Facile Generation and Trapping of α-Oxo-*o*-quinodimethane; a Synthesis of 3-Aryl-3,4-dihydroisocoumarins

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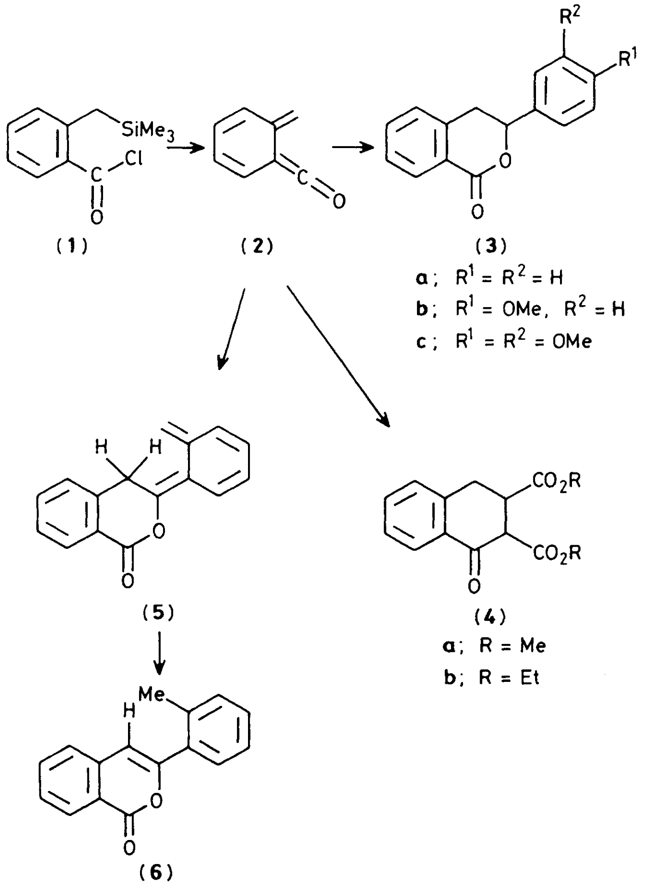
Treatment of *o*-(trimethylsilylmethyl)benzoyl chloride (**1**) with fluoride ions in the presence of aromatic aldehydes and alkyl fumarates gives 3-aryl-3,4-dihydroisocoumarins (**3**) and substituted α-tetralones (**4**), respectively.

α-Oxo-*o*-quinodimethanes (**2**) are intermediates of considerable interest which on suitable [2 + 4] trapping give functionalised bicyclic systems. These intermediates (**2**) have been generated by thermolysis of benzocyclobutenones[1] and homophthalic anhydrides.[2] We have found that desilylation of *o*-(trimethylsilylmethyl)benzoyl chloride (**1**) provides a convenient route to them.[3]

Treatment of the acid chloride[4] (**1**) with CsF in refluxing acetonitrile (or Bu_4NF in tetrahydrofuran or CH_2Cl_2) containing aromatic aldehydes furnished 3-aryl-3,4-dihydroisocoumarins.[5] With benzaldehyde, (**3a**) was obtained [38%, m.p. 88—90 °C (lit.[5] 87—89 °C)]; *p*-anisaldehyde, (**3b**) [51%, m.p. 108—109 °C (lit.[5] 109 °C)]; veratraldehyde (**3c**) [62%, m.p. 101—102 °C, δ_H ($CDCl_3$) 3.19 (m, 2H, CH_2), 3.99



(s, 6H, 2 × OMe), 5.55 (dd, 1H, CH), 7.35 (m, 6H, ArH), 8.25 (d, 1H, ArH)].

Under similar conditions, alkyl fumarates formed adducts (**4**) in moderate yield: with dimethyl fumarate, (**4a**) [48%, m.p. 87—88 °C (lit.[1], 86—88 °C)]; diethyl fumarate, (**4b**)† [60%, m.p. 54—55 °C, δ_H (CCl_4) 1.15 (t, 3H, CO_2Et), 1.35 (t, 3H, CO_2Et), 3.24 (m, 2H, $ArCH_2$), 3.68—4.53 (m, 6H, 2 × CO_2CH_2, COCHCO, COCH), 7.32 (m, 3H, ArH), 7.96 (d, 1H, ArH)]. When dimethyl acetylenedicarboxylate was employed trapping proceeded inefficiently (*ca.* 10% yield by n.m.r. spectroscopy). In desilylations carried out in the presence of methyl acrylate and acrylonitrile, or without any addend, the isocoumarin (**6**) was the predominant product [40%, m.p. 63—65 °C, δ_H (CCl_4) 2.48 (s, 3H, Me), 6.49 (s, 1H, =CH), 7.31 (m, 7H, ArH), 8.25 (d, 1H, ArH)]. Formation of (**6**) can be rationalised in terms of self trapping of (**2**) followed by a 1,5-hydrogen shift in the dimer (**5**).

The reactions were carried out in refluxing acetonitrile (4.5 h) using the acid chloride, CsF, and the dienophile in the molar ratio 1:1.2:3. The yields are for pure compounds isolated through chromatography and/or crystallisation.‡

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References

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3 Generation of an imino analogue of (**2**) has been described recently; Y. Ito, E. Nakajo, and T. Saegusa, *Tetrahedron Lett.*, 1984, **25**, 5139. We are grateful to a referee for bringing to our notice a related publication on reaction of F^- with methyl-*o*-(trimethylsilylmethyl)benzoate; A. Aono, Y. Terao, and K. Achiwa, *Chem. Lett.*, 1985, **3**, 339. We have also observed that products derived from the intermediate (**2**) are formed on desilylation of corresponding esters and benzene sulphonic anhydrides.

4 W. R. Bergmark, M. Medaor, J. Issacs, and M. Thim, *Tetrahedron*, 1983, **39**, 1109.

5 For importance and methods for synthesis of this class of compounds see; M. Watanabe, M. Sahara, M. Kubo, S. Furukawa, R. J. Billedeau, and V. Snieckus, *J. Org. Chem.*, 1984, **49**, 742.

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† Obtained as a keto–enol mixture which on crystallisation from hexane gave the pure keto form.

‡ All new compounds gave satisfactory analytical and spectral data.