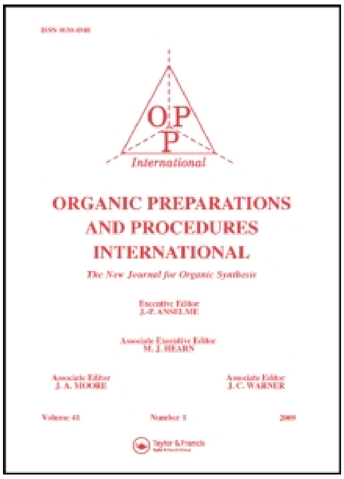

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A NEW ROUTE TO 1,2-INDANEDIONE

H. Harry Szmant[a]; Raghunath Nanjundiah[a]
[a] Department of Chemistry and Chemical Engineering, University of Detroit, Detroit, Mich

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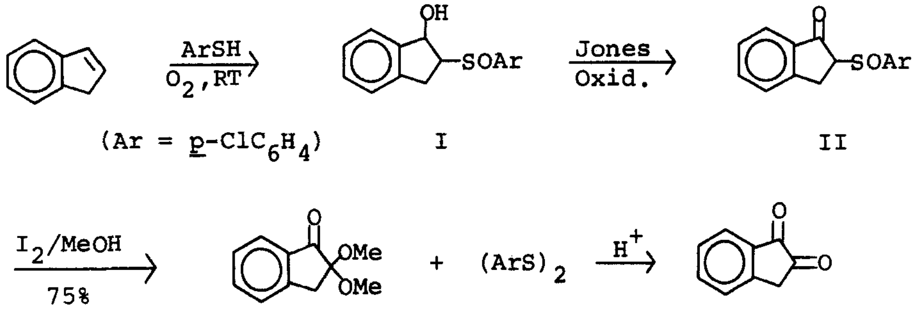
A NEW ROUTE TO 1,2-INDANEDIONE

H. Harry Szmant* and Raghunath Nanjundiah
Department of Chemistry and Chemical Engineering
University of Detroit, Detroit, Mich. 48221

The facile conversion of indene to a mixture of isomeric β-hydroxy sulfoxides (I)[1] which are readily oxidized to β-keto sulfoxides II coupled with the ready conversion of II to α-keto acetate[2] suggested a convenient three-step route from indene to 1,2-indanedione (IV) and its β-monoketal III.



III

IV

EXPERIMENTAL

1-Hydroxy-2-p-chlorophenylsulfinylindane (I). - Equimolar amounts (0.16 mole) of freshly distilled indene and p-chlorothiophenol were dissolved in 350 ml of isooctane. Oxygen was bubbled for 48 hours through the reaction mixture kept at room temperature. The mixture of the isomeric β-hydroxy sulfoxides was filtered, washed with isooctane and recrystallized from ethanol. Mp. 138-152°, yield: 85-90%. The mixture of the three isomers was used in the synthetic applications described below.

<u>1-Keto-2-p-chlorophenylsulfinylindane (II)</u>. - Jones' reagent - prepared by dilution of a solution of 26.72 g of chromium trioxide in 23 ml of conc. sulfuric acid with water to the volume of 100 ml - was added dropwise to a solution of 2 g of I in 40 ml of reagent grade acetone until the color of the top layer changed from green to brown. The solvent was removed under vacuum and the residue was extracted with chloroform. The extract was washed with water until the top layer was clear, dried over anhydrous sodium sulfate and evaporated to give 80% of II, mp. 160-162°, ir (cm^{-1}) 1720, 1610, 1580, 1020, 750; nmr ($CDCl_3$) δ 3-4 (m,3), 7.5-8 (m,8). <u>Anal</u>. Calc'd. for $C_{15}H_{11}O_2SCl$: C, 61.85; H, 3.78; S, 10.99. Found: C, 61.87; H, 3.82; S, 11.16.

<u>1-Keto-2,2-dimethoxyindane (III)</u>. - A solution of 1.5 g of II and 0.8 g of iodine in 20 ml of methanol was heated to reflux for 90 min. The solvent was removed under vacuum and the residue was extracted with chloroform. The extract was washed first with a saturated solution of sodium thiosulfate and then with water, dried over anhydrous sodium sulfate and concentrated to give a residue which was chromatographed on 80 g of alumina (F-20). The material was eluted with hexane, a mixture of hexane and benzene and finally benzene. The hexane fraction gave a quantitative yield of <u>p</u>-chlorophenyl disulfide, mp. 72-73°, lit[3] mp. 71-72°, and the hexane-

benzene fraction produced a 75% yield of III, bp. 114°/3 mm, mp. 54-56°; nmr ($CDCl_3$) δ 3.2 (s,2), 3.6 (s,6), 7.4 (m,4). Anal. Calc'd. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.48; H, 6.06.

The mono-2,4-dinitrophenylhydrazone was prepared by treatment of III with the DNPH reagent for 5 min., mp. 180-185°. Anal. Calc'd. for $C_{17}H_{16}O_4N_4$: C, 55.74; H, 2.75; N, 15.00. Found: C, 55.35; H, 2.67; N, 15.29. The treatment of III with the DNPH reagent overnight gave the bis-2,4-dinitrophenylhydrazone, mp. 240°.

Anal. Calc'd. for $C_{21}H_{14}O_8N_8$: C, 49.81; H, 2.78; N, 22.12. Found: C, 50.11; H, 2.81; N, 21.47.

Treatment of III with hydrogen peroxide (30%) in acetic acid at room temperature gave homophthalic acid, while with o-phenylenediamine in methanol, indenoquinoxaline, mp. 162-163°, lit.[4] mp. 164-165° was obtained.

1,2-Indanedione (IV). - A solution of 0.5 g of III in 40 ml of ethanol was refluxed for 30 min. in the presence of a few drops of sulfuric acid. The solvent was removed under vaccum and the yellow residue was extracted with chloroform. The extract was washed with water, dried over anhydrous sodium sulfate and concentrated. IV was recrystallized from benzene, mp. 110-115°, lit.[4] mp. 95-115°, yield: 80%.

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REFERENCES

1. T. L. Moore, J. Org. Chem., 32, 2786 (1967).
2. H. H. Szmant et.al., J. Org. Chem., 37, 447 (1972); Tetrahedron, 32, 2665 (1976).
3. E. Hoggarth and W. A. Sexton, J. Chem. Soc., 815 (1947).
4. Elsevier's Encyclopedia, V.12A, p.220 (1948).

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