Notes

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Chemistry of Lactones. IV. Conversion of α-Benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide into 4-Phenyl-2-naphthoic Acid by Intramolecular Alkylation

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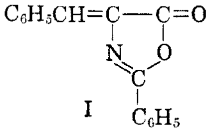
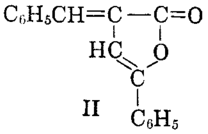
Received February 9, 1959

As part of our research on highly conjugated lactone systems, we have previously reported[2] the reaction of the azlactone, 2-phenyl-4-benzylidene-5(4H)-oxazolone (I) with benzene in the presence of anhydrous aluminum chloride. Although azlactones often resemble cyclic anhydrides in their chemical behavior, I did not act as an acylating agent under these conditions. The reaction followed a different course, the 1,4 addition of benzene to the α,β-unsaturated carbonyl system.

In a continuation of our comparative studies of I and the structurally analogous α-benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (II),[3] with which it is isoelectronic, we have also examined the behavior of II under Friedel-Crafts conditions.

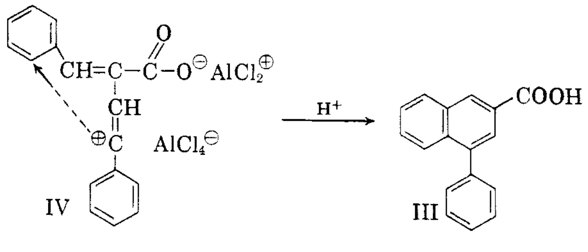

I


II

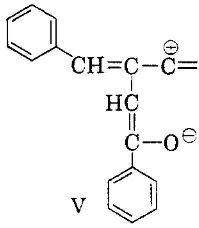
II reacted in the presence of excess benzene and anhydrous $AlCl_3$ to give a 71% yield of a substance (III), whose elemental analysis and molecular weight (determined by neutralization equivalent) indicated that it was a carboxylic acid isomeric with II. The infrared and ultraviolet spectra of III offered additional evidence that this compound was a substituted aromatic acid. III exhibited a strong band at 1695 cm.$^{-1}$, which may be attributed to the carbonyl stretching mode of aromatic carboxylic acids.[4] The weak band at 2600 cm.$^{-1}$ is characteristic of the hydrogen-bonded —OH moiety of the carbonyl group.[5] 2-Naphthoic acid also possessed bands at these frequencies.

In the ultraviolet, the intense K band at 245 mμ (ε 31,000) and the less intense B-band at 290 mμ (ε 7990) are also in general agreement with the spectra of compounds of this type.[6]

On the basis of possible ring opening reactions of the butenolide under these conditions and of the data previously cited, it appeared plausible that III was 4-phenyl-2-naphthoic acid, formed *via* an *intramolecular alkylation* reaction. Thus, the butenolide could readily be converted to a resonance-stabilized carbonium ion (IV), which, by electrophilic attack at the ortho position, would form III:



Decisive evidence for the structure of III was obtained by its decarboxylation to 1-phenylnaphthalene, which was identified by its physical properties and by its conversion to 4-nitro-1-phenylnaphthalene. There was no evidence of any product which could be obtained *via* an incipient acylium ion V (*i.e.*, by inter- or intramolecular acylation). Such an intermediate would be formed by the alternate mode of ring opening of II.



The butenolide failed to react when $AlCl_3$ was replaced by polyphosphoric acid, but when the original procedure was carried out using anisole in place of benzene, III was again the sole product isolated, though only in 50% yield. This result further emphasizes the intramolecular nature of this reaction.

Whereas the isomeric 1-phenyl-2-naphthoic and 4-phenyl-1-naphthoic acids[7] are known, 4-phenyl-2-naphthoic acid (having a considerably higher melting point) has, to our knowledge, not been de-

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[1] From the M. S. thesis of L. H. M., April, 1959.

[2] R. Filler and L. M. Hebron, *J. Org. Chem.*, **23**, 1815 (1958).

[3] R. Filler and L. M. Hebron, *J. Am. Chem. Soc.*, **81**, 391 (1959).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 168.

[5] Ref. 4, p. 163.

[6] Benzoic acid, for example, exhibits comparable maxima at 230 mμ and 270 mμ. A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," 2nd ed., Edward Arnold, Ltd., London, 1957, p. 141.

[7] *Chemical Abstracts* nomenclature.

scribed previously and would appear to be quite difficult to obtain by any other means. It seems clear that we have available an excellent method for preparing certain substituted naphthalene compounds from selected β,γ-unsaturated lactones. The scope and limitations of the method are being explored further.

Other striking differences in chemical behavior between I and II have been observed and these will be discussed in a forthcoming paper.

EXPERIMENTAL[8]

Reaction of α-benzylidene-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (II) with benzene. In a 2-l., round bottomed flask, fitted with a mechanical stirrer, dropping funnel, and reflux condenser, were placed 19.8 g. (0.15 mol.) of anhydrous aluminum chloride in 250 ml. of dry, thiophene-free benzene. The mixture was cooled to 10–20° and stirred for 1 hr. To this mixture was added dropwise with stirring a solution containing 12.4 g. (0.05 mol.) of II in 250 ml. of dry benzene, the temperature being maintained at 10–20° during the addition. The mixture turned brick-red. When all of the butenolide had been added, the mixture was stirred for an additional 3 hr. at room temperature. The complex was decomposed with dilute hydrochloric acid and the resulting mixture extracted with ether. The ether layer was washed with dilute sodium bicarbonate solution and water and then dried over anhydrous magnesium sulfate. Upon evaporation of the solvent on steam bath, a yellowish white solid was obtained. Crystallization from 95% ethanol gave 8.5 g. (70.8%) of white needles of 4-phenyl-2-naphthoic acid (III), m.p. 262.5–263.5°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.83. Found: C, 82.52; H, 4.81. Mol. wt. calcd.: 248. Found: 248 (neut. equiv.).

λ_{max}^{EtOH} 245 mμ (ϵ 31,000), 290 mμ (ϵ 7990). Infrared absorption at 1695 cm.$^{-1}$ (s) and 2600 cm.$^{-1}$ (w).

Reaction of II with anisole. In a 500-ml. round bottomed flask, fitted with a mechanical stirrer, dropping funnel, and reflux condenser, were placed 4.7 g. (0.036 mol.) of anhydrous aluminum chloride and 3.8 g. (0.036 mol.) of anisole in 65 ml. of methylene chloride. The mixture was stirred for 1 hr. at 10°. To this mixture was added dropwise with stirring a solution containing 3 g. (0.012 mol.) of II in 100 ml. methylene chloride, the temperature being maintained at 10–20° during the addition. When all of the butenolide had been added, the mixture was stirred for an additional 3 hr. at room temperature. The complex was decomposed with 250 ml. of dilute (1:15) hydrochloric acid and the two layers which formed were separated, the water layer was washed with methylene chloride and the combined extracts were washed with dilute acid and water until neutral to litmus. Excess methylene chloride was removed by evaporation on a steam bath. The product was crystallized from 95% ethanol to give 1.5 g. (50%) of white needles, m.p. 258–260°.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.83. Found: C, 82.57; H, 5.17.

Mixed melting point with the product obtained with benzene showed no depression. The ultraviolet and infrared spectra were also identical.

Decarboxylation of 4-phenyl-2-naphthoic acid (III). III [8.13 g. (0.033 mol.)] and 0.648 g. (0.0028 mol.) of copper chromite in 10 ml. of quinoline were heated under slow reflux for 7 hr. The mixture was treated with 100 ml. of ether and washed with several portions of dilute hydrochloric acid followed by sodium bicarbonate solution and water. The ether layer was dried over anhydrous magnesium sulfate.

The ether was removed by evaporation and 1-phenylnaphthalene was obtained as a viscous oil, b.p. 333–335° at 748 mm., $n_D^{23.4}$ 1.6654 (reported b.p. 334–336°,[9] n_D^{18} 1.6692[10]).

Nitration of 1-phenylnaphthalene. To 3 ml. of a 50-50 mixture of fuming nitric acid and glacial acetic acid, cooled in an ice bath, was added dropwise 0.25 ml. of 1-phenylnaphthalene. The solution was mixed and poured over ice. The 4-nitro-1-phenylnaphthalene thus obtained was crystallized from petroleum ether to give yellow crystals melting at 129–130° (reported[11] m.p. 129–130°).

Spectral measurements and analyses. Infrared spectra were obtained on a Perkin-Elmer 21 spectrophotometer, using chloroform as solvent. Ultraviolet spectra were measured in 95% ethanol using a Beckman DK-2 spectrophotometer. Microanalyses were conducted by Micro-Tech Laboratories, Skokie, Ill.

Acknowledgment. The authors gratefully acknowledge the financial assistance of the Research Corp. and the Philip D. Armour Cancer Fund.

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[8] M.p.'s are corrected.

(9) R. Weiss and K. Woidich, *Monatsh.*, 46, 455 (1925).

(10) W. Davies, N. W. Gamble, aud W. E. Savage, *J. Chem. Soc.*, 4678 (1952).

(11) R. T. Arnold, C. Collins, and W. Zenk, *J. Am. Chem. Soc.*, 62, 983 (1940).

Aluminum Iodide as a Friedel-Crafts Catalyst[1]

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Received April 1, 1959

A comparison of aluminum iodide with aluminum chloride and aluminum bromide as catalysts in typical Friedel-Crafts alkylations and acylations seems not to have been reported. The absence of such an investigation may be due, in part, to the well known sensitivity of aluminum iodide to air and moisture.[4]

Aluminum iodide was prepared by two methods which minimize contact with air and moisture. Comparisons have been made with aluminum chloride and aluminum bromide as catalysts in the isopropylation, succinoylation, and benzoylation of benzene. The results of these experiments are summarized in Table I. The reactions using aluminum chloride reported in this table are each the best of several made to determine conditions which give moderately good yields. The alkylations with aluminum bromide and aluminum iodide (Method B) represent the average of two runs. Although aluminum iodide acts as a catalyst in all these reactions,

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(1) Based on part of the Ph.D. thesis of B.N.C., University of Connecticut, 1958.

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(4) G. W. Watt and J. L. Hall, *Inorganic Syntheses*, McGraw-Hill Book Company, Inc., New York, N. Y., 1953, Vol. IV, p. 119.