
THE OXIDATION OF β -AROYL PROPIONIC ACIDS BY SODIUM HYPOCHLORITE¹

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As part of a general study of the applicability of the Friedel and Crafts Reaction to qualitative organic chemistry, the oxidation of β -aroyl propionic acids has been investigated. The β -aroyl propionic acids have been recommended as derivatives of aryl hydrocarbons by Reinheimer and Taylor (1954). If these acids could be oxidized to the corresponding benzoic acid, a second derivative of the original hydrocarbon would become available.

MATERIALS AND METHODS

Procedures for the oxidation of a keto containing side chain without simultaneously oxidizing other side chains generally require the use of hypochlorite. Several procedures were recommended in the literature. Zaki and Fakim (1942) used an alkaline NaOBr solution. This procedure was not regarded as suitable, for the reagent was expensive and had to be prepared immediately before use. Fieser and Bradsher (1936) used NaOCl in an acid solution. They noted that chlorination of the benzene ring occurred if the ring were sufficiently activated. While the aromatic rings in this series of aroyl propionic acids were not highly activated, this chlorination reaction might possibly interfere. Short, Stromberg and Wiles (1936) were able to avoid ring chlorination by the use of alkaline hypochlorite solution. An adaptation of their procedure was employed.

The details of the modified procedure of Short, Stromberg and Wiles are as follows: An oxidizing solution was prepared by dissolving 2 gm. of NaOH in 40 ml. of 5.25 percent NaOCl and diluting to 100 ml. with water. One gm. of the β -aroyl propionic acid was dissolved in 100 ml. of the NaOCl solution and was warmed in a water bath for 20 to 30 minutes. After the reaction mixture had been refluxed for an additional one-half hour, the hot solution was filtered and cooled to room temperature. The acid product was precipitated by bubbling in sulfur dioxide for 4 to 5 minutes. The crude derivative was separated by filtration, washed several times with cold water and finally recrystallized from ethanol or an ethanol water mixture.

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The yields which are reported in table 1 were taken on material that was dried for 24 hours in a vacuum dessicator; all melting points reported were taken with a calibrated thermometer.

DISCUSSION AND RESULTS

The results of this oxidation procedure are collected in table 1 and table 2. In table 1 β -keto acids and their oxidation products are listed according to the boiling point of the parent hydrocarbon from which they were derived. The oxidation products provide satisfactory derivatives of the original hydrocarbon

TABLE 1
Oxidation products of aroyl propionic acids of aromatic hydrocarbons

| Aromatic Hydrocarbons | B.P. °C | M.P. of Aroyl Propionic Acid, °C | Crude Yield % | M.P. °C Derivative | |
|----------------------------|---------|----------------------------------|---------------|--------------------|-------------------------------|
| | | | | Observed | Literature |
| Benzene | 80 | 116.5-17.5 | 64.8 | 121.7(1x) | 121.7 (Beilstein, 1926) |
| Toluene | 111 | 127.0-28.5 | 69.7 | 180.5-81(2x) | 180 (Beilstein, 1926) |
| Ethyl Benzene | 135 | 107.0-08.5 | 57.6 | 111-12(1x) | 110-11 (Beilstein, 1926) |
| m-Xylene | 139 | 112.0-13.0 | 74.0 | 125.1-26.6(2x) | 126 (Beilstein, 1926) |
| o-Xylene | 142 | 130.0-31.0 | 91.3 | 165.9-65.9(1x) | 166 (Beilstein, 1926) |
| Cumene | 153 | 139.5-41.5 | 73.8 | 116.6-18.0(1x) | 116-18 (Beilstein, 1926) |
| n-Propylbenzene | 158 | 120.5-22.5 | 59.3 | 141.4-41.9(1x) | 140-41 (Beilstein, 1926) |
| Mesitylene | 164 | 109-09.5 | 60.4 | 148-50(1x) | 147-49 (Beilstein, 1926) |
| tert-Butylbenzene | 169 | 123.5-25 | 82.2 | 164.1-65.2(3x) | 164 (Beilstein, 1926) |
| sec-Butylbenzene | 173 | 95.5-96.5 | 54 | 92.5-93.5(1x) | 91-92 (Marvel, 1943) |
| n-Butylbenzene | 182 | 111-12.5 | 82.6 | 101-102(1x) | 102.5-03 (Beilstein, 1926) |
| Tetralin | 206 | 121-22 | 60.1 | 152.2-53.0(3x) | 154 (Heilbrun, 1953) |
| Phenylcyclohexane | 237 | 136-36.5 | 96.9 | 191.5-93.5(3x) | 198 (Bordroux, 1938) |
| β -Methylnaphthalene | 32* | 165-66 | 77 | 228.5-30.5(2x) | 228-30 (Heilbrun, 1953) |
| Diphenyl | 70* | 183.5-85 | 66.6 | 223.5-24.5(1x) | 224 (Beilstein, 1926) |
| Naphthalene | 80* | 172-73 | 82.9 | 182-83(1x) | 182-82.5 (Beilstein, 1926) |
| Acenaphthene | 95* | 209-210 | 78.1 | 217-17.5(1x) | 217 (Beilstein, 1926) |
| Fluorene | 115* | 212-13 | 52.2 | Sublimes | Sublimes (Beilstein, 1926) |

*Melting point.

(x) represents the number of recrystallizations.

TABLE 2
Oxidation products of aroyl propionic acids

| Original Aromatic Hydrocarbon Used | M.P. °C of Keto Acid | M.P. °C of Oxidation Product |
|------------------------------------|----------------------|------------------------------|
| sec-Butylbenzene | 95.5-96.5 | 92.5-93.5 |
| Ethyl benzene | 107.5-08.5 | 111-12 |
| Mesitylene | 109-09.5 | 148-50 |
| n-Butylbenzene | 111-13.5 | 101-02 |
| m-Xylene | 112-13 | 125.1-26.6 |
| Benzene | 116.5-17.5 | 121.7 |
| n-Propylbenzene | 120.5-22.5 | 141.4-41.9 |
| Tetralin | 121-22 | 152.2-53 |
| tert-Butylbenzene | 123.5-25 | 164.1-65.2 |
| Toluene | 127.5-28.5 | 180.5-81 |
| o-Xylene | 130-31 | 165.4-65.9 |
| Phenylcyclohexane | 136-36.5 | 191.5-93.5 |
| Cumene | 139.5-41.5 | 116.6-18 |
| β -Methylnaphthalene | 165-66 | 228.5-30.5 |
| Naphthalene | 172-73 | 182-83 |
| Diphenyl | 187.5-88 | 223.5-24.5 |
| Acenaphthene | 209-10 | 217-17.5 |
| Fluorene | 212-13 | Sublimes over 260 |

for: a) the procedure is simple and the yields are fair to good; b) the products are generally pure, so that only one or two recrystallizations are required to obtain a sharp melting point; c) the melting points are high, and the melting point difference between successive members of the series is sufficient for positive identification; d) the melting point of the product is considerably different from that of the reactant in all but two cases.

The data obtained from the oxidation of this series of keto acids may be arranged to show that the keto acids may also be identified by means of the melting points of the oxidation products. This arrangement is presented in table 2, in which the keto acids are listed according to melting point. The oxidation products are suitable as derivatives of the keto acids for essentially the same reasons as presented above.

SUMMARY

The oxidation of β -aroyl propionic acids was successful in 17 of 18 trials. The substituted benzoic acids obtained are recommended as suitable derivatives for both the original hydrocarbon and the β -aroyl propionic acids.

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