[Contribution from the Department of Chemistry of the Punjab University and the Department of Organic Chemistry, Indian Association for the Cultivation of Science]

FRIEDEL-CRAFTS REACTION INVOLVING UNSATURATED KETONES AND ESTERS. II. CONVENIENT SYNTHESES OF SOME ALKYLNAPHTHALENES

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In Part I of this series (1) it was reported that naphthalene condenses with ethyl allylacetate in the presence of aluminum chloride in carbon disulphide to give a satisfactory yield of ethyl 4-(β-naphthyl)valerate. The present communication describes the results of our study on the Friedel-Crafts alkylation of benzene, toluene, and *m*-xylene with ethyl allylacetate, which constitutes a convenient route to a variety of alkylnaphthalenes.

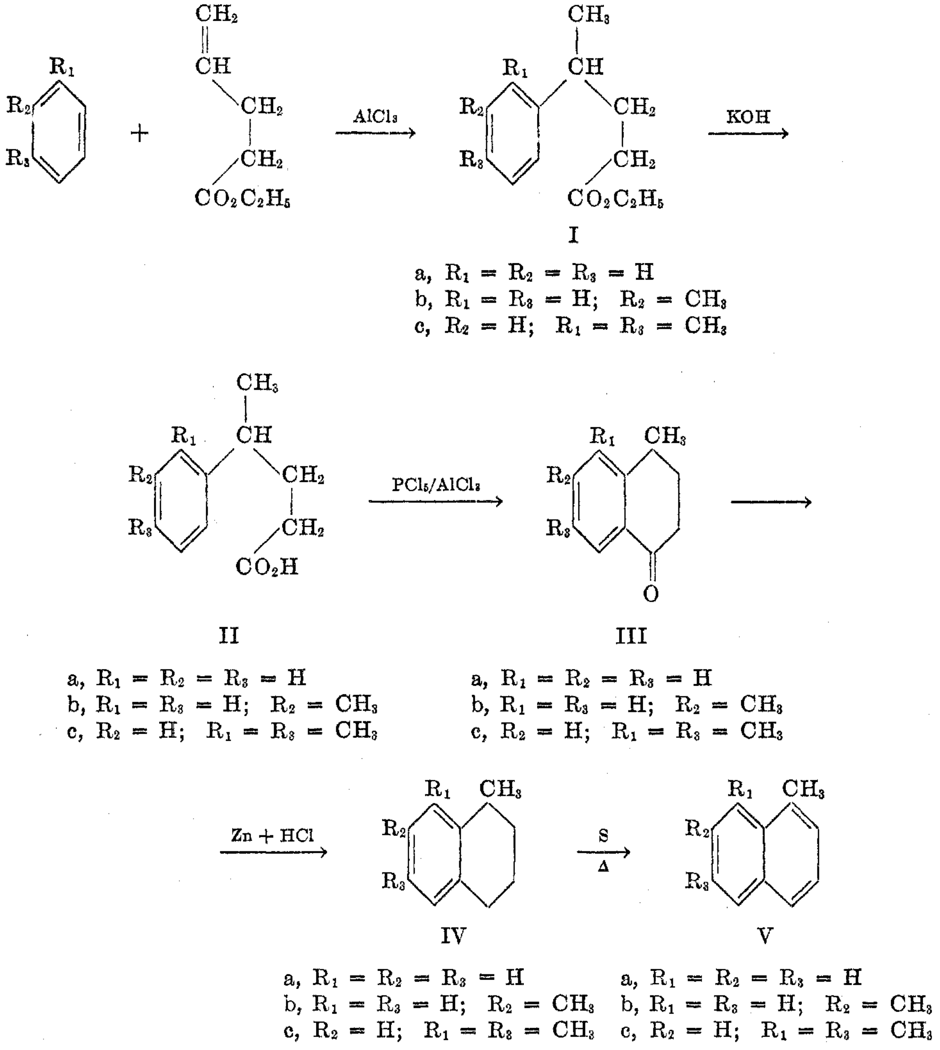
Benzene on being subjected to the aluminum chloride-catalyzed reaction at 0–5° with ethyl allylacetate gave a 93% yield of ethyl 4-phenylvalerate (Ia) which was quantitatively hydrolyzed to the corresponding acid (IIa). Cyclization of the acid (IIa) was effected by Johnson's inverse cyclization process (2) when an excellent yield of 4-methyl-1-tetralone (IIIa) was obtained. Similar convenient routes to tetralones have been recently reported (3, 11). The ketone (IIIa) was reduced by the Clemmensen method and the resulting tetralin derivative (IVa) was dehydrogenated with sulphur to afford 1-methylnaphthalene (Va) (4).

The method was then extended to the possibility of a new synthesis of 4-(*p*-tolyl)valeric acid which is an important intermediate in the synthesis of cadalene (5). But toluene reacted with ethyl allylacetate to give an excellent yield of ethyl 4-(*m*-tolyl)valerate (Ib) which was hydrolyzed to the corresponding acid (IIb). The proof of the structure of the product (Ib) was obtained by the alkaline permanganate oxidation of the acid (IIb) to isophthalic acid, identified through its dimethyl ester. The crude oxidized product failed to respond to the phthalein test and a search for terephthalic acid through crystallization of the crude esterified product was futile showing the absence of any significant amount of *ortho* and/or *para* isomers in the Friedel-Crafts condensation product.

Furthermore, the S-benzylisothiuronium salt of the acid (IIb) was proved to be identical with that of an authentic sample of 4-(*m*-tolyl)valeric acid which was synthesized unequivocally from *m*-tolylmagnesium bromide and ethyl levulinate through the usual sequence of reactions.

Colonge and Grimaud (6), on the other hand, have reported a *para* orientation in the above Friedel-Crafts condensation. This is indeed very interesting particularly since the temperature employed by these authors is higher than that in the present investigation. However, the recent observations of Chaudhuri (7) on the aluminum chloride-catalyzed reaction between toluene and γ-valerolactone support our results. Anomalies in the orientation in di- or tri-alkylation have been explained on the basis of the reversibility of the Friedel-Crafts alkylation (8). Again, normal alkylation to form the 1,2,4-trialkyl derivative, followed by elimination of the alkyl group at the 1-position was postulated (9) in order to account for the abnormal *m*-alkylation.

FORMULAE



I

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_2 = H$; $R_1 = R_3 = CH_3$

II

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_2 = H$; $R_1 = R_3 = CH_3$

III

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_2 = H$; $R_1 = R_3 = CH_3$

IV

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_2 = H$; $R_1 = R_3 = CH_3$

V

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_2 = H$; $R_1 = R_3 = CH_3$

In view of the above observations with toluene it was of interest to study the behavior of *meta*-xylene under comparable conditions, when ethyl 4-(2′,4′-dimethylphenyl)valerate (Ic) was obtained in 82% yield. The orientation in this product was established by the alkaline permanganate oxidation of the corresponding acid (IIc) to benzene-1,2,4-tricarboxylic acid. The acids (IIb and IIc) were subjected to the same sequence of reactions as in the case of (Ib), and 1,7-dimethylnaphthalene (Vb) and 1,6,8-trimethylnaphthalene (Vc) were obtained through the corresponding tetralone (IIIb and IIIc) and tetralin derivatives (IVa and IVb) respectively. 1,7-Dimethylnaphthalene (Vb) was identified by the mixture melting point of its picrate with an authentic sample of the picrate of 1,7-dimethylnaphthalene prepared according to Barnett and Sanders (10).

The orientation in the Friedel-Crafts product from *m*-xylene and ethyl allylacetate, although in agreement with the parallel observation by Mosby (11), is in contradistinction to our expectations in view of our experience with toluene. It was expected that the Friedel-Crafts alkylation of toluene and xylene would give rise to mixtures of isomers of different orientations (12). But the close proximity of the crude melting points of the solid derivatives, prepared in the course of this investigation, to those recorded in the literature, indicates the homogeneity of the Friedel-Crafts products.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Analyses marked with an asterisk (*) are by Drs. Weiler and Strauss, Oxford.

Ethyl 4-phenylvalerate (Ia). Anhydrous aluminum chloride (20.8 g., 2 moles) was added in five portions during 45 minutes to dry thiophene-free benzene (80 cc.) placed in a three-necked flask fitted with a mercury-sealed stirrer, a thermometer, and a calcium chloride guard tube. The mixture was stirred vigorously and chilled to 0–5°. After the addition of each lot of anhydrous aluminum chloride, 2 g. of ethyl allylacetate was added (10 g. in all; 1 mole). The temperature was not allowed to go beyond 5°. After the additions were complete, the mixture was stirred for three hours more at 5°. It was then decomposed with iced hydrochloric acid, and the benzene layer was washed with dilute hydrochloric acid, sodium carbonate solution, water, and then dried over sodium sulphate. The solvent being removed, the residue was distilled under reduced pressure when 15 g. (93.2%) of ethyl 4-phenylvalerate (Ia) was obtained, b.p. 134–136°/7 mm.

Anal. Calc'd for $C_{13}H_{18}O_2$: C, 75.72; H, 8.74.
Found: C, 75.34; H, 8.89.

4-Phenylvaleric acid (IIa). The above ester (IIa, 15 g.) was hydrolyzed by refluxing it for about 12 hours with alcoholic caustic potash (7.5 g. of potassium hydroxide, 5 cc. of water and 165 cc. of ethanol). After removing most of the alcohol, the mixture was diluted with water and was worked up in the usual way, when 4-phenylvaleric acid was obtained as colorless, mobile oil, b.p. 140°/3 mm.; yield, 12 g. (92%).

Anal. Calc'd for $C_{11}H_{14}O_2$: C, 74.15; H, 7.86.
Found: C, 73.82; H, 7.62.

The *S-benzylisothiuronium* derivative was prepared in the usual way and was crystallized from 50% ethanol, m.p. 150–151°.

*Anal.** Calc'd for $C_{19}H_{24}N_2O_2S$: N, 8.13. Found: N, 8.05.

4-Methyl-1-tetralone (IIIa). Phosphorus pentachloride (14.24 g., 1.1 moles) was placed in a 100-cc. distillation flask and covered with dry thiophene-free benzene. The acid (IIa; 11 g., 1 mole), dissolved in dry thiophene-free benzene (25 cc.) was added in two portions and the acid chloride of IIa was thus prepared. The benzene and phosphorus oxychloride were removed under reduced pressure. The acid chloride thus obtained was dissolved in dry thiophene-free benzene (30 cc.), cooled, and added all at once to a cold suspension of anhydrous aluminum chloride (9.06 g., 1.1 moles) in petroleum ether (50 cc.). On warming to room temperature (24°) the reaction started with a vigorous evolution of hydrogen chloride. When the vigor of the reaction subsided, the mixture was just warmed on the water-bath at 50° and removed, and the reaction was allowed to proceed as such; this was repeated 3 to 4 times till all the aluminum chloride had dissolved. The mixture was dark-brown in color. It was decomposed with iced hydrochloric acid and worked up in the usual way, when 8.5 g. (86.7%) of the desired ketone (IIIa) was obtained, b.p. 144°/17 mm.

Anal. Calc'd for $C_{11}H_{12}O$: C, 82.50; H, 7.50.
Found: C, 82.62; H, 7.36.

The *semicarbazone* was prepared in the usual way and was crystallized as colorless leaflets from ethanol, m.p. 209–210° [lit. (16) m.p. 210°].

*Anal.** Calc'd for $C_{12}H_{15}N_3O$: N, 19.35. Found: N, 19.00.

The *2,4-dinitrophenylhydrazone* was prepared in the usual manner and was crystallized from ethyl acetate, m.p. 218–219° [lit. (16) m.p. 218°].

*Anal.** Calc'd for $C_{17}H_{16}N_4O_4$: N, 16.47. Found: N, 16.10.

1-Methyltetralin (IVa). The ketone (IIIa, 8 g.) was reduced with amalgamated zinc (20 g.), concentrated hydrochloric acid (35 cc.), water (17 cc.), toluene (30 cc.), and acetic acid (1 cc.) by refluxing for 36 hours. After each six hours 8 cc. of concentrated hydrochloric acid was added. The reaction mixture was then worked up in the usual way and 6.6 g. (83%) of 1-methyltetralin was obtained, boiling at 87–88°/7 mm.

Anal. Calc'd for $C_{11}H_{14}$: C, 90.41; H, 9.59.
Found: C, 90.13; H, 9.46.

1-Methylnaphthalene (Va). 1-Methyltetralin (IVa, 6.6 g.) was dehydrogenated with sulphur (3 g.) at 180° for about 6 hours. The product was then steam-distilled and the distillate was worked up for 1-methylnaphthalene, b.p. 110°/12 mm.; yield 4 g. (66%).

Anal. Calc'd for $C_{11}H_{10}$: C, 92.96; H, 7.04.
Found: C, 92.63; H, 6.84.

The *picrate* was prepared in the usual way and was crystallized as orange-red needles from ethanol, m.p. 141–141.5° [lit. (17) m.p. 141–142°].

*Anal.** Calc'd for $C_{17}H_{13}N_3O_7$: N, 11.32. Found: N, 11.20.

Ethyl 4-(m-tolyl)valerate (Ib). Toluene (80 cc.) was subjected to an aluminum chloride-catalysed reaction with ethyl allylacetate (15 g., 1 mole) and anhydrous aluminum chloride (31.2 g., 2 moles) exactly according to the conditions employed for the preparation of Ia, and 21 g. (81%) of ethyl 4-(*m*-tolyl)valerate (Ib), boiling at 140–141°/7 mm., was obtained.

Anal. Calc'd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09.
Found: C, 76.47; H, 9.21.

4-(m-Tolyl)valeric acid (IIb). The ester (Ib, 21 g.) was hydrolyzed with alcoholic caustic potash (potassium hydroxide, 10 g.; water, 6 cc.; and ethyl alcohol, 220 cc.) by refluxing for about 12 hours and then was worked up in the usual way to give the acid (IIb) as a colorless mobile liquid, b.p. 180–182°/13 mm.; yield 18 g. (98%).

Anal. Calc'd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33.
Found: C, 74.64; H, 8.48.

The *S-benzylisothiuronium salt* was prepared in the usual way and was crystallized from 50% ethanol, m.p. 140–141°.

*Anal.** Calc'd for $C_{20}H_{26}N_2O_2S$: N, 7.82. Found: N, 7.75.

Oxidation of 4-(m-tolyl)valeric acid with alkaline potassium permanganate. The above acid (IIb, 1 g.) was oxidized by alkaline potassium permanganate in the usual way (13) when about 0.65 g. of isophthalic acid was obtained. This was esterified with diazomethane and the dimethyl ester, b.p. 120°/10 mm., was crystallized from dilute methanol; yield, 0.6 g.; m.p. 67–68° [lit. (14) m.p. 68–69°], undepressed when mixed with an authentic sample of dimethyl isophthalate.

Anal. Calc'd for $C_{10}H_{10}O_4$: C, 61.86; H, 5.16.
Found: C, 62.05; H, 5.45.

4,6-Dimethyl-1-tetralone (IIIb). The acid (IIb, 18 g.) was cyclized in the same manner as in the preparation of IIa, using 21.6 g. of phosphorus pentachloride and 13.8 g. of anhydrous aluminum chloride, when 15 g. (92%) of the tetralone (IIIb), b.p. 120°/2 mm., was obtained as a colorless oil.

Anal. Calc'd for $C_{12}H_{14}O$: C, 82.79; H, 8.04.
Found: C, 82.65; H, 8.26.

The *semicarbazone* was prepared in the usual way and was crystallized from ethanol, m.p. 223–224°.

*Anal.** Calc'd for $C_{13}H_{17}N_3O$: N, 18.18. Found: N, 17.80.

The *2,4-dinitrophenylhydrazone* was prepared in the usual manner and was crystallized as red needles from a mixture of dry benzene and alcohol, m.p. 202–203°.

*Anal.** Calc'd for $C_{18}H_{18}N_4O_4$: N, 15.81. Found: N, 15.50.

1,7-Dimethyltetralin (IVb). The ketone (IIIb, 7 g.) was reduced with amalgamated zinc (18 g.), concentrated hydrochloric acid (30 cc.), toluene (25 cc.), glacial acetic acid (1 cc.), and water (14 cc.) by refluxing for 36 hours at 120–140°. After every six hours 5 cc. of concentrated hydrochloric acid was added. The reaction mixture was worked up in the usual way when the tetralin derivative (IVb) was obtained, b.p. 100°/6 mm.; yield, 5.5 g. (85%).

Anal. Calc'd for $C_{12}H_{16}$: C, 90.00; H, 10.00.
Found: C, 89.82; H, 9.84.

1,7-Dimethylnaphthalene (Vb). The tetralin derivative (IVb, 5.5 g.) was dehydrogenated with sulphur (2.5 g.) as in the case of 1-methylnaphthalene, when 3.8 g. (70%) of 1,7-dimethylnaphthalene, b.p. 117–120°/17 mm., was obtained.

Anal. Calc'd for $C_{12}H_{12}$: C, 92.31; H, 7.69.
Found: C, 92.06; H, 7.62.

The *picrate* was prepared in the usual way and was crystallized as lemon-yellow needles from ethanol, m.p. 120–121° [lit. (10) m.p. 121°] undepressed when mixed with an authentic sample (10).

*Anal.** Calc'd for $C_{18}H_{15}N_3O_7$: N, 10.90. Found: N, 11.00.

4-Methyl-4-(m-tolyl)butyrolactone. Ethyl levulinate (21.6 g.) in 200 cc. of benzene was reacted upon in the cold with *m*-tolylmagnesium bromide (prepared from 26 g. of *m*-bromotoluene and 3.5 g. of magnesium in 200 cc. of ether). After the reaction mixture was allowed to stand for one hour it was refluxed on the water-bath for half an hour, then cooled and worked up in the usual way. The solvent was removed and the residue was refluxed with 100 cc. of concentrated hydrochloric acid and the oil was extracted with ether. The ethereal extract was washed with sodium bicarbonate solution and then with 10% caustic potash solution. The caustic potash extract was acidified and the resulting oil was taken up in ether and worked up in the usual way when 12.5 g. of the above lactone, b.p. 180–182°/4 mm. was obtained.

Anal. Calc'd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37.
Found: C, 75.56; H, 7.12.

4-(m-Tolyl)valeric acid. The above lactone (12.0 g.) was reduced by refluxing for 16 hours at 130–140° with hydriodic acid (*d.* 1.7, 65 g.) and red phosphorus (8.0 g.). The cooled and diluted reaction mixture was taken up in ether and the ethereal extract was washed twice with water and then with dilute sodium bicarbonate solution. The bicarbonate extract was acidified with 2 *N* sulphuric acid and the resulting oil was taken up in ether; the ethereal layer was washed with water, sodium thiosulphate solution, and again with water and dried. The solvent was removed and the residue on distillation *in vacuo* gave 6 g. of a colorless viscous oil, b.p. 120–121°/2 mm.

Anal. Calc'd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33.
Found: C, 74.84; H, 8.21.

The *S-benzylisothiuronium salt* prepared in the usual way and crystallized from alcohol melted at 140° undepressed when mixed with *S-benzylisothiuronium salt* of IIb.

Ethyl 4-(2′,4′-dimethylphenyl) valerate (Ic). *m*-Xylene (120 cc.) was subjected to an aluminum chloride-catalyzed reaction with ethyl allylacetate (20 g.) and anhydrous aluminum chloride (41.6 g.) exactly as for Ia and 30 g. (82.2%) of the ester (Ic) was obtained, b.p. 134–136°/2 mm.

Anal. Calc'd for $C_{15}H_{22}O_2$: C, 76.92; H, 9.40.
Found: C, 76.67; H, 9.56.

4-(2′,4′-Dimethylphenyl)valeric acid (IIc). The above ester (Ic, 30 g.) was hydrolyzed by refluxing with alcoholic potash (potassium hydroxide, 15 g.; water, 9 cc.; ethanol, 330 cc.) for about 12 hours. After working up in the usual way, the acid (IIc) was obtained as colorless oil, b.p. 200°/22 mm.; yield, 25 g. (94.6%).

Anal. Calc'd for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74.
Found: C, 75.60; H, 8.52.

The *S-benzylisothiuronium salt* was prepared in the usual way and was crystallized from 50% ethanol, m.p. 119–120°.

*Anal**. Calc'd for $C_{21}H_{28}N_2O_2S$: C, 67.47; H, 7.52.
Found: C, 67.89; H, 7.34.

Oxidation of 4-(2',4'-dimethylphenyl)valeric acid with alkaline potassium permanganate. The above acid (IIc, 1 g.) was oxidized in the usual way (13) when *benzene*-1,2,4-tricarboxylic acid (trimellitic acid) was obtained in 70% yield. It was crystallized from dilute ethanol, m.p. 227–228° [lit. (15) m.p. 228°].

Anal. Calc'd for $C_9H_6O_2$: C, 51.43; H, 2.85.
Found: C, 51.62; H, 2.46.

4,5,7-Trimethyl-1-tetralone (IIIc). The acid (IIc, 25 g.) was converted into its acid chloride with phosphorus pentachloride (27.9 g.) and then cyclized using 17.7 g. of anhydrous aluminum chloride in the same manner as for IIIa, and 20 g. (87.7%) of the ketone (IIIc) was obtained, b.p. 158–160°/10 mm.

Anal. Calc'd for $C_{13}H_{16}O$: C, 82.98; H, 8.51.
Found: C, 83.16; H, 8.18.

The *semicarbazone* was prepared in the usual manner and was crystallized from ethanol, m.p. 225–226° [lit. (11) m.p. 221.6–222.4°].

*Anal.** Calc'd for $C_{14}H_{19}N_3O$: N, 17.14. Found: N, 17.10.

The *2,4-dinitrophenylhydrazone* was prepared in the usual way and was crystallized from ethyl acetate, m.p. 231–232° [lit. (11) m.p. 232.5°].

*Anal.** Calc'd for $C_{13}H_{20}N_4O_4$: N, 15.21. Found: N, 14.80.

1,6,8-Trimethyltetralin (IVc). The ketone (IIIc, 20 g.) was reduced with amalgamated zinc (40 g.), concentrated hydrochloric acid (70 cc.), toluene (40 cc.), acetic acid (2 cc.), and water (34 cc.) by refluxing for 34 hours at 120–140°. After working up in the usual way, 16.1 g. (87%) of the product (IVc) was obtained, b.p. 120–122°/8 mm.

Anal. Calc'd for $C_{13}H_{18}$: C, 89.66; H, 10.34.
Found: C, 89.28; H, 10.21.

1,6,8-Trimethylnaphthalene (Vc). The above tetralin derivative (IVc, 16.1 g.) was dehydrogenated with 6 g. of sulphur in the same way as in the case of 1,7-dimethylnaphthalene, and 11 g. (73.3%) of the desired product (Vc) was obtained, b.p. 140–144°/8 mm.

Anal. Calc'd for $C_{13}H_{14}$: C, 91.76; H, 8.24.
Found: C, 91.42; H, 8.01.

The *picrate* was prepared in the usual way and was crystallized as orange-red needles from ethanol, m.p. 124–125° [lit. (11) m.p. 125°].

*Anal.** Calc'd for $C_{19}H_{17}N_3O_7$: N, 10.52. Found: N, 10.20.

SUMMARY

Aluminum chloride-catalyzed reactions between ethyl allylacetate and benzene, toluene, and *m*-xylene have been studied, and a convenient route to substituted tetralones and naphthalenes has been developed.

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