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

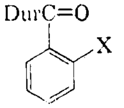
o-Vinylation of Hindered Diaryl Ketones by Use of Vinylmagnesium Bromide

REYNOLD C. FUSON AND MEHM TIN MON[1]

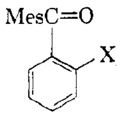
Received July 5, 1960

Hindered *o*-methoxy diaryl ketones react with vinylmagnesium bromide to give the corresponding vinyl ketones. When the leaving group is phenoxyl the yield of the vinyl ketone is higher. The structure of these ketones was determined by reference to the ethyl compounds made from them by hydrogenation. The action of vinylmagnesium bromide on 1-mesitoyl-4-methoxynaphthalene and 1-naphthyl triphenylmethyl ketone has been studied.

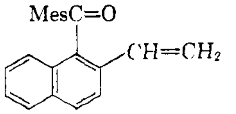
In connection with the problem of 1,6 addition involving the side chain[2] it appeared that an easy route to the vinyl ketone needed might be found in the reaction of hindered *o*-methoxy diaryl ketones with vinyl Grignard reagents. The first compound to be studied was duryl *o*-methoxyphenyl ketone (Ia) which was treated with vinylmagnesium bromide. When 4 to 16 molar equivalents of the reagent and a long reaction time were employed, several products were formed. Apparently duryl *o*-vinylphenyl ketone (Ie) which was first formed had partly undergone secondary reactions under the influence of the excess Grignard reagent. The desired ketone (Ie) was obtained in 40–42% yield by using 1.5 to 2 moles of the reagent to one mole of the methoxy ketone, a short reaction time, and a fairly large amount of tetrahydrofuran. This procedure served also to make duryl *o*-isopropenylphenyl ketone (If), mesityl *o*-vinylphenyl ketone (IIa), and 1-mesitoyl-2-vinylnaphthalene (III) in satisfactory yields. The yield of the vinylated product was increased when a phenoxyl substituent was used in place of the methoxyl as a leaving group. Thus, *o*-duroylstyrene was realized in a 64% yield by treating duryl *o*-phenoxyphenyl ketone (Ib) with vinylmagnesium bromide. When duryl *o*-bromophenyl ketone (Ic) was treated with this reagent, debromination[3] occurred, and benzoyldurene (Id) was isolated.



Ia. X = OCH_3. Ib. X = OC_6H_5
Ic. X = Br. Id. X = H
Ie. X = $CH{=}CH_2$. If. X = $C(CH_3){=}CH_2$
Ig. X = C_2H_5



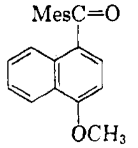
IIa. X = $CH{=}CH_2$
IIb. X = C_2H_5



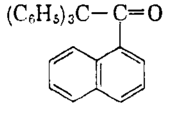
III

The structures of *o*-duroylstyrene and *o*-mesitoylstyrene were established by reference to duryl *o*-ethylphenyl ketone (Ig) and mesityl *o*-ethylphenyl ketone (IIb), respectively, to which they could be readily transformed by hydrogenation. The saturated ketones were made, in turn, by treating the corresponding methoxy ketones with the ethyl Grignard reagent. Duryl *o*-isopropylphenyl ketone had been synthesized previously by two independent methods.[2]

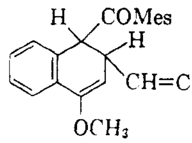
The ability of vinylmagnesium bromide to add to hindered ketones in the conjugate manner has been studied with 1-mesitoyl-4-methoxynaphthalene (IV) and 1-naphthyl triphenylmethyl ketone (V). From the reaction of the vinyl Grignard reagent with the ketone (IV) 1-mesitoyl-4-methoxy-2-vinyl-1,2-dihydronaphthalene (VI) was obtained in 50% yield. This dihydro compound readily decolorized bromine in carbon tetrachloride and 1% potassium permanganate solution. The action of vinylmagnesium bromide on the ketone V under drastic conditions gave, however, mainly the cleavage product, triphenylmethane, and a reduction product which may be triphenylmethyl-1-naphthylmethane.



IV



V



VI

EXPERIMENTAL[4]

Vinylmagnesium bromide.[5,6] Part of a solution of 5 g. of anhydrous vinyl bromide gas in 20–30 ml. of tetrahydrofuran, freshly redistilled from lithium aluminum hydride, was added to 1 g. of magnesium turnings blanketed with dry nitrogen. The mixture was stirred vigorously; an exothermic reaction usually started within 5 min. If a more dilute solution of vinyl bromide in tetrahydrofuran was employed, the mixture had to be heated gently to start the reaction. The rest of the solution was then added slowly to keep the solvent at gentle reflux, a Dry Ice–acetone condenser being used for cooling. When the addition was complete the mixture was heated

---

[1] Deputationist of the government of the Union of Burma.

[2] R. C. Fuson, W. D. Emmons, and S. G. Smith, Jr., *J. Am. Chem. Soc.*, **77**, 2503 (1955).

[3] R. C. Fuson and M. D. Armstrong, *J. Am. Chem. Soc.*, **63**, 2650 (1941).

[4] All melting points are corrected.

[5] H. Normant, *Compt. rend.*, **239**, 1510 (1954).

[6] H. Normant, *Bull. soc. chim. France*, **1957**, 728.

under reflux for 15–30 min. and cooled. The yield of the Grignard reagent, determined by titration,[7] was 95%.

Reaction of vinylmagnesium bromide with duryl o-methoxyphenyl ketone. The Grignard reagent, prepared from 2 g. (0.08 g.-atom) of magnesium and 10 g. of vinyl bromide in 50 ml. of tetrahydrofuran, was filtered through glass wool under nitrogen pressure into a solution of 11 g. (0.04 mole) of duryl *o*-methoxyphenyl ketone[8] in 125 ml. of tetrahydrofuran. The mixture was stirred under nitrogen at room temperature for 10 min., cooled in an ice bath, and treated with 25 ml. of cold, saturated ammonium chloride solution. The product was extracted with ether; the ether layer was washed and dried over anhydrous sodium sulfate. Removal of the solvent left a yellow oil which was subjected to chromatography, alumina serving as the adsorbent. Elution with cyclohexane followed by recrystallization of the product from absolute ethanol gave duryl *o*-vinylphenyl ketone as colorless crystals, m.p. 132.5–133.5°; yield 4.2–4.4 g. (40–42%). The infrared spectrum[9] contains bands at 1657 cm.$^{-1}$, attributed to a conjugated carbonyl group, at 918, 980, and 1622 cm.$^{-1}$, attributed to a vinyl group, and at 826, 878, and 950 cm.$^{-1}$, attributed to a duryl group.

Anal.[10] Calcd. for $C_{19}H_{20}O$: C, 86.31; H, 7.62. Found: C, 86.51; H, 7.67.

Elution of the column with ether gave 0.1 g. of a colorless powder which, when crystallized repeatedly from chloroform-methanol, melted at 216–218°. Its infrared spectrum shows a strong carbonyl absorption at 1650 cm.$^{-1}$, an alcoholic absorption at 3435 cm.$^{-1}$, and weak absorption bands at 922, 975, and 1625 cm.$^{-1}$ characteristic of a vinyl group. This compound appears to be a dimer of *o*-duroylstyrene.

Anal. Calcd. for $C_{38}H_{40}O_2$: C, 86.31; H, 7.62. Found: C, 86.24; H, 7.74.

In one run, employing the normal addition of a solution of 0.01 mole of duryl *o*-methoxyphenyl ketone in 30 ml. of tetrahydrofuran to 0.04 mole of the vinyl Grignard reagent, a colorless compound, m.p. 245–249°, was isolated in addition to *o*-duroylstyrene. Its infrared spectrum is very similar to that of the product melting at 216–218°.

Reaction of vinylmagnesium bromide with duryl o-phenoxyphenyl ketone. To a solution of 33 g. (0.1 mole) of duryl *o*-phenoxyphenyl ketone[11] in 300 ml. of tetrahydrofuran was added, slowly with stirring, the vinyl Grignard reagent made from 3.6 g. (0.15 g.-atom) of magnesium and 20 g. of vinyl bromide in 90 ml. of the same solvent. The reaction mixture was stirred for an additional 12 min., cooled, and decomposed with cold ammonium chloride solution. The organic layer was washed and concentrated; the solid product was crystallized twice from ethanol to give pure duryl *o*-vinylphenyl ketone m.p. 132.5–133.5°; yield 16.9 g. (64%).

Reaction of vinylmagnesium bromide with duryl o-bromophenyl ketone. A solution of 6.34 g. (0.02 mole) of the bromo ketone[8] in 50 ml. of tetrahydrofuran was added dropwise during a period of 1.6 hr. to 0.08 mole of vinylmagnesium bromide in 35 ml. of the solvent. The reaction was slightly exothermic causing a gentle reflux. A curdy, yellow precipitate began to appear toward the end of the addition period. The mixture was diluted with 20 ml. of the solvent, stirred at 25° for 10 hr., and heated under reflux 1 hr. longer. Then 15 ml. of ammonium chloride solution was added. The ether extracts were washed and dried. Removal of ether gave a dark red oil which shows a carbonyl absorption (1670 cm.$^{-1}$) in the infrared spectrum. Chromatographic treatment of the oil yielded 1 g. (21%) of colorless, cubic crystals, m.p. 118–119.5°. A mixed melting point with an authentic sample of duryl phenyl ketone, m.p. 119–120°, was not depressed.

Duryl o-ethylphenyl ketone. (a) A solution of 0.445 g. of duryl *o*-vinylphenyl ketone in 25 ml. of purified tetrahydrofuran was treated with hydrogen over 0.5 g. of platinum oxide for 12 hr. at room temperature and a pressure of 150 lb. The product was crystallized from aqueous ethanol to give a quantitative yield of duryl *o*-ethylphenyl ketone, colorless plates, m.p. 120–121°. The infrared spectrum has a carbonyl peak (1663 cm.$^{-1}$), but no vinyl absorption.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.66; H, 8.32. Found: C, 85.39; H, 8.42.

(b) To a solution of a Grignard reagent, made from 0.5 g. of magnesium, 3.65 g. of redistilled ethyl bromide, and 20 ml. of tetrahydrofuran, was added in the course of 20 min. a solution of 1.34 g. of duryl *o*-methoxyphenyl ketone in 25 ml. of the same solvent. The reaction mixture darkened gradually during an additional 30 min. of stirring at 25°. It was cooled to 0° and treated with 25 ml. of saturated ammonium chloride solution. Fractional crystallization of the products from ethanol gave 100 mg. of colorless crystals, m.p. 230–232°. A mixture melting point determination and a comparison of infrared spectra showed it to be 9,10-dihydro-9,10-dihydroxy-9,10-didurylphenanthrene.[8] When the mother liquor was concentrated duryl *o*-ethylphenyl ketone crystallized as colorless plates, m.p. 120–121°; yield 700 mg. Its infrared spectrum is identical with that of the sample obtained by hydrogenation of *o*-duroylstyrene; also a mixture melting point was not depressed.

Duryl o-isopropenylphenyl ketone. A Grignard reagent was prepared from 2 g. (0.08 g.-atom) of magnesium, 10 g. of 2-bromopropylene and 150 ml. of tetrahydrofuran in a manner similar to that used in making vinylmagnesium bromide. The reagent was filtered into a solution of 11 g. (0.04 mole) of duryl *o*-methoxyphenyl ketone in 150 ml. of tetrahydrofuran. The purple mixture was stirred an additional 10 min. and worked up as usual. The resultant organic material was subjected to chromatography; the duryl *o*-isopropenylphenyl ketone was present in the fractions obtained by elution of the column with cyclohexane and cyclohexane-ether mixtures. Repeated recrystallization of the product from ethanol and from cyclohexane gave colorless crystals, m.p. 145.5–146.5°; reported m.p. 145–147°.[3] The yield was 6.7 g. (58.7%). No depression was observed in a mixture melting point with the authentic sample. The infrared spectrum contains bands at 820, 873, 890, 925, 943, 1003, 1635, 1670, and 3090 cm.$^{-1}$ in agreement with the assigned structure.

Mesityl o-vinylphenyl ketone. Mesityl *o*-methoxyphenyl ketone[12] was made in an improved yield (94%) by heating a mixture of mesityl *o*-bromophenyl ketone with a 5*N* solution of sodium methoxide for 48 hr. under reflux. A solution of 0.04 mole of this ketone in 150 ml. of tetrahydrofuran was treated for 12 min. with 0.08 mole of vinylmagnesium bromide. The product was passed through a column of 200 g. of alumina, elution being accomplished with cyclohexane. Mesityl *o*-vinylphenyl ketone was obtained in the form of long colorless crystals, m.p. 99–100°; yield 5.8 g. (58%). The infrared spectrum indicates the presence of a conjugated carbonyl function (1655 cm.$^{-1}$), an ethylenic linkage (1620 cm.$^{-1}$), and a mesityl group (850, 910, and 955 cm.$^{-1}$).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.38; H, 7.25. Found: C, 86.42; H, 7.53.

Mesityl o-ethylphenyl ketone. (a) A solution of 0.5 g. (0.002 mole) of *o*-mesitoylstyrene in 50 ml. of purified dioxane was treated with hydrogen in the presence of 0.1 g. of platinum oxide in an Adams microhydrogenation apparatus. The vol-

---

[7] H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, 51, 1576 (1929).

[8] R. C. Fuson and R. O. Kerr, *J. Org. Chem.*, 19, 373 (1954).

[9] The infrared spectra were determined by Mr. Brian Cloonan, Mr. Paul McMahon, Mrs. Mary Verkade, and Miss Charlene Leubke.

[10] The microanalyses were performed by Mr. Josef Nemeth, Miss Claire Higham, Mrs. A. S. Bay, and Miss Jane Liu.

[11] R. C. Fuson and W. S. Friedlander, *J. Am. Chem. Soc.*, 76, 4989 (1954).

[12] R. C. Fuson and C. Hornberger, Jr., *J. Org. Chem.*, 16, 637 (1951).

ume of hydrogen taken up in 1 hr. and 30 min. was 44.8 ml. (0.002 mole). The product isolated was sublimed at 97–102° and 0.5 mm. pressure and recrystallized from aqueous ethanol to give colorless needles, m.p. 79–80°; yield 0.37 g. (74%). The infrared spectrum shows a carbonyl absorption at 1660 cm.$^{-1}$

Anal. Calcd. for $C_{13}H_{20}O$: C, 85.68; H, 7.99. Found: C, 85.42; H, 8.15.

(b) A solution of 1.5 g. of mesityl *o*-methoxyphenyl ketone in 50 ml. of anhydrous ether was added to a Grignard reagent made from 0.24 g. of magnesium, 2 ml. of redistilled ethyl iodide, and 35 ml. of anhydrous ether. The mixture was stirred for 5 min. and treated at 0° with 10 ml. of saturated ammonium chloride solution. Chromatographic separation of the products gave 0.18 g. of mesityl *o*-ethylphenyl ketone, m.p. 81–81.5°, 0.7 g. of the starting methoxy ketone, and 0.07 g. of *o*-(*o'*-mesitoylphenyl) phenylmesitylcarbinol, m.p. 237–239.5°.[13]

1-Mesitoyl-2-methoxynaphthalene. A modification of the procedure of Fuson and Fang[14] was used. The experiment was carried out at 0° for 23.5 hr. in the presence of a limited amount of anhydrous aluminum chloride and a large volume of carbon disulfide. From 50.4 g. (0.276 mole) of mesitoyl chloride, and 39.6 g. (0.250 mole) of 2-methoxynaphthalene was obtained 49.5 g. (65.7%) of 1-mesitoyl-2 methoxynaphthalene, m.p. 126–127°. A mixture melting point with an authentic sample was not lowered. The infrared spectrum contains bands assignable to a conjugated carbonyl group (1663 cm.$^{-1}$), an aryl ether group (1235 cm.$^{-1}$), a 1,2-disubstituted naphthalene ring (820 and 750 cm.$^{-1}$), and a mesityl group (852 cm.$^{-1}$).

1-Mesitoyl-2-vinylnaphthalene. To a solution of 20 g. of 1-mesitoyl-2-methoxynaphthalene in 150 ml. of tetrahydrofuran was added in 2 min. a Grignard reagent made from 3 g. of magnesium, 15 g. of vinyl bromide, and 100 ml. of tetrahydrofuran. The reaction was slightly exothermic. The red mixture was stirred for an additional 10 min. and treated with 30 ml. of cold saturated ammonium chloride solution. Concentration of the organic phase followed by chromatographic treatment gave colorless rectangular crystals of 1-mesitoyl-2-vinyl-naphthalene, m.p. 75–76°; yield 10.8 g. (54.5%). The infrared spectrum contains bands at 910, 980, 1620, and 1820 cm.$^{-1}$, attributed to a vinyl group, and at 1653 cm.$^{-1}$, attributed to a carbonyl group. The compound also took up a molecule of hydrogen in an Adams microhydrogenation apparatus.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.71; H, 6.46.

Reaction of vinylmagnesium bromide with 1-mesitoyl-4-methoxynaphthalene. A solution of 3.04 g. (0.01 mole) of the ketone, made in 75.3% yield by the Friedel-Craft condensation of 1-methoxynaphthalene with mesitoyl chloride, in 60 ml. of tetrahydrofuran was added slowly over 50 min. to a solution of 0.08 mole of vinylmagnesium bromide in 60 ml. of tetrahydrofuran. The dark green mixture was then heated under reflux for 2 hr. during which time it turned dark red. Treatment of the mixture with saturated ammonium chloride solution and chromatographic separation of the reaction products as usual gave colorless cubic crystals of 1-mesitoyl-2-vinyl-4-methoxy-1,2-dihydronaphthalene which, after being recrystallized six times from cyclohexane and twice from ethanol, melted at 121.5–122.5°, yield 1.65 g. (50%). The infrared spectrum has bands at 1693 cm.$^{-1}$ attributed to a carbonyl group, at 855 cm.$^{-1}$ attributed to a mesityl group, and at 920, 1000, 1615, and 1648 cm.$^{-1}$, attributed to ethylenic double bonds. The compound readily decolorized bromine in carbon tetrachloride and 1% potassium permanganate solution.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.09; H, 7.28. Found: C, 83.12; H, 7.15.

Reaction of vinylmagnesium bromide with 1-naphthyltriphenylmethyl ketone. To 0.08 mole of vinylmagnesium bromide in 35 ml. of tetrahydrofuran was added in the course of 55 min. a solution of 2.99 g. (0.0075 mole) of 1-naphthyltriphenylmethyl ketone,[15] in 30 ml. of tetrahydrofuran. The greenish mixture was heated at 66° for 24 hr. during which time a brown precipitate appeared gradually, and 20 ml. of tetrahydrofuran was added. At the end of the reflux period the solution was dark red. Cold saturated ammonium chloride solution (50 ml.) was added and the mixture was heated under reflux in a stream of nitrogen for 10 hr. to ketonize any conjugate addition product present. The organic layer was washed, dried over anhydrous sodium sulfate, and concentrated to a yellow oil. Chromatographic separation of the oil gave 0.4 g. (22%) of triphenylmethane, m.p. 89–90°, and 1.24 g. (43%) of a hydrocarbon, m.p. 154–155°. This same hydrocarbon was obtained as the main product along with triphenylmethane when 1-naphthyltriphenylmethyl ketone was treated for 24 hr. in boiling anisole with 15 molar equivalents of methylmagnesium iodide.[16] A mixture melting point of the two samples of the hydrocarbon showed no depression. Its infrared spectrum has bands assignable to aromatic hydrogen (3060 cm.$^{-1}$), aliphatic hydrogen (shoulder near 2900 cm.$^{-1}$), monosubstituted phenyl (695 cm.$^{-1}$), and an α-substituted naphthalene ring (795, 770, 757, and 742 cm.$^{-1}$). The information about this hydrocarbon suggests that it may be triphenylmethyl-1-naphthylmethane.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.70; H, 6.29. Found: C, 93.79; H, 6.11.

URBANA, ILL.

---

[13] R. C. Fuson and C. Hornberger, Jr., *J. Org. Chem.*, **16**, 631 (1951).

[14] R. C. Fuson and F. T. Fang, *J. Am. Chem. Soc.*, **77**, 3781 (1955).

[15] R. C. Fuson and K. D. Berlin, *J. Am. Chem. Soc.*, **81**, 2130 (1959).

[16] Private communication from Dr. K. D. Berlin.