cm.$^{-1}$). The only bands in the range 700–900 cm.$^{-1}$ are those assigned to mono- and *o*-substituted phenyl. In mixture melting point determinations the compound depressed the melting points of both the starting material and 1-naphthyl trityl ketone.

*Anal.* Calcd. for $C_{36}H_{30}O$: C, 90.34; H, 6.32. Found: C, 90.16; H, 6.18.

When a mixture of 0.030 g. of platinum oxide, 0.20 g. (0.0005 mole) of 1-naphthyl trityl ketone and 30 ml. of sodium-dried thiophene-free benzene was subjected to hydrogenation under the conditions employed with the phenylated compound, the ketone was recovered nearly quantitatively. An attempted high-pressure hydrogenation (1000 lb. per sq. in.) of 1-naphthyl trityl ketone also failed, starting material again being recovered unchanged.

URBANA, ILL.

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(19) R. A. Friedel, M. Orchin and L. Reggel, THIS JOURNAL, **70**, 199 (1948).

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

# Reactions of Amines. IV. Pyrolysis of Dialkyl N-Alkylphosphoramidates[1,2]

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The preparation of six dialkyl N-alkylphosphoramidates is described. The pyrolysis at 350–400° of these phosphoramidates gave mixtures of olefin and tertiary amine.

The pyrolysis of N-alkylacetamides to olefins[1,4] appears to require temperatures 100° or more above those required for the pyrolysis of the corresponding alkyl acetates, whereas the pyrolysis of alkyl phosphates[5] requires temperatures of 50–100° less than those for the acetates. Since the foregoing reactions are not necessarily related mechanistically, it may not be valid to predict that the pyrolysis of dimethyl N-alkylphosphoramidates to olefins should require lower pyrolysis temperatures than the N-alkylacetamides. Nevertheless, the work described in this communication was undertaken to test such a prediction.

While this work was in progress two other studies of the pyrolysis of phosphoramidates were described. Thus, Gerrard and Jeacocke[6] reported that heating dialkyl N-arylphosphoramidates to 240–250° gave about 95% yields of N-alkylanilines. According to their results the phosphoramidates of primary aromatic amines gave almost exclusively the secondary alkylarylamine. The latter results have been challenged recently by Cadogan,[7] who obtained largely the tertiary dialkylarylamine in similar pyrolyses. Codogan reported also that

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(1) Paper III, THIS JOURNAL, **80**, 4588 (1958).

(2) This work was supported in part by grant G-3689 of the National Science Foundation.

(3) Minnesota Mining and Manufacturing Co. Fellow, 1955–1956.

(4) W. J. Bailey and C. N. Bird, *J. Org. Chem.*, **23**, 996 (1958).

(5) H. E. Baumgarten and R. A. Setterquist, *ibid.*, **78**, 2605 (1957).

(6) W. Gerrard and G. J. Jeacocke, *Chemistry & Industry*, 1538 (1954).

(7) J. I. G. Cadogan, *J. Chem. Soc.*, 1079 (1957).