[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORY, GENERAL ANILINE AND FILM CORP.]

5,7-DIMETHYL-3,4-DIHYDRO-1(2*H*)-NAPHTHALENONE

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In view of the rearrangement undergone by γ-(2,4-dimethylphenyl)valeric acid (I) (1) during cyclization by hot polyphosphoric acid (Fig. 1), it was thought worthwhile to reinvestigate the cyclization of γ-(2,4-dimethylphenyl)butyric acid (V). This acid has previously been prepared by the succinoylation of *m*-xylene followed by a Clemmensen reduction of the γ-ketoacid (2–4), and also by a Reformatzky reaction on 2,4-dimethylacetophenone with subsequent extension of the acid side chain (5).

Some ambiguity exists in the literature regarding 5,7-dimethyl-3,4-dihydro-1(2*H*)-naphthalenone (VI) and its derivatives. Krollpfeiffer and Schäfer (6) describe the cyclization of V to VI by (a) treating V with concentrated sulfuric acid, and (b) converting V to the acid chloride and heating this *in vacuo*. Each method gave apparently the same tetralone (VI), m.p. 49–50°, and they report a semicarbazone melting at 234–235°. Baddeley (7), who obtained a compound to which he assigned structure VI, by heating 5,8-dimethyl-3,4-dihydro-1(2*H*)-naphthalenone with anhydrous aluminum chloride at 170°, gives the melting point of the semicarbazone as 245°. Heilbron (5) gives only a boiling point for VI, and the m.p. of the semicarbazone as 243–246°, while Barnett and Sanders (2) report VI melts at 50°. Tucker, *et al.* (4) found VI to melt at 46°, and report a 2,4-dinitrophenylhydrazone melting at 270–271°. From these data it might be concluded that the cyclization of V to VI is probably not attended by any rearrangement regardless of the cyclizing agent employed, although incontrovertible evidence is lacking due to discrepancies in the melting points reported for the products and derivatives.

The route of the present synthesis is shown in Figure 2. The reduction of the carbonyl group in keto acids similar to IV by hydrogenation over palladium-charcoal has been described by Horning (8) and was found applicable to IV, although somewhat superior results were obtained by preparing the catalyst *in situ*[2] from palladium chloride. Cyclization of V to VI was effected by (a) treating V with PCl_5 followed by $SnCl_4$, and (b) heating V with polyphosphoric acid to 130°. Each method afforded the same tetralone (VI), as demonstrated by the melting points of the tetralone and two of its derivatives, and most conclusively, by comparison of the x-ray diffraction patterns of each.

Thus it has been shown that no rearrangement attends the cyclization of V with hot polyphosphoric acid, in contrast to I. Such a rearrangement presumably would involve separation of the side chain as a carbonium ion. The moiety thus

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formed in the case of V would be a primary carbonium ion, whereas in the case of I it would be secondary. As secondary carbonium ions are generally considered to be more stable than primary ones, the absence of any rearrangement in the cyclization of V may be attributable to this factor. On the other hand, it is possible that a more facile extrusion of the side chain is favored by the steric repulsion of the adjacent methyl groups in I, or a combination of this and the preceding factor may be responsible for the rearrangement of I and not of V. Further information on the exact mechanism operating in these cases might be obtained from an investigation of the product formed by cyclizing γ-(4-methylphenyl)-valeric acid with hot polyphosphoric acid.

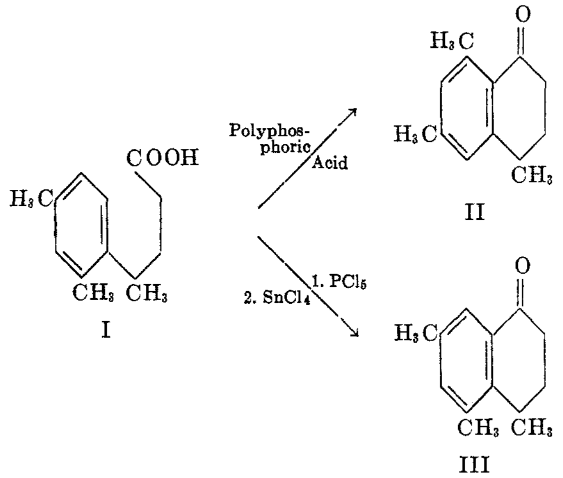

Figure 1

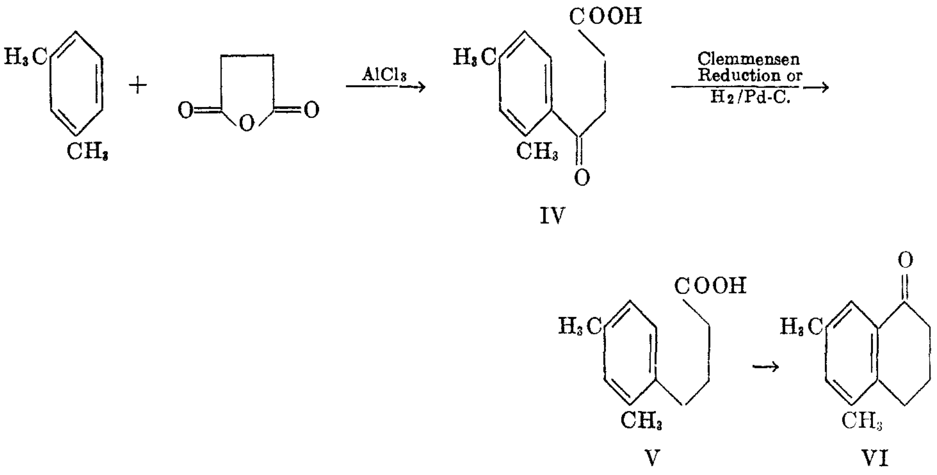

Figure 2

EXPERIMENTAL[3, 4]

β-(2,4-Dimethylbenzoyl)propionic acid (IV). In a 1-liter flask equipped with a Hershberg stirrer, solid addition tube, and reflux condenser with hydrogen chloride trap, were placed 265 g. (2.5 moles) of *m*-xylene (Eastman No. 275) and 100 g. (1.0 mole) of succinic anhydride (Eastman No. 868). The mixture was stirred, and 300 g. (2.2 moles) of powdered anhydrous aluminum chloride was added gradually. When it had all been added, the mixture was refluxed a few minutes, then allowed to stir for one hour while cooling to room temperature. Hydrolysis was accomplished with ice and dilute hydrochloric acid, and the semisolid product layer was separated, washed well with water, and then steam-distilled from excess potassium hydroxide solution. The alkaline residue from the distillation was adjusted approximately to *p*H 7–8 with dilute hydrochloric acid, treated with charcoal, then filtered from the charcoal and precipitated aluminum salts, and the filtrate was acidified with hydrochloric acid. The precipitated product was filtered, washed with cold water and pressed dry, then dissolved in hot benzene and decanted from the remaining water. The benzene solution was treated with charcoal, filtered and cooled, whereupon it deposited 126 g. (61% yield) of white crystals, m.p. 110.2–113.6°. Evaporation of the benzene mother liquor gave an additional 12 g. of less pure material. Recrystallization of the main batch from a small volume of hot benzene gave 124 g. (60% yield) of white leaves, m.p. 111.6–113.6°.

Since the primary purpose of this preparation was to obtain IV in high purity, no effort was made to improve the yield. By working up the mother liquors and extracting the discarded precipitate of aluminum salts, additional product could doubtless have been obtained.

γ-(2,4-Dimethylphenyl)butyric acid (V). To a suspension of 51.5 g. (0.25 mole) of the keto acid IV in 200 ml. of reagent glacial acetic acid in a 500-ml. glass hydrogenation bottle, was added 1.0 g. of palladium chloride and 1.0 g. of Norit. The bottle was put into a Parr hydrogenation apparatus and shaken at 40 p.s.i. (gauge pressure). A pressure drop of 16 p.s.i. occurred during the first 1.5 hours, then the rate showed appreciably. The heating unit of the bomb was adjusted to keep the mixture at 50°, and the bomb was repressured to 40 p.s.i. and allowed to shake overnight, when the total pressure drop was 47 p.s.i. While still warm, the contents of the bomb were shaken with 2.0 g. of Norit and filtered through a sintered glass filter directly into a 300-ml. distillation flask with Claisen head and capillary regulator. The acetic acid was removed and the product was distilled *in vacuo*, giving 46.4 g. (96.5% yield), b.p. 128–129°/0.35 mm., which solidified in the receiver. The product was dissolved in 200 ml. of boiling cyclohexane, treated with Norit, filtered, and cooled, whereupon there was obtained 41 g. (85% yield) of white lusterous laminae, m.p. 77.8–79.0°.

5,7-Dimethyl-3,4-dihydro-1(2H)-naphthalenone (VI); *Cyclization with* PCl_5-$SnCl_4$. A solution of 19.2 g. (0.10 mole) of pure V in 50 ml. of chloroform was added slowly to a warmed and stirred slurry of 21.0 g. (0.10 mole) of phosphorus pentachloride in 50 ml. of chloroform. The resulting clear solution was warmed and stripped of chloroform and phosphorus oxychloride *in vacuo*, leaving 21.0 g. (100% of theory for the acid chloride) of a pale brown oil. This residue was dissolved in 50 ml. of thiophene-free benzene and cooled in an ice-bath to 5°. A cooled (5°) solution of 25 ml. (approximately 0.2 mole) of stannic chloride in 50 ml. of thiophene-free benzene was added in one lot to the acid chloride solution. Hydrogen chloride was evolved and the temperature rose to 40°. The mixture was allowed to stand in the ice-bath 15 minutes, then hydrolyzed with ice and the product was extracted well with ether. The combined ether extracts were washed with dilute hydrochloric acid, dilute sodium bicarbonate solution, and water and dried over magnesium sulfate. Removal of

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[3] Melting points were taken in Pyrex capillaries using a Hershberg melting-point apparatus and Anschütz thermometers.

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the solvents *in vacuo* left a pale yellow oil which crystallized on cooling, giving 16.5 g. (95%) of crude product. This material was dissolved in hot 30–65° petroleum ether, treated with charcoal, filtered, and reduced to a small volume. The crystals so obtained were recrystallized from 20–40° petroleum ether. They then melted at 50.0–50.4°.

Anal. Calc'd for $C_{12}H_{14}O$: C, 82.7; H, 8.04.
Found: C, 82.7; H, 8.02.

The *semicarbazone*, after one recrystallization from ethanol melted at 241–242° dec.

Anal. Calc'd for $C_{13}H_{17}N_3O$: C, 67.50; H, 7.41; N, 18.17.
Found: C, 67.42; H, 7.34; N, 18.25.

The *2,4-dinitrophenylhydrazone* was recrystallized once from ethyl acetate. The melting point appeared to depend on the temperature of the heating bath upon introduction of the capillary. Thus, if put into the bath at 260° it melted at 268.8-269.4°, but when inserted at 267°, it melted at 272–273°.

Anal. Calc'd for $C_{18}H_{18}N_4O_4$: C, 61.0; H, 5.09; N, 15.82.
Found: C, 61.05; H, 5.14; N, 15.81.

5,7-Dimethyl-3,4-dihydro-1(2H)-naphthalene (VI); *Cyclization with polyphosphoric acid.* To 300 g. of polyphosphoric acid, warmed to 100° and stirred mechanically, there was added in one lot, 19.2 g. (0.10 mole) of pure V. No appreciable increase in the temperature of the mixture accompanied solution. The mixture was stirred and heated to 130° for five minutes, then cooled to 100° and poured into water. On standing overnight, the supernatant oily layer crystallized. The solid was separated, dissolved in ether, and the solution was washed with sodium bicarbonate solution and dried with magnesium sulfate. Removal of the ether left an oil which crystallized readily. After purification as in the preceding experiment, the tetralone formed hard white needles, m.p. 49.6–50.6°.

A mixture melting point determination with the product of the preceding experiment showed no significant depression. The semicarbazone and 2,4-dinitrophenylhydrazone purified as before melted at 241–242.4° and 268.4–269° respectively. The mixture melting point of each of these derivatives with that obtained from the tetralone prepared by the stannic chloride cyclization, gave no depression. The x-ray diffraction pattern of this tetralone was identical with that obtained from the stannic chloride cyclization product.

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REFERENCES

(1) MOSBY, *J. Am. Chem. Soc.*, **74,** 2564 (1952).
(2) DE B. BARNETT AND SANDERS, *J. Chem. Soc.*, 434 (1933).
(3) FIESER, *et al.*, *J. Am. Chem. Soc.*, **70,** 3200 (1948).
(4) TUCKER, WHALLEY, AND FORREST, *J. Chem. Soc.*, 3194 (1949).
(5) HEILBRON AND WILKINSON, *J. Chem. Soc.*, 2537 (1930).
(6) KROLLPFEIFFER AND SCHÄFER, *Ber.*, **56,** 620 (1923).
(7) BADDELEY, *J. Chem. Soc.*, 233 (1944).
(8) HORNING AND REISNER, *J. Am. Chem. Soc.*, **71,** 1036 (1949).