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Synthesis of 2,2-Dichloroindane-1,3-diones from 1,4-Naphthoquinones

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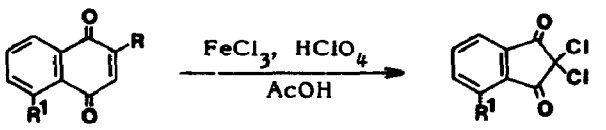
Abstract: Reaction of 1,4-naphthoquinone (1) and its derivatives (2 and 3) with iron(III) chloride in the presence of perchloric acid affords 2,2-dichloroindane-1,3-dione (5) while 5-hydroxy-1,4-naphthoquinone (4) gives 2,2-dichloro-4-hydroxyindane-1,3-dione (6).

Reaction of iron(III) salts with variety of organic substrates give varying products. Formation of biaryls and diarylmethanes have been reported[1] from the reaction between iron(III) chloride and methylbenzene . Iron(III) salts have also been reported to oxidise p-xylene[2] and p-methoxytoluene[3]. Similar reaction was applied to flavonoids[4] when 5-hydroxy-4',7-dimethoxyflavone selectively gave 6-chloro and 8-chloro derivatives instead of diaryl methane or diaryl while 4'-hydroxy-5,7-dimethoxyflavone gave diarylmethane[5]. We have observed a novel reaction when 1,4-naphthoquinone and its derivatives are treated with iron(III) chloride in the presence of perchloric acid to give 2,2-dichloroindane-1,3-dione and its derivatives. In all the cases studied, it has been observed that one of the quinonoid methine carbons is lost resulting in dichlorodiketo product. Out of the two quinonoid methine carbons the substituted one is lost in all the cases studied. The reaction is of unique type and can be used for the economic synthesis of 2,2-dichloroindane-1,3-dione (5) and is a better method compared to the reported one[6].

Each of the 1,4-naphthoquinones (1, 2 and 3) (2 mmol) was refluxed with ferric chloride (3 mmol) and 66% perchloric acid (1 ml) in acetic acid (10 ml) for 6 hours. The reaction mixture was cooled, and poured into ice cold water. The precipitate was filtered and washed with water. On purification by passing over a column (silica gel, petroleum ether) it gave 5 as offwhite crystals; yield 95%; m.p. 124-25°C (lit.[6] 124°C); IR (KBr) ν_{max} 1730, 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.05 (s, aromatic protons) and m/e 216($M^{\dot{+}}$+2; 66%), 214($M^{\dot{+}}$; 100%), 179($M^{\dot{+}}$-Cl). The reaction with compound 4 gave 2,2-dichloro-4-hydroxyindane-1,3-dione (6): yield 50%; m.p. 159°C, IR(KBr) ν_{max} 1715, 1760, 3360 cm^{-1}; ^1H NMR ($CDCl_3$+TFA) δ 7.45(d, 1H, J=10 Hz, C_6-H), 7.6(d, 1H, J = 10 Hz, C_5-H), 7.90(d, 1H, J = 10 Hz, C_7-H); m/e 232($M^{\dot{+}}$+2; 66%), 230($M^{\dot{+}}$; 100%); 195($M^{\dot{+}}$-Cl), 167, 139.



1 R = R^1 = H

2 R = CH_3; R^1 = H

3 R = OH; R^1 = H

4 R = H; R^1 = OH

5 R^1 = H

6 R^1 = OH

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