

A Photobisdecarbonylation Route to Isoindenes: a New Synthesis of 2,2-Dimethyl- and 2,2-Spirocyclopentyl-isoindene

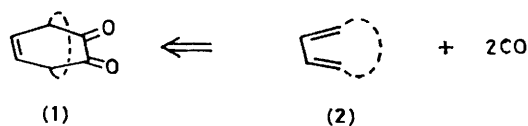
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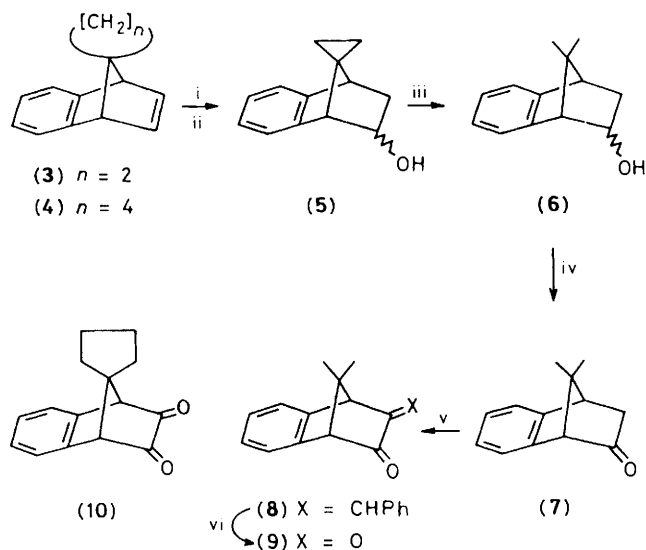
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The title isoindenes have been prepared by u.v. photolysis of the appropriate 7,7-disubstituted benzonorbornene-2,3-diones, the syntheses of which are described.

The α -dicarbonyl bridge can be used as a protecting group for conjugated dienes, according to the retrosynthetic analysis shown in Scheme 1. The α -dicarbonyl group is characterised by high thermal stability yet can be removed readily by u.v. photolysis.¹ This has been employed by ourselves² and others³ for the preparation of bicyclo[4.2.0]octa-2,4,7-trienes, which



Scheme 1



Scheme 2. Reagents: i, B_2H_6 ; ii, $\text{NaOH-H}_2\text{O}_2$; iii, $\text{H}_2\text{-Pt}$; iv, CrO_3 ; v, PhCHO-NaOMe ; vi, $\text{O}_3\text{-Me}_2\text{S}$.

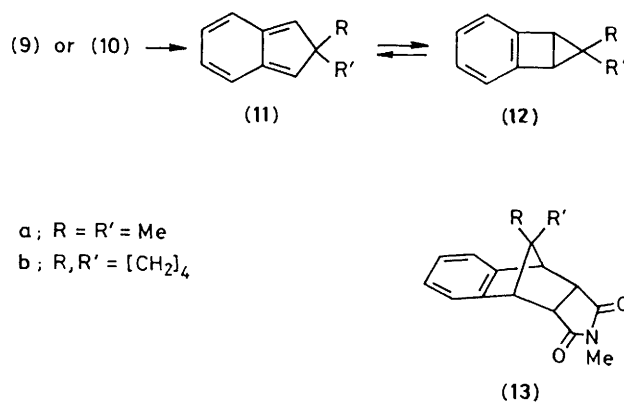
are not readily accessible by other routes. The present report details synthetic aspects of the photobisdecarbonylation of 7,7-disubstituted benzonorbornene-2,3-diones as a route to isoindenes, another highly reactive system.⁴

The synthesis of the photosubstrate (9) required for use in the preparation of the known 2,2-dimethylisoindene^{4,5} was achieved according to the steps outlined in Scheme 2. The selective hydrogenolysis of the cyclopropyl group in (5) or the related ketone† to introduce the *gem*-dimethyl group is a key step since it avoids the tedious preparation of 2,2-dimethylcyclopentadiene.⁶ The orange-yellow α -dione (9), m.p. 81–82 °C, was prepared from the ketone (7), m.p. 66–70 °C, via the isopropylidene derivative (8), m.p. 120–121.5 °C, and subsequent ozonolysis according to standard procedures⁷ in an overall yield of 90%.

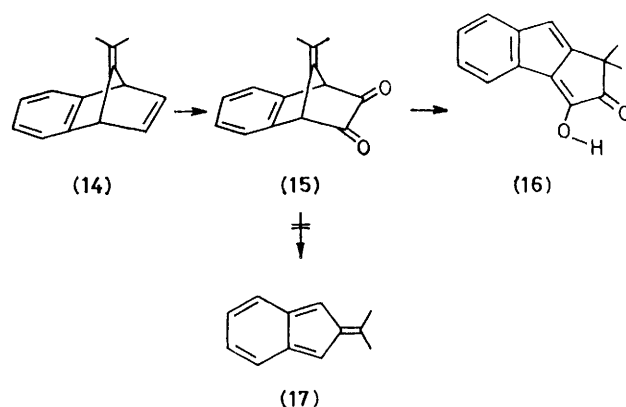
Irradiation‡ of the *gem*-dimethyldione (9) was carried out in $(\text{CD}_3)_2\text{CO}$ solution at 0 °C to yield the bicyclic valence isomer (12a) (cooled to –40 °C for storage). Careful monitoring of the reaction failed to show the intermediacy of isoindene (11a) but separate irradiation experiments on the preformed isoindene (11a) indicated that this was possible since it was transformed very rapidly into the valence isomer (12a) under the reaction conditions. The isoindene (11a) was formed thermally from (12a) at 0 °C or more rapidly at room temperature and could be isolated by distillation. The spectral characteristics [u.v., λ_{max} hexane, 360, 378, 399, 410 inf., 420, and 424 nm; ^1H n.m.r., $(\text{CD}_3)_2\text{CO}$, δ 1.15 (s, Me), 6.20 (dd, J 7.1, 3.3 Hz, 4-H, 7-H), 6.23 (s, 1-H, 3-H), and 6.66 (dd, J 7.1, 3.3 Hz, 5-H, 6-H)] were identical with those reported.⁵ Isoindene (11a) was characterised by conversion into the cycloadduct (13a), m.p. 122 °C, on treatment with *N*-methylmaleimide (Scheme 3). The same adduct was formed directly upon u.v. irradiation‡ of the α -dione (11a) in the presence of *N*-methylmaleimide, or by separate irradiation‡

† In contrast with the norcamphor series (N. J. Turro and G. L. Farrington, *J. Am. Chem. Soc.*, 1980, **102**, 6056) hydrogenolysis of this ketone yielded (7) together with an isomeric mixture of alcohols (6).

‡ Medium pressure American Hanovia (450 W) Hg lamp, Vycor filter, freeze/thaw degassed.



Scheme 3



Scheme 4

of the valence isomer (12a) and *N*-methylmaleimide at –40 °C (no reaction occurred in the absence of light).

Application of this method to the yellow-orange α -dione (10), m.p. 73–74 °C, yielded the spirocyclopentylisoindene (12b) [u.v., λ_{max} hexane, 363 inf., 384, 404, 426, and 429 nm; ^1H n.m.r., $(\text{CD}_3)_2\text{CO}$, δ 1.0–2.0 (m, cyclopentane), 6.2 (dd, J 6.7, 3.0 Hz, 4-H, 7-H), 6.3 (s, 1-H, 3-H), and 6.6 (dd, J 6.7, 3.0 Hz, 5-H, 6-H)]. The bicyclic form (12b) was the product obtained in the u.v. irradiation‡ step, the isoindene (11b) being formed only after thermal isomerisation. Isoindene (11b) was too unstable§ to be isolated in pure form but readily formed an *endo*-adduct (13b) with *N*-methylmaleimide, m.p. 160 °C.

Attempts to extend this method to the production of 2-methyleneisoindene (isobenzofulvene)⁸ (17) were not successful (Scheme 4). Irradiation‡ of the red α -dione (15),¶ m.p. 191–193 °C, yielded the oily oxo-enol (16), which resisted further photolysis under a wide range of conditions and so stultified any hopes of generating isobenzofulvene by this route.

This paper offers firm evidence that the photobisdecarbonylation process is effective in the production of the isoindenes

§ Spirocyclopentylisoindene (11b) undergoes 1,3-rearrangement when set aside overnight to yield 2,3,4,4a-tetrahydro-1*H*-fluorene [^1H n.m.r. 270 MHz in CHCl_3 : δ 0.8–3.0 (8H, m, methylene protons), 3.05 (1H, dd, J 6.1, 12.1 Hz, 4a-H), 6.37 (1H, br. s, 9-H), and 7.0–7.4 (4H, m, arom.)].

¶ Prepared in two steps from (14) by *cis*-hydroxylation (OsO_4 , Bu^tOOH), m.p. 208–210 °C, followed by oxidation (*N*-chlorosuccinimide, Me_2S , NEt_3), m.p. 191–193 °C.

(11a,b) albeit *via* their valence isomer. This should find ready application in synthesis in view of the ease of production of the required α -diones. Indeed a very recent report by Rubin⁹ on the synthesis of norcaradiene by a photobisdecarbonylation procedure further emphasises this.

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