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ADAMANTANOID DIENONES

By Robert S. Atkinson and James E. Miller
(Department of Chemistry, Leicester University, Leicester LE1 7RH)

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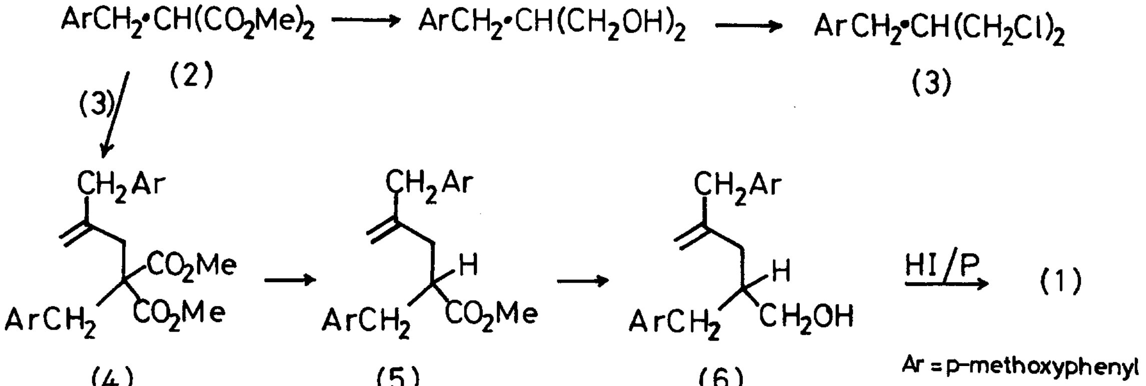
Intramolecular participation of a phenolate anion with displacement of a suitably located leaving group has been used to synthesise a variety of polycyclic dienones.[1] Acid treatment of the latter leads to phenols by the dienone-phenol rearrangement. We have synthesised the phenolic iodide (1) and subjected it to conditions necessary for Ar_1 6 participation.[2] The successful route to (1) is shown in Scheme 1 which advantageously uses dimethyl p-methoxybenzylmalonate (2) as a common starting material for both halves of the molecule.



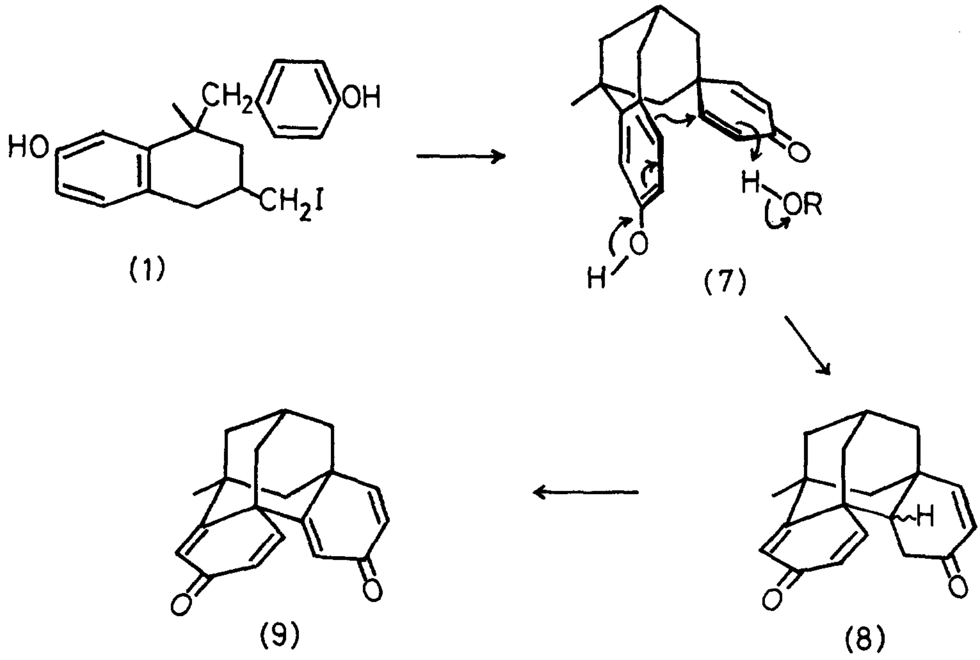
Scheme 1

The use of (3) as an alkylating agent is noteworthy since elimination of HCl in the reaction (either before or after reaction of (3) with the malonate (2)) occurs in the presence of a second mole of base with production of the non-conjugated olefin. Decarbomethoxylation[3] of the diester (4) (m.p. 50.5-51.5°) gave the monoester (5) which was reduced to alcohol (6) (m.p. 59-60°). Heating alcohol (6) in concentrated hydriodic acid in the presence of a little red phosphorus gave the unstable iodide (1) (45%) as a glass whose n.m.r. spectrum revealed the presence of both stereoisomers in a ∿3:1 ratio.

Reaction of (1) at 170° with potassium t-butoxide in t-butanol (sealed tube) gave two different dienones depending upon the concentration of base used : with 2.5 equivalents, the expected phenolic dienone (7) was isolated, m.p. 216-219° i.r. (Nujol) 3190, 1655, 1610, 1580 cm^{-1}; n.m.r. δ (CD_3COCD_3) 8.10 (1H, s br. exch. D_2O), 7.1-6.6 (4H, m), 6.28 (1H, dd, J 12.5 x 2.5 Hz), 6.00 (1H, dd, J 10 x 2.5 Hz), 5.60 (1H, dd, J 12.5 x 2.5 Hz), 3.4-1.4 (9H, m), 1.30 (3H, s). If only 1 equivalent of base was used, a product, m.p. 237-239° was obtained, formulated as the adamantanoid dienone (8); i.r. (Nujol) 1665, 1655, 1625, 1600 cm^{-1}; n.m.r.

δ ($CDCl_3$) 6.72 (2H, d, J 10 Hz), 6.38 (1H, dd, J 10 x 2 Hz), 6.32 (1H, s), 5.94 (1H, d, J 10 Hz), 2.6-1.4 (12H, m), 1.09 (3H, s).

Although the yields of (7) and (8) from the iodide (1) were consistently low (12%), we suspect that the epimer of (1) with p-methoxybenzyl and iodomethyl groups cis, necessary for formation of (7), is that present in the lesser amount.



An adamantane skeleton for (8) is assigned from a consideration of the mechanism involved in its formation from (7) (arrows). The stereochemistry of the cyclohexenone ring fusion in (8) is unknown but after dehydrogenation with DDQ in dioxane, the bis-dienone (9) is obtained, m.p. 195-202° in which all six dienone ring protons are visible at different chemical shifts in the n.m.r. spectrum:[4] δ ($CDCl_3$) 7.09 (1H, d, J 10 Hz), 6.79 (1H, d, J 10 Hz), 6.51 (1H, dd, J 10 x 1.5 Hz), 6.29 (1H, dd, J 10 x 1.5 Hz), 6.18 (1H, d, J 1.5 Hz), 6.12 (1H, d, J 1.5 Hz), 2.6-1.4 (9H, m), 1.24 (3H, s).

A dienone-phenol rearrangement of (9) would be expected to be difficult since the resulting rigid (homoadamantyl) framework necessitates a bent phenol ring. Consequently, it was not surprising to find that (9) was unaffected by standing in trifluoroacetic acid for one week: simple dienones suffer rearrangement under these conditions within hours.

References

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