

NOTE

Aromatization of Stobbe Reaction Products

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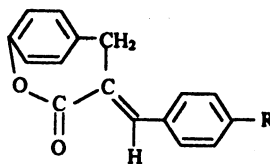
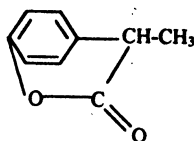
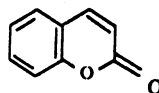
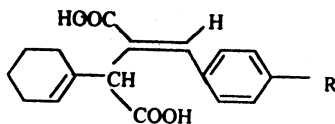
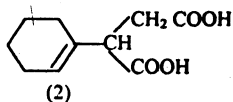
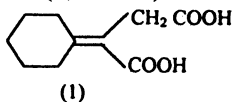
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Stobbe condensation products (diacids) of dimethylsuccinate and dimethyl itaconate with cyclohexanone aromatize into aromatic lactones when N-bromosuccinimide (NBS) in CCl_4 with benzoylperoxide is used but give back the original acids when sulphur in xylene is the reagent for aromatization.

Key Words: Aromatization, Stobbe reaction, Products.

Aromatization reactions have been particularly important in the proof of structure of many cyclic natural products like steroids and terpenes. Aromatization of six-membered alicyclic ring to aromatic phenyl ring is a common feature and can be achieved in a number of ways. The cyclohexane ring with an exo-double bond in cyclohexylidenesuccinic acid (1)^{1,2} and the same with endo-double bonds in cyclohexenylsuccinic acid (2)^{1,2} and 1-cyclohexenyl-1-carboxy-3-arylprop-2-ene-2-carboxylic acid (3)^{2,3} aromatizes into a phenyl ring when N-bromosuccinimide (NBS) and benzoyl-peroxide in CCl_4 is used⁴ for 2 h under boiling conditions. The reaction products are lactones bearing an aromatized phenyl ring obtained in quantitative yield.

Aromatization is not possible under reflux for 8 h with sulphur in xylene⁵ and the original acids (1, 2 and 3) are obtained back.



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Aromatisation with sulphur in xylene: Diacid (1, 2 or 3) (1.0 g) and elemental sulphur (1.0 g) in xylene (10.0 mL) were mixed and refluxed for 8 h. The reaction mixture was extracted in benzene in ice and washed with 10% ice cold aq. sodium carbonate solution which on acidification with conc. HCl gave back the original diacid.

Aromatisation with NBS and benzoylperoxide in CCl₄: Diacid (1, 2 or 3) (1.0 g), N-bromosuccinimide (1.0 g), benzoylperoxide (0.2 g) and CCl₄ (250.0 mL) were mixed and refluxed for 2 h. The reaction mixture was cooled in ice and filtered. The filtrate was washed with 10% ice-cold aq. sodium carbonate solution repeatedly, then with ice-cold water and dried over anhydrous sodium sulphate. On concentration with n-hexane, white crystals of lactones (4, 5, 6a) and lemon yellow crystals of lactone (6b) were obtained in quantitative yield, m.p. 102°C (4), 101°C (5), 101°C (6a) and 103°C (6b).

The absence of alicyclic protons in the PMR spectra of all the products show that aromatization is total. Only aromatic protons at 6.40 to 8.23 δ for (4), a methyl peak at 1.26 δ and >CH-peak as deshielded quartet at 1.68–2.30 δ for (5) and a methylene peak 1.25 δ^* for (6) confirm the respective lactonic structures of the products. The aromatic lactonic structures for products (4, 5 and 6) are further confirmed from IR spectra which show peaks at 1792 and 1765 ν (C=O lactone) and 1180 cm^{-1} ν (C—O str. lactone) for (4), at 1770 ν (C=O lactone) and 1175 cm^{-1} ν (C—O str. lactone) for (5), at 1790 and 1765 ν (C=O lactone) and 1180 cm^{-1} ν (C—O str. lactone) for (6a) and at 1765 ν (C=O lactone) and 1175 cm^{-1} ν (C—O str. lactone) for (6b).

Aromatization can be accomplished most easily if there are already one or two double bonds in the ring or if the ring is fused to an aromatic ring. The above reactions also reflect the stability of the Stobbe condensation products which aromatize only in the presence of very potent reagents.

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* Though this methylene falls in the deshielding zone of the aromatized phenyl ring, it shows shielding due to the facing Ar group.