Anal. Calcd. for $C_{16}H_{20}O$: C, 84.12; H, 8.83. Found: C, 84.32; H, 9.28.

The **semicarbazone** of V readily was prepared and was obtained after crystallization from aqueous ethanol as flat white crystals, m. p. 222°.

Anal. Calcd. for $C_{17}H_{23}N_3O$: C, 71.55; H, 8.12. Found: C, 71.81; H, 8.31.

A mixture of the semicarbazone of V and the semicarbazone of IV melted below 200°.

9-Phenyldecalin, VI.—The reduction of V was carried out according to a method worked out by Baker.[14] A solution of V (6.0 g., 0.027 mole) in absolute alcohol (15 ml.) was boiled with 85% hydrazine hydrate (4 ml.) for four hours. The volatile material was removed and powdered potassium hydroxide (13 g.) was added. The flask containing the reaction mixture was then placed in a heating bath and the temperature was raised slowly. Nitrogen evolution, which began at 130°, was complete when the bath temperature reached 230°. When the flask had cooled, water was added and the organic layer was separated by benzene extraction. The benzene was removed and the residue distilled. There was obtained 4.0 g. (70%) of a colorless oil; b. p. 97–98° (0.3 mm.); $n^{20}{}_{\text{D}}$ 1.5532. On standing the oil crystallized to a white solid, m. p. 52–53°.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.41; H, 10.44.

The **sulfonamide derivative** of VI was prepared according to the method of Huntress and Carten.[15] It was obtained by crystallization from aqueous ethanol as fluffy, white plates; m. p. 161–162°.

Anal. Calcd. for $C_{16}H_{23}NO_2S$: C, 65.50; H, 7.90. Found: C, 65.56; H, 7.94.

1-Phenyloctalin.—Decalone-1 (40 g., 0.26 mole), prepared by the chromic acid oxidation[16] of decalol-1,[17] was dissolved in ether (100 ml.). The ether solution was then added dropwise to a 3 *M* phenylmagnesium bromide solution (100 ml.). The reaction mixture was boiled under reflux for twenty minutes and was then hydrolyzed by slowly adding a dilute iced solution of hydrochloric acid. The ether layer was separated and the ether removed. The residual oil was boiled under reflux with 25 ml. of a 20% solution of sulfuric acid for two hours. The organic layer was then separated and distilled. There was obtained 24.0 g. (46%) of a colorless oil; b. p. 92–95° (0.1 mm.); $n^{20}{}_{\text{D}}$ 1.5610.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.33; H, 9.73.

1-Phenyldecalin.—The 1-phenyloctalin (18 g.) was shaken with 1 g. of 10% palladium-on-charcoal catalyst under a pressure of three atmospheres of hydrogen. Hydrogenation was complete after twenty-four hours. Distillation of the product gave 16 g. (90%) of a colorless oil; b. p. 103–104° (0.3 mm.); $n^{20}{}_{\text{D}}$ 1.5420.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.89; H, 10.51.

The **sulfonamide** derivative of 1-phenyldecalin was prepared as before and was obtained, after crystallization from aqueous ethanol, as hard white plates, m. p. 154–158°.

Anal. Calcd. for $C_{16}H_{23}NO_2S$: C, 65.50; H, 7.90. Found: C, 65.37; H, 7.82.

A mixture of the sulfonamide of VI and the sulfonamide of 1-phenyldecalin was found to melt at 115–125°.

Summary

It has been shown that compounds having an angular aryl group can be synthesized without great difficulty. The synthesis of 10-phenyldecahydroquinoline and of 9-phenyldecalin is described.

URBANA, ILLINOIS RECEIVED JUNE 11, 1946

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[14] B. R. Baker, Doctoral Dissertation, University of Illinois, 1940.

[15] Huntress and Carten, THIS JOURNAL, **62**, 511 (1940).

[16] This was carried out according to the procedure used for the oxidation of 3-methoxycyclohexanol-1 by Marvel and Walton, *J. Org. Chem.*, **7**, 88 (1942).

[17] Musser and Adkins, THIS JOURNAL, **60**, 664 (1938).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Stobbe Condensation with Methyl *p*-Tolyl Ketone. A Synthesis of Cadalene

BY WILLIAM S. JOHNSON AND A. RUSSELL JONES[1]

In previous communications[2] we described a method involving the use of the Stobbe condensation for the introduction of a propionic acid side-chain at the site of the carbonyl group of a ketone. When applied to 2-acetylnaphthalene, this chain-lengthening process gave rise to a useful intermediate for the synthesis of 1,4-dimethylphenanthrene.[2a] In the present work the chain-lengthening process has been applied similarly to methyl *p*-tolyl ketone, I, and the product has been employed in a new synthesis of cadalene, VI.

Cadalene has been synthesized previously by various schemes involving from seven to eleven steps.[3] The highest over-all yield reported was about 3%. In the present synthesis cadalene was obtained as the picrate in about 25% over-all yield in six steps from methyl *p*-tolyl ketone. The reactions which were employed are indicated in the accompanying flow sheet. Although the intermediates II through V have been previously known, the present synthesis affords a new and easy source of these substances.

The condensation between the ketone I and diethyl succinate proceeded readily under the influence of potassium *t*-butoxide. The crude oily half ester thus was obtained in 90% yield, and undoubtedly consisted of a mixture of isomers. Decarbethoxylation with hydrobromic and acetic acid afforded crystalline γ-methyl-γ-*p*-tolylbutyrolactone, II, in 85% yield (75% after purification for reduction). This material was cleaved with dilute sodium hydroxide and the resulting aqueous solution of the salt of the hydroxy acid III was hydrogenated over copper–chromium oxide catalyst. The per cent. conversion to γ-*p*-

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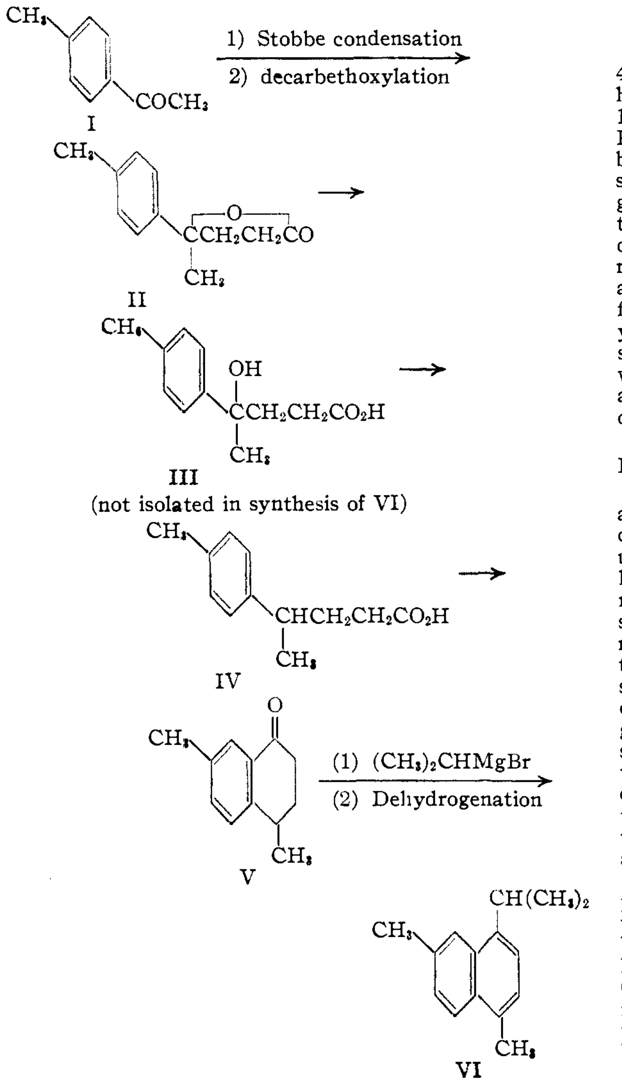
[1] Sterling-Winthrop Research Institute Fellow, 1946–1947.

[2] (a) Johnson, Goldman and Schneider, THIS JOURNAL, **67**, 1357 (1945); (b) W. S. Johnson, H. C. E. Johnson and Petersen, *ibid.*, **67**, 1360 (1945); (c) Johnson and Petersen, *ibid.*, **67**, 1366 (1945).

[3] (a) Ruzicka and Seidel, *Helv. Chim. Acta*, **5**, 369 (1922); (b) Barnett and Cook, *J. Chem. Soc.*, 22 (1933); (c) Bardhan and Banerji, *ibid.*, 476 (1935); (d) N. N. Chatterjee, *J. Ind. Chem. Soc.*, **13**, 588 (1936); (e) Dutta, *ibid.*, **18**, 233 (1941).



tolylvaleric acid, IV, proved to be quite variable (10–90%, but usually about 60%), possibly due to the presence of catalyst poisons which were difficult to remove. Considering recovered lactone, however, the yield was practically quantitative. Clemmensen reduction of the lactone gave IV in 48% yield, while phosphorus and hydriodic acid effected reduction in about 62% yield. The cyclization of IV with hydrogen fluoride gave 4,7-dimethyltetralone-1, V, in 91% yield. The carbinol which was formed by the interaction of this ketone with isopropylmagnesium bromide was dehydrated giving an oily hydrocarbon which was readily separated from unchanged ketone by selective adsorption on alumina. The conversion was 44% while the yield based upon recovered starting material was 64%. Dehydrogenation of the hydrocarbon fraction over palladium–charcoal afforded an oil from which cadalene picrate was formed in 64% yield. The trinitrobenzene complex and the styphnate were also prepared for further characterization.

Experimental Part[4]

γ-Methyl-γ-*p*-tolylbutyrolactone (II).—To a solution of 4.3 g. (0.11 mole) of potassium in 100 cc. of *t*-butyl alcohol was added 26.1 g. (0.15 mole) of diethyl succinate and 13.4 g. (0.10 mole) of methyl *p*-tolyl ketone (Eastman Kodak Company grade). An additional 15–20 cc. of *t*-butyl alcohol was used to aid in the transfer. The yellow solution was allowed to reflux in an atmosphere of nitrogen for forty-five minutes, and the resulting orange solution was cooled to room temperature and acidified with dilute hydrochloric acid. The alcohol was removed under reduced pressure, and the residual oil was taken up in ether and washed with 3% potassium hydroxide solution. Acidification of the alkaline extracts afforded 23.5 g. (90% yield) of pale yellow oily half-ester. After standing for several days the material partially crystallized. A sample was distilled at reduced pressure and the fraction boiling at 165–166° (0.2–0.3 mm.), which represented about 40% of the product, was analyzed.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.86; H, 7.04.

A solution of 22.7 g. of the crude half-ester in 90 cc. of acetic acid (distilled from potassium permanganate), 70 cc. of 48% hydrobromic acid and 20 cc. of water was boiled under reflux in an all-glass apparatus. After three hours the rate of evolution of gas (which was roughly measured by collection over saturated sodium chloride solution) had become quite slow; so the acid solvents were removed under reduced pressure. The residual oil was taken up in ether, washed with 5% potassium carbonate solution, followed by saturated salt solution, and dried over anhydrous sodium sulfate. Evaporation of the ether gave 15.0 g. of a thick yellow oily lactone which turned to a soft crystalline mass on standing. The harder portions of the material melted at 43–45°. An additional 0.5 g. of crude lactone was obtained by retreating the acidic material recovered from the potassium carbonate washings with 9 cc. of acetic acid, 6.5 cc. of 48% hydrobromic acid and 2.5 cc. of water for thirty-five minutes (refluxing). Distillation of the total crude material under reduced pressure gave almost colorless lactone, m. p. 48–49° with softening at 46.5°; yield, 14.0 g. or 85%. For the hydrogenation it was usually found desirable to recrystallize the distilled product from petroleum ether (b. p. 60–68°). The total yield of this purified material was 75%; m. p. 48.5–50°. The best sample which was obtained had the m. p. 51.3–52° (reported[5] 52°). Rupe and Steinbach[5] have prepared the lactone II by sulfuric acid cyclization of γ-methyl-γ-*p*-tolylisocrotonic acid which was obtained by the interaction of methylmagnesium halide and ethyl γ-*p*-toluylpropionate. Their over-all yield was about 55%.[6]

γ-*p*-Tolylvaleric Acid (IV).—This substance has been prepared previously in about 74% yield by the reduction of the lactone II with phosphorus and hydriodic acid.[5] It has also been obtained by catalytic hydrogenation of γ-methyl-γ-*p*-tolylisocrotonic acid.[6]

In the present work IV was obtained by a procedure similar to that which was used for the preparation of γ-(2-naphthyl)-valeric acid.[2a] The most satisfactory of a number of experiments is reported below.

A mixture of 9.5 g. of the pure lactone and a slight excess of 1 *N* sodium hydroxide solution was warmed and swirled until solution was effected. Acetic acid was added until the solution was only faintly basic to litmus, and the solution was filtered into a bomb where the hydrogenation was conducted in the presence of 2.0 g. of copper–chromium oxide catalyst and at an initial hydrogen pressure of 170 atmospheres for two hours at 200°. The filtered solution was acidified with hydrochloric acid and the mixture was boiled for one hour to lactonize any unreduced hydroxy acid. (Preliminary experiments with the pure hydroxy acid showed that such a treatment effected

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[4] All melting points are corrected.

[5] Rupe and Steinbach, *Ber.*, **44**, 584 (1911).

[6] See Rupe and Schütz, *Helv. Chim. Acta*, **9**, 992 (1926).

quantitative lactonization.) The resulting oil was taken up in ether and washed with saturated sodium bicarbonate solution. Acidification of the combined alkaline extracts liberated the oily acid IV which was taken up in ether, washed with water followed by saturated salt solution, and dried over anhydrous sodium sulfate. Evaporation of the ether gave 8.6 g. (90% yield) of pale yellow oil which crystallized on cooling in ice; m. p. 28–30.5°. This material was satisfactory for the cyclization step. Further purification by distillation under reduced pressure gave a colorless product, m. p. 28–30.5° (reported[5] 32°); b. p. 173–174°, 9 mm. (reported[5] 173–174°, 9 mm.).

The ether solution from which the acid IV was extracted retained the lactone II. The amount of crystalline lactone recovered (1 g. in this experiment) was generally the theoretical amount.

Various methods of purifying the material for hydrogenation were investigated, but none was found which gave as good results as direct recrystallization. Thus when the distilled lactone was pretreated with Raney nickel, the conversion on hydrogenation was 36%. It was discovered that the sodium salt of the hydroxy acid III could be recrystallized nicely from a solution of sodium chloride. Such a treatment gave a perfectly colorless product which was reduced, however, only to the extent of 54–56%.

4,7-Dimethyl-1-keto-1,2,3,4-tetrahydronaphthalene (V).—The cyclization of γ-*p*-tolylvaleric acid has been effected by sulfuric acid in 78% yield,[3e] and by the action of aluminum chloride on the acid chloride in 72% over-all yield.[6,7]

In the present work the acid IV (9.6 g.) was cyclized with excess anhydrous hydrogen fluoride. After standing overnight in a platinum vessel, the mixture was evaporated in a current of air and the residue was taken up in ether and washed with saturated sodium bicarbonate solution, followed by saturated salt solution. Evaporation of the dried (over anhydrous sodium sulfate) solution afforded 8.5 g. of dark oily ketone which was distilled under reduced pressure; yield 7.9 g. or 91% of colorless oil, b. p. 97° (0.4–0.5 mm.). The ketone is reported to boil at 145–152° (15 mm.),[7] at 146.5–147° (11.5 mm.)[6] and at 118° (4 mm.).[3e]

The semicarbazone, after recrystallization from alcohol, melted at 196–197°. It is reported to melt at 194–195°[6,7] and at 195–196°.[3e]

The **2,4-dinitrophenylhydrazone**, prepared in alcohol with hydrochloric acid, was obtained in the form of small red blades from ethyl acetate–chloroform; m. p. 244–244.3° (dec.) with shrinking at 242.5°.

Anal. Calcd. for $C_{18}H_{18}O_4N_4$: C, 61.01; H, 5.12. Found: C, 61.08; H, 5.32.

Cadalene (VI).—Dutta[3e] has prepared this hydrocarbon by the addition of isopropylmagnesium iodide to the ketone V, followed by dehydrogenation with selenium; no yield was given.

In the present work a solution of 7.03 g. of the ketone V in 25 cc. of ether was added to a cooled solution of *iso*-propylmagnesium bromide (from 26.3 g. of isopropyl bromide and 5.3 g. of magnesium) in 300 cc. of ether. During the addition the temperature was maintained below 0°. The mixture was then stirred at 0° for about fourteen hours, refluxed for four hours, and finally was allowed to stand at room temperature for thirty-six hours. The cooled mixture was treated with saturated ammonium chloride solution, and evaporation of the ether gave 6.51 g. of pale yellow oil. A portion (2.81 g.) of this material was heated just to boiling with a crystal of iodine, and the mixture was cooled, dissolved in 40–60° petroleum ether and adsorbed on a column of activated alumina. The material was then fractionally eluted with portions of petroleum ether, petroleum ether–benzene (in decreasing ratios) benzene, benzene–ether (in decreasing ratios), ether and finally methanol. In this way there were isolated in the following order: 1.53 g. of colorless hydrocarbon fraction, 0.96 g. of unreacted ketone (at least 94% pure as indicated by formation of the 2,4-dinitrophenylhydrazone), and 0.09 g. of yellow oil which partially solidified on standing. Dehydrogenation of 0.51 g. of the hydrocarbon fraction with 0.05 g. of 30% palladium–charcoal[8] at 300° was complete in a few minutes, 95% of the calculated volume of gas being evolved. The ether-soluble material (0.45 g.) was heated to boiling with a solution of 1.2 g. of picric acid in 15 cc. of alcohol. The total amount of picrate isolated amounted to 0.70 g. (a 41% over-all yield from V accounting for recovered V), m. p. 113–114.5°. A sample purified by repeated recrystallization from alcohol had the m. p. 115–116° (reported,[3a,b,e] 114–115°).

Anal. Calcd. for $C_{21}H_{21}O_7N_3$: C, 59.01; H, 4.95. Found: C, 59.06; H, 4.72.

A purified sample of the styphnate melted at 139.5–140.5° and is reported to melt at 139°[3a] and 140°.[3b]

The **trinitrobenzene complex** after repeated recrystallization from alcohol had the m. p. 111.5–113° (reported,[9] 112–113°).

Anal. Calcd. for $C_{21}H_{21}O_6N_3$: C, 61.31; H, 5.15. Found: C, 61.30; H, 5.06.

In one experiment the crude Grignard product was chromatographed without preliminary dehydration. Dehydration occurred nevertheless either in working up the Grignard product or during the chromatographic analysis, since a hydrocarbon fraction was obtained which gave highly pure cadalene picrate, m. p. 114–116°, in 94% yield. The over-all yield from V, accounting for recovered ketone, was 36%.

Summary

A previously described method for the introduction of a propionic acid side-chain at the site of the carbonyl group of a ketone has been applied to methyl *p*-tolyl ketone. The steps involve a Stobbe condensation with diethyl succinate, decarbethoxylation of the half-ester with hydrobromic and acetic acid and reduction of the resulting lactone to give γ-methyl-γ-*p*-tolylbutyric acid.

This acid has been used to synthesize cadalene as follows: cyclization gave 4,7-dimethyl-1-keto-1,2,3,4-tetrahydronaphthalene which on treatment with isopropylmagnesium bromide, followed by dehydrogenation afforded cadalene in six steps from methyl *p*-tolyl ketone.

MADISON, WISCONSIN RECEIVED NOVEMBER 12, 1946

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[7] Mayer and Stamm, *Ber.*, **56**, 1424 (1923).

[8] Linstead and Thomas, *J. Chem. Soc.*, 1130 (1940).

[9] Plattner and Magyar, *Helv. Chim. Acta*, **24**, 191 (1941).