by the selective hydrogenation over Lindlar's catalyst of the triple bond of 2-methyl-5-hexen-3-yn-2-ol. The alcohol was obtained in 83% yield, b.p. 47–52° (8 mm.), n_D^{21} 1.4560; reported: 78–80° (12 mm.), n_D^{20} 1.4566.

Cyclization of 2-methyl-3,5-pentadien-2-ol. The cyclization was carried out according to the method of Zonis.[1] In a 1-l. flask was heated for 10 hr. at 100° a solution of 2-methyl-3,5-hexadiene-2-ol and 120 ml. of 25% sulfuric acid. The reaction mixture was then distilled until only a clear aqueous phase was collected. The distillate was neutralized with 10% sodium carbonate solution and the organic material separated and dried over potassium carbonate. This product was then distilled and separated into four fractions shown in Table I. This table also lists the gas chromatographic analysis and physical properties of these fractions. Fractions 1 and 3 did not show active hydrogen by the sodamide method nor did they yield maleic anhydride or *N*-phenylmaleimide derivatives.

Ithaca, N. Y.

[Contribution from the Chemistry Department, Northwestern University]

peri-Substituted Naphthalenes. IV. The Tetrahydro-8-isopropyl-1-naphthoic Acids[1]

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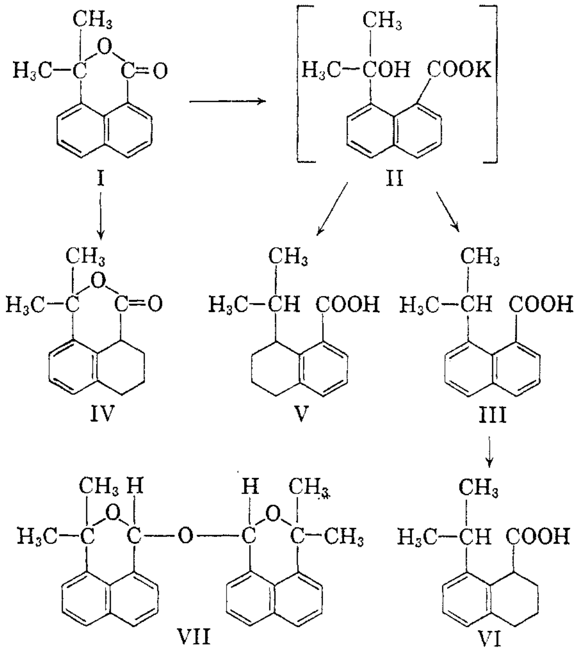
Received April 8, 1960

3,3-Dimethyl-1,8-naphthalide may be reduced by appropriate use of nickel-aluminum alloy and sodium metal to give tetrahydro-3,3-dimethyl-1,8-naphthalide (IV), 8-isopropyl-1-naphthoic acid (III), 5,6,7,8-tetrahydro-8-isopropyl-1-naphthoic acid (V), or 1,2,3,4-tetrahydro-8-isopropyl-1-naphthoic acid (VI). A nickel-aluminum alloy reduction was also employed in a simplified synthesis of 2-isobutylbenzoic acid. Tetrahydro acid V isomerized readily in sulfuric acid or liquid hydrogen fluoride to a neutral aldol-type product. Neither 5,6,7,8-tetrahydro-1-naphthoic acid nor 2-isobutylbenzoic acid underwent a transformation of this type under comparable conditions. The unusual lability of compound V is ascribed to the particular geometrical relationship existing between the carboxyl group and the alkyl side chain in compound V.



It has been shown that 8-isopropyl-1-naphthoic acid (III) yields an aldal (VII) when treated with sulfuric acid or hydrogen fluoride.[1] This reaction involves a hydrogen transfer from the isopropyl group to the neighboring carbonyl group. The present paper concerns the preparation and acid treatment of three related compounds—5,6,7,8-tetrahydro-8-isopropyl-1-naphthoic acid (V), 1,2,3,4-tetrahydro-8-isopropyl-1-naphthoic acid (VI), and 2-isobutylbenzoic acid (IX)—in which the relative positions of the carboxyl and isopropyl groups are similar to that in 8-isopropyl-1-naphthoic acid.

Synthesis and structure. Acids V and VI, as well as acid III and lactone IV, could be obtained by appropriate reduction of 3,3-dimethyl-1,8-naphthalide (I). The direct action of a coarse, granular grade of Raney nickel-aluminum alloy[3] on an alkaline ethanol-water solution of lactone I afforded (10%) the tetrahydrolactone (IV). This lactone was also formed, and in somewhat better yield (31%) when an ethanol solution of I was treated with sodium. By saponifying compound I with potassium hydroxide in triethylene glycol prior to addition of the alloy the course of the reaction could be altered. In this case reduction with the granular grade of alloy yielded isopropylnaphthoic acid III[1] (16–29%) and a small amount of V. When the saponification product was similarly treated with the more active, finely powdered nickel-aluminum alloy[4] in place of the granular alloy, tetrahydro acid V was the principal product (48%). Tetrahydro acid VI was prepared (57%) by reduction of acid III with sodium and boiling amyl alcohol. The isomeric tetrahydroisopropylnaphthoic acids melted at the same temperature; however, the mixture

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(1) For the previous paper in this series see R. L. Letsinger, W. J. Vullo, and A. S. Hussey, *J. Am. Chem. Soc.*, **81**, 1965 (1959).

(2) Standard Oil Company of Indiana Fellow, 1957–1958. Sinclair Oil Company Harvey Fellow, 1956–1957.

(3) Procured from the Gilman Paint and Varnish Co., Chattanooga, Tenn.

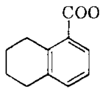
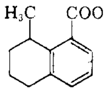
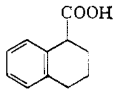
(4) Procured from the Raney Catalyst Co., Chattanooga, Tenn.

melting point was markedly depressed and their spectra differed in many respects.

The positions of the reduced rings in IV, V, and VI were established by means of the ultraviolet spectra. Pertinent information is summarized in Table I.

TABLE I

ULTRAVIOLET SPECTRAL DATA[a]

Compound	λ_{max}	log ϵ	λ_{max}	log ϵ
	236	3.6	282	3.0
 [b]	233	3.6	281	3.1
V	236	3.7	283	3.0
	264	2.6	272	2.6
VI	263	2.6	—	—
IV	267	2.32	274	2.64

[a] Ultraviolet spectra were taken with a DK-2 Beckman instrument with 95% ethanol as a solvent. [b] See ref. 5.

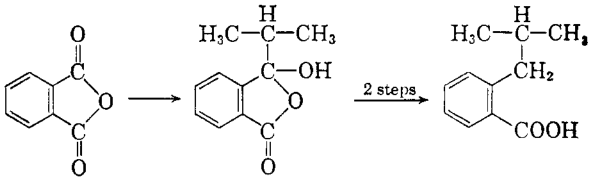
The similarity of the spectra of V and 5,6,7,8-tetrahydro-1-naphthoic acid on the one hand, and of VI and 1,2,3,4-tetrahydro-1-naphthoic acid on the other, permits an unambiguous structural assignment of the two new acids. Also, the data in Table I suggest that the carbonyl group in lactone IV is joined to the nonaromatic ring. In support of this conclusion, IV absorbs at 5.8 μ in the infrared, as expected for a compound with non-conjugated lactone carbonyl, whereas the related aromatic compound, I, absorbs at 5.9 μ.

Cason and Wordie[5] previously used the ultraviolet spectra of the tetrahydronaphthoic acids as references for establishing the structure of 5,6,7,8-tetrahydro-8-methyl-1-naphthoic acid, one of the products of a catalytic reduction of 1,8-naphthalic anhydride. The excellent agreement between the spectrum of their product and that of compound V further supports the structural assignments.

Independent evidence for the structure of acid VI may be derived from the mode of its formation. A search of the literature reveals that all cases of reduction of naphthoic acid or the substituted naphthoic acids by sodium in the presence of hydroxylic solvents are reported to afford the 1,2,3,4-tetrahydro-1- or 2-naphthoic acids; *i.e.*, the reduction occurred in the ring bearing the carboxyl group. These cases included the reduction of 1-naphthoic acid,[6,7] 2-naphthoic acid,[6] 1-methyl-2-naphthoic acid,[8] 4-ethoxy-1-naphthoic acid,[9] and naphthostyril.[10] Thus reduction of 8-isopropyl-1-naphthoic acid by sodium in amyl alcohol would be expected to yield the 1,2,3,4-tetrahydro isomer, a conclusion in agreement with that drawn from the ultraviolet spectral data.

In contrast to the sodium reductions, the course of the nickel-aluminum alloy reductions cannot at present be reliably predicted. Thus, although the reduction of potassium 8-hydroxyisopropyl-1-naphthoate (II) by the alloy yielded principally the 5,6,7,8-tetrahydro acid (V), the reduction of potassium 1-naphthoate under similar conditions produced the 1,2,3,4- and the 5,6,7,8-tetrahydro-1-naphthoic acid in yields of 44% and 16%, respectively. Furthermore, the reduction of 1,8-naphthalide by the same type of reagent gave 1,2,3,4-tetrahydro-8-methyl-1-naphthoic acid as the only reported isolated reduction product.[5,11]

2-Isobutylbenzoic acid has been described by Mann and Stewart, who prepared it incidently in connection with some studies on the chemistry of 2-methoxymethylaniline.[12] As their procedure involved seven steps from 2-bromobenzyl bromide, another shorter synthesis was developed.



VIII IX

The reaction of diisopropylcadmium with phthalic anhydride afforded (37%) a monoisopropyl adduct (VIII), which is formulated as the hydroxyphthalide rather than the keto acid, as the infrared spectrum of the solid contained a band at 3.0 μ (O—H) and a single band at 5.72 μ in the carbonyl region. A Clemmensen reduction converted VIII to 3-isopropylphthalide in 76% yield. The same transformation was also accomplished in 61% yield by heating VIII with an alkaline suspension of nickel-aluminum alloy. Reduction of the phthalide to isobutylbenzoic acid (IX) was accomplished (36%) by saponifying the phthalide of triethylene glycol at 160–170° and reducing with nickel-aluminum alloy.

Acid treatment. Tetrahydro-acid V proved to be more sensitive than 8-isopropyl-1-naphthoic acid

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(5) J. Cason and J. D. Wordie, *J. Org. Chem.*, **15**, 608 (1950).

(6) W. V. Sowinski, *Ber.*, **24**, 2358 (1891).

(7) W. Kay and A. Morton, *J. Chem. Soc.*, **105**, 1565 (1914).

(8) K. v. Auwers, *Ber.*, **58**, 151 (1925). K. v. Auwers and K. Moller, *J. prakt. Chem.*, **109**, 124, 143 (1925).

(9) O. Kamm, H. B. McClugage, and A. W. Landstrom, *J. Am. Chem. Soc.*, **39**, 1247 (1925).

(10) G. Schroeter and H. Rossler, *Ber.*, **35**, 4218 (1902).

(11) R. C. Fuson and G. Munn, *J. Am. Chem. Soc.*, **71**, 1870 (1949).

(12) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 4127 (1954). See F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2819 (1954) and F. C. Holliman and F. G. Mann, *J. Chem. Soc.*, 1634 (1947) for preparation of the intermediates.

to the action of sulfuric acid. Indeed, concentrated sulfuric acid rapidly converted V to water soluble products. In 94.7% sulfuric acid at room temperature, however, compound V reacted to give a neutral, water insoluble oil(X) in 51–61% yield. The same material (identical infrared spectrum) was obtained quantitatively when V was treated with liquid hydrogen fluoride. This product showed no carbonyl or hydroxyl absorption in the infrared; however, it reacted readily with 2,4-dinitrophenylhydrazine in acidic solution to give an orange-red hydrazone derivative, the analysis of which agreed with the formula $C_{20}H_{22}O_6N_4$. Dehydrogenation of the oil at 250–270° in the presence of palladium afforded a low yield of 3,3-dimethyl-1,8-naphthalide (I). It therefore seems plausible, although it has not been proved, that the neutral product is an aldal analogous in structure to compound VII.

The reaction of V is particularly striking when one considers the behavior of 5,6,7,8-tetrahydro-1-naphthoic acid and 2-isobutylbenzoic acid. The former differs from V only in having hydrogen in place of the isopropyl group at the 8-position; the latter possesses an alkyl group which, with respect to the carboxyl group, is equivalent to the side chain in V except for the greater rotational freedom. Yet neither the tetrahydronaphthoic acid nor the isobutylbenzoic acid were altered by sulfuric acid under the conditions which transformed V to XI. It is therefore apparent that the isopropyl group is directly involved in the reaction of V and that it must be held in a particular position with respect to the neighboring carboxyl group in order for the hydrogen transfer to take place. The situation is similar to that for the 1,5-aryl migrations, for 8-benzhydryl-1-naphthoic acid readily isomerizes to 1-phenylhydroxymethyl-8-benzoylnaphthalene hemiketal,[13] whereas no evidence of a phenyl shift could be found with the more flexible system, 2-benzhydrylphenylacetic acid.[14]

Both 1,2,3,4-tetrahydro-8-isopropylnaphthoic acid and 1,2,3,4-tetrahydro-1-naphthoic acid reacted readily with sulfuric acid. As no water insoluble products were obtained, however, no conclusions concerning hydrogen transfer reactions can be drawn for these substances.

EXPERIMENTAL[15]

Tetrahydro-3,3-dimethyl-1,8-naphthalide (IV). (*a*) *Nickel aluminum alloy reduction.* 3,3-Dimethyl-1,8-naphthalide[1] (1.0 g.) was dissolved in a hot solution of 9 g. of potassium hydroxide in 40 ml. of ethanol and 30 ml. of water. While the solution was rapidly stirred at 58–70°, 5.0 g. of granular Raney nickel-aluminum catalyst[3] was slowly dropped in. It was necessary to add more ethanol to keep the lactone in solution. The mixture was heated at 70–75° for an additional 45 min., then filtered while hot (the filter cake was pyrophoric when dry). The filtrate was added to concd. hydrochloric acid, the resulting suspension extracted with ether, and the ether layer washed with aqueous sodium hydroxide, dried, and evaporated. The residual solid, m.p. 103–112°, was recrystallized first from hexane, then from methanol-water, yielding 0.102 g. (10%) of tetrahydro-3,3-dimethyl-1,8-naphthalide (IV); m.p. 122–123°. The analytical sample, obtained by further recrystallization, melted at 125–125.5°. No carboxylic acid was obtained as a product of this reduction.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.47; H, 7.46. Found: C, 77.37; H, 7.31.

(*b*) *Sodium amalgam reduction.* To a refluxing solution of the lactone (0.636 g.) in 50 ml. of ethanol and 5 ml. of water was slowly added (2 hr.) 34 g. of 2% sodium amalgam. The reaction mixture was kept slightly acidic by portionwise addition of sulfuric acid (2 g. sulfuric acid in 10 ml. of water). Stirring and refluxing were continued for an additional 2 hr.; then the supernatant solution was decanted into water and extracted with ether. From this was isolated 0.200 g. (31%) of dimethyltetrahydronaphthalide, IV; m.p. 119–121°; the infrared absorption was the same as for the product from procedure (a), and a mixture melting point showed no depression.

5,6,7,8-Tetrahydro-8-isopropyl-1-naphthoic acid (V). Lactone I (6.00 g.) was saponified by heating overnight at 145° in 450 g. of triethylene glycol containing 60 g. of potassium hydroxide. Additional alkali (48 g. of potassium hydroxide in 100 ml. of water) was added; then, with the temperature at 95–97° and good stirring, 24 g. of powdered Raney nickel-aluminum alloy[4] was added in portions. Small amounts of capryl alcohol were occasionally added to reduce foaming. After standing overnight at room temperature the mixture was warmed, filtered, and the filtrate poured into concd. hydrochloric acid. The mixture was extracted with ether and the ether layer extracted with several portions of sodium carbonate solution. The acids obtained upon acidification were separated by crystallization from petroleum hexane into two portions: (a) 5,6,7,8-tetrahydro-8-isopropyl-1-naphthoic acid, 1.45 g., m.p. 113.5–114.2°, and (b) a low melting mixture, 2.6 g. Portion (b) was dissolved in 100 ml. of 12% potassium hydroxide solution and subjected to the action of 6.15 g. of powdered nickel-aluminum alloy at steam bath temperature. From this second reduction was obtained 1.5 g. of pure tetrahydro acid, making a total of 2.95 g. (48%) of this product. The analytical sample melted at 114.5–115.2°; infrared absorption, 3.4 (strong) 3.8, 5.95 (strong), 6.3, 6.86, 7.7, 7.86 (strong), 8.66, 10.54, 12.75, 13.12 (strong) μ.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; neut. equiv. 214. Found: C, 76.79; H, 8.11; neut. equiv. 215.

This tetrahydro acid was converted to the acid chloride with thionyl chloride, and the acid chloride was treated with concd. ammonium hydroxide to give the tetrahydroisopropylnaphthamide, m.p. 116–117°; infrared absorption, 3.0, 3.1, 3.4, 6.0, 6.13, 6.85 μ.

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81. Found: C, 77.08; H, 8.82.

1,2,3,4-Tetrahydro-8-isopropyl-1-naphthoic acid (VI). Sodium (3 g.), in small pieces, was dropped into a refluxing solution of 600 mg. of 8-isopropyl-1-naphthoic acid in 50 ml. of dry amyl alcohol. After all the sodium had dissolved, the mixture was poured into water. The two layers were separated and the aqueous phase, after thorough washing with ether, was acidified and extracted with ether. From this extract was obtained a solid which, after recrystallization (treatment with charcoal), was colorless and melted at 114–115°. The purified sample weighed 350 mg. (57%). When the reaction was carried out in ethanol in place of amyl alcohol the yield was only 15%. Like acid V, VI did not decolorize permanganate or bromine in carbon tetrachloride, indicating the absence of any dihydro compounds.

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(13) R. L. Letsinger and P. T. Lansbury, *J. Am. Chem. Soc.*, **81**, 940 (1959).

(14) R. L. Letsinger, J. D. Jamison, and A. S. Hussey, *J. Org. Chem.*, in press.

(15) The microanalyses were performed by Miss H. Beck.

That V and VI were different compounds was shown by the mixture melting point (melting started at 90°) and the distinctly different infrared spectrum; VI absorbed strongly at 3.42, 5.90, 8.21, and 12.75 μ and no bands occurred in the 12.8–13.4 μ region where V absorbed. Conversely, V had only a very weak band (8.28 μ) in the 7.9–8.4 μ region.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.66; H, 8.31.

The tetrahydronaphthoic acids. In order to learn more about the course of the alloy reductions, 1-naphthoic acid was used as a substrate. In this case a solution made up with 3.8 g. of 1-naphthoic acid, 21 g. of potassium hydroxide, and 160 ml. of water was treated, at 80°, with 11.4 g. of the finely powdered Raney nickel-aluminum alloy, added in small portions. On working up the reaction mixture in the usual way 3.2 g. of an acid mixture, m.p. 69–75°, was obtained. Chromatography of a 1.0 g. sample on silica gel with a chloroform-benzene solvent yielded two substances; (a) 0.20 g., m.p. 147–149° (eluent solvent, 20% chloroform) and (b) 0.54 g., m.p. 79–81° (eluent solvent, 50% chloroform). Recrystallization of these two fractions from petroleum hexane gave 5,6,7,8-tetrahydro-1-naphthoic acid, m.p. 149.5–150°, lit.,[16] m.p. 150° and 1,2,3,4-tetrahydro-1-naphthoic acid, m.p. 84°, lit.,[17] m.p. 85°, respectively.

A sample (0.0300 g.) of 5,6,7,8-tetrahydro-1-naphthoic acid was dissolved in 3 ml. of sulfuric acid (prepared from 49 g. of concd. sulfuric acid and 1 ml. of water) and allowed to stand for 2 hr. at 22°. The solution was pale tan in color. On pouring onto ice 0.0266 g. of the tetrahydro acid, m.p. 149–150°, was recovered. A similar sulfuric acid solution of 1,2,3,4-tetrahydro-1-naphthoic acid was a rich yellow color. It yielded no precipitate when diluted.

Acid induced rearrangement of 5,6,7,8-tetrahydro-8-isopropyl-1-naphthoic acid (Product X). *(a) Use of hydrogen fluoride.* Tetrahydro acid V (0.60 g.) was allowed to stand at ice temperature in 20 g. of liquid hydrogen fluoride for 45 min. and then at room temperature for 45 min. The dark red solution was then poured onto ice and the resulting solution extracted with benzene. Extraction of the benzene layer with alkali and acidification yielded no organic acids, showing that the tetrahydroisopropylnaphthoic acid had reacted completely. Evaporation of the benzene layer left 0.6 g. of a neutral oil (X) which could not be induced to crystallize. Chromatographic separation gave only a series of oils, all of which gave positive tests with 2,4-dinitrophenylhydrazine. The infrared spectra of all fractions were essentially the same and had no bands characteristic of hydroxyl, carboxyl, or carbonyl groups or carbon-carbon double bonds; there was strong absorption at 9.1, 9.3, 9.7, and 10.0 μ, suggestive of ether type bonds. A 2,4-dinitrophenylhydrazone derivative melted after several recrystallizations from ethanol at 176.5–177.5°.

Anal. Calcd. for $C_{20}H_{22}O_5N_4$: N, 14.06. Found: N, 14.28.

After several further recrystallizations the sample melted at 180–183°. The existence of stereoisomers may account for the difficulty of obtaining a sharp melting derivative as well as for the oily nature of X.

Anal. Calcd. for $C_{20}H_{22}O_5N_4$: C, 60.29; H, 5.57. Found: C, 59.80, 60.64; H, 5.59, 5.61.

(b) Use of sulfuric acid. Tetrahydro acid V (0.50 g.) was added to a solution of 1.0 g. of water in 49 g. of sulfuric acid. The acid slowly dissolved, giving a dark red solution. After the mixture had stood for 2 hr. at room temperature, it was poured onto ice and worked up as in the hydrogen fluoride experiment. The neutral oil (X) weighed 0.292 g. (61%) and no starting acid could be recovered. The infrared spectrum of the oil was the same as the spectrum for the product from the hydrogen fluoride experiment.

The use of concd. sulfuric resulted in water soluble products. Thus, from a 1 hr. reaction of 200 mg. of V in 25 ml. of concd. sulfuric acid at 0° was obtained 66 mg. of starting material (V) and only a trace of neutral organic product. Longer reaction times or higher temperatures resulted in lower recoveries of V.

In contrast to the reactivity of Compound V in strong acids, the acid chloride was stable when treated with stannic chloride in carbon disulfide, and a high yield of the acid was recovered on hydrolysis.

Dehydrogenation of product X. The aldal type product (X) from the sulfuric acid reaction (0.244 g.) was heated at 250–270° with a mixture of 25 mg. of palladium black and 25 mg. of 10% palladium on charcoal. Within 3 hr. 10.3 ml. of hydrogen had been evolved and hydrogen evolution had ceased. The gummy products were taken up in ether, filtered to remove palladium, and the ether evaporated. The residual oil partially crystallized overnight in the form of long needles, which after recrystallization melted at 110–111.5° (11 mg.). This product was identified as 3,3-dimethyl-1,8-naphthalide by its spectrum and a mixture melting point determination.

3-Hydroxy-3-isopropylphthalide (VIII). This compound was prepared by the general procedure of de Benneville,[18] the quantities of reagents being 92 g. of isopropyl bromide, 18.5 g. of magnesium, 60.5 g. of anhydrous calcium chloride, and 89 g. of finely powdered phthalic anhydride. A 37.5% yield (based on phthalic anhydride) was obtained; m.p. 121.5–122.5°; lit.,[19] m.p. 120–121°; neut. equiv. found, 196; neut. equiv. calcd., 192.

A sample of the hydroxyphthalide was dissolved in concd. sulfuric acid, allowed to stand in solution 2 hr., and poured onto chopped ice. A quantitative yield of 3-isopropenylphthalide, m.p. 95–96° (lit.[19] m.p. 96°) was obtained.

Anal. Calcd. for $C_{11}H_{10}O$: C, 75.84; H, 5.79. Found: C, 76.15; H, 5.82.

2-Isobutylbenzoic acid. Concentrated hydrochloric acid (150 ml.) was added over an 8-hr. period to a refluxing, well stirred mixture of hydroxylactone VIII (5.7 g.), acetic acid (25 ml.), hydrochloric acid (25 ml.), and zinc amalgam (prepared from 50 g. of 20 mesh zinc and 5 g. of mercuric chloride). After an additional 16 hr. of reflux the liquid was decanted and extracted with benzene. From the benzene extract was obtained a neutral oil (none of the alkyl benzoic acid was isolated), tentatively identified as 3-isopropylphthalide because it absorbed at 5.69 μ (chloroform solvent) and did not absorb in the hydroxyl region. This same (by infrared) product was obtained in 61% yield by heating an aqueous solution of hydroxyphthalide (VIII) with 20 g. of potassium hydroxide to 75–85° and then adding 15 g. of the granular nickel-aluminum alloy[3] over an hour period. Filtration, acidification of the filtrate and ether extraction yielded the lactone (2.8 g.).

The isopropylphthalide (2.2 g.) was saponified by heating at 160–170° for 18 hr. with 66 g. of triethylene glycol and 8.8 g. of potassium hydroxide; then 60 ml. of water and 7.5 g. of potassium hydroxide were added, the mixture was heated to 95°, and 8.8 g. of finely powdered Raney nickel-aluminum alloy[4] was added (90-min. period) to the well stirred solution. After 3 hr. of additional stirring the mixture was allowed to cool to room temperature and to stand overnight. It was then worked up as the preparation for tetrahydro acid V to give 0.80 g. (36%) of 2-isobutylbenzoic acid, m.p. 62–63.3°; melting point after recrystallization from hexane-ether, 64–65°; lit.,[12] m.p. 64–65°.

A solution of 2-isobutylbenzoic acid (0.600 g.) in concd. sulfuric acid was allowed to stand for 2 hr. at room temperature and then poured onto ice; 0.550 g. (92%) of the isobutylbenzoic acid was recovered, m.p. 63.4–64°. From a solution of 0.75 g. of the acid in 20 g. of liquid hydrogen fluoride which had stood 45 min. at 0° and then 45 min. at room temperature was recovered 0.60 g. (80%) of isobutyl-

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[16] J. v. Braun, *Ann.*, **451**, 29 (1927).

[17] A. Baeyer, *Ann.*, **266**, 184 (1891).

[18] P. L. de Benneville, *J. Org. Chem.*, **6**, 462 (1941).

[19] W. Roser, *Ber.*, **17**, 2777 (1884).

benzoic acid, m.p. 63.5–64°. A trace of a neutral oil was isolated from this reaction but it failed to give a test with 2,4-dinitrophenylhydrazine reagent.

In connection with the preparation of isobutylbenzoic acid it may be noted that an attempt to reduce 7.06 g. of 3-hydroxy-3-isopropylphthalide with hydrazine hydrate (5 ml.) and sodium hydroxide (5 g.) in diethylene glycol (80 ml.) by the Huang-Minlon procedure[20] yielded, instead of a reduction product, 6 g. (87%) of a crystalline solid, m.p. 154–156°; melting point after recrystallization from benzene-hexane, 158–159°; infrared absorption, 3.14, 3.28, 3.34, 6.04 (very strong), 12.68, 13.28 μ. The analysis, mode of formation, and spectrum indicate that this product is 4-isopropylphthalazone.

Anal. Calcd. for $C_{11}H_{12}ON_2$: C, 70.19; H, 6.43; N, 14.89. Found: C, 69.57; H, 6.36; N, 14.93.

EVANSTON, ILL.

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[20] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, THE HEBREW UNIVERSITY]

Experiments in the 4-Arylcycloalk-2-en-1-one Series. V[1]

ERNST D. BERGMANN AND S. YAROSLAVSKY

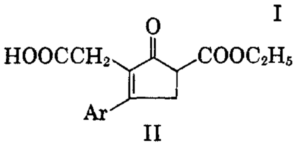
Received April 13, 1960

Some new cases are reported, in which the Stobbe reaction of γ-keto esters leads to cyclopent-2-enone derivatives.

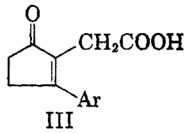
Recently, it has been reported[2] that the Stobbe condensation of ethyl 3-benzoylpropionate (Ia) with diethyl succinate leads unexpectedly to 4-carbethoxy-5-oxo-2-phenylcyclopent-1-enylacetic acid (IIa). Elimination of the 4-carbethoxy group gave 5-oxo-2-phenylcyclopent-1-enylacetic acid (IIIa), characterized by its conversion into 4-hydroxy-3′-oxo-1,2-cyclopentenonaphthalene (IV), which had been prepared before by a different route.

It had escaped our attention that Turner[3] had observed the analogous reaction with methyl β-(5,6,7,8-tetrahydro-2-naphthoyl)propionate (Ib), yielding 5-oxo-2-(5,6,7,8-tetrahydro-2-naphthyl)cyclopent-1-enylacetic acid (IIIb).[4,5] In fact, the reaction seems to be general for esters of 3-aroylpropionic acids. Thus, ethyl 3-(2-naphthoyl)propionate (Ic) gave with diethyl succinate in the presence of sodium hydride an oily acidic product, to which according to the spectrum formula (IIc) was assigned. It could not be isolated in pure form, but was converted, by treatment with boiling alcoholic sulfuric acid, into ethyl 2-(2-naphthyl)-5-oxocyclopent-1-enylacetate and, by subsequent hydrolysis, to the corresponding acid (IIIc) which had the same melting point as a product which Robinson[6] had obtained by a different route and to which he assigned formula (IIIc). This was confirmed by conversion of the compound into 4-acetoxy-3′-oxo-1,2-cyclopentenophenanthrene (V), a compound possessing the steroid skeleton. The oily product obtained from ethyl 3-(*p*-anisoyl)propionate (Id) and diethyl succinate was obviously 4-carbethoxy-2-(*p*-methoxyphenyl)-5-oxocyclopent-1-enylacetic acid (IId), as it could be converted into ethyl 2-(*p*-methoxyphenyl)-5-oxocyclopent-1-enylacetate and the corresponding acid (IIId) which had been prepared before by Turner by a different route.[7] It was cyclized by boiling acetic anhydride to 4-acetoxy-6-methoxy-3′-oxo-1,2-cyclopentenonaphthalene (VI).

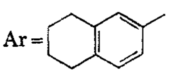
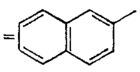
$ArCOCH_2CH_2COOC_2H_5$
I



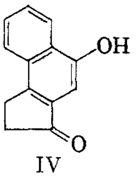
II



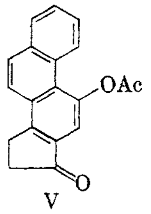
III

a, Ar = C_6H_5 b, Ar =

c, Ar =


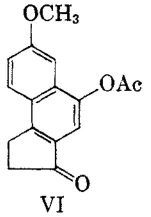
d, Ar = *p*-$CH_3O\cdot C_6H_4$



IV



V



VI

In Table I, the ultraviolet spectra of compounds IIIa, c, and d, of their 2,4-dinitrophenylhydrazones, and of IV, V, and VI are compared. In III, the naphthyl and even more the *p*-methoxyphenyl

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[1] Part IV. E. D. Bergmann and S. Yaroslavsky, *Tetrahedron*, **82**, in press.

[2] E. D. Bergmann, S. Yaroslavsky, and H. Weiler-Feilchenfeld, *J. Am. Chem. Soc.*, **81**, 2775 (1959).

[3] D. L. Turner, *J. Am. Chem. Soc.*, **75**, 1257 (1953).

[4] We are indebted to Dr. D. L. Turner, Jefferson Medical College, Philadelphia, for drawing our attention to his paper.

[5] Another example which—at least formally—belongs to this group is the Stobbe reaction of 2-carbethoxymethyl-1-hydrindone. B. P. Sen, A. Chatterjee, S. K. Gupta, and B. K. Bhattacharyya, *J. Indian Chem. Soc.*, **35**, 751 (1958) [*Chem. Abstr.*, **53**, 16086 (1959)].

[6] R. Robinson, *J. Chem. Soc.*, 1390 (1938).

[7] D. L. Turner, *J. Am. Chem. Soc.*, **71**, 612 (1949). The same acid has recently been described by G. S. Grinenko and V. I. Maksimov [*Zhur. Obshcheĭ Khim.*, **28**, 528 (1958); *Chem. Abstr.*, **52**, 14544 (1958)], m.p. 146°. Turner and we both observed a melting point of 132°.