

Photobisdecarbonylation of Benzonorbornene-2,3-dione at Low Temperatures: Isolation and Characterisation of Novel Isoindene (2*H*-indene) Dimers

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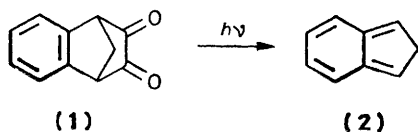
Photolysis of benzonorbornene-2,3-dione in acetone at -60°C yields a diastereomeric mixture of 1-(indanyl)-1*H*-indenes considered to arise from $[8\pi + 8\pi + 2\sigma]$ -cyclodimerisation of isoindene: these structures have been confirmed by synthesis, and full stereochemical assignments made following conversion into dihydro-derivatives.

The transient existence of isoindenes has long been postulated;¹ the main evidence in their support as reaction intermediates being the isolation of $[4\pi + 2\pi]$ -cycloadducts,^{1,2} or iron tricarbonyl complexes,³ and an elegant labelling study involving the trapping of $[2\text{-}^2\text{H}]$ isoindene.⁴ Subsequently a limited number of routes to stable isoindenes, *e.g.* 2,2-dimethyl-1,3-diphenylisoindene⁵ or 2,2-dimethylisoindene⁶ have appeared. In the accompanying communication we showed that isoindenes can be generated by an alternative route employing the photobisdecarbonylation of benzonorbornene-2,3-diones.⁷

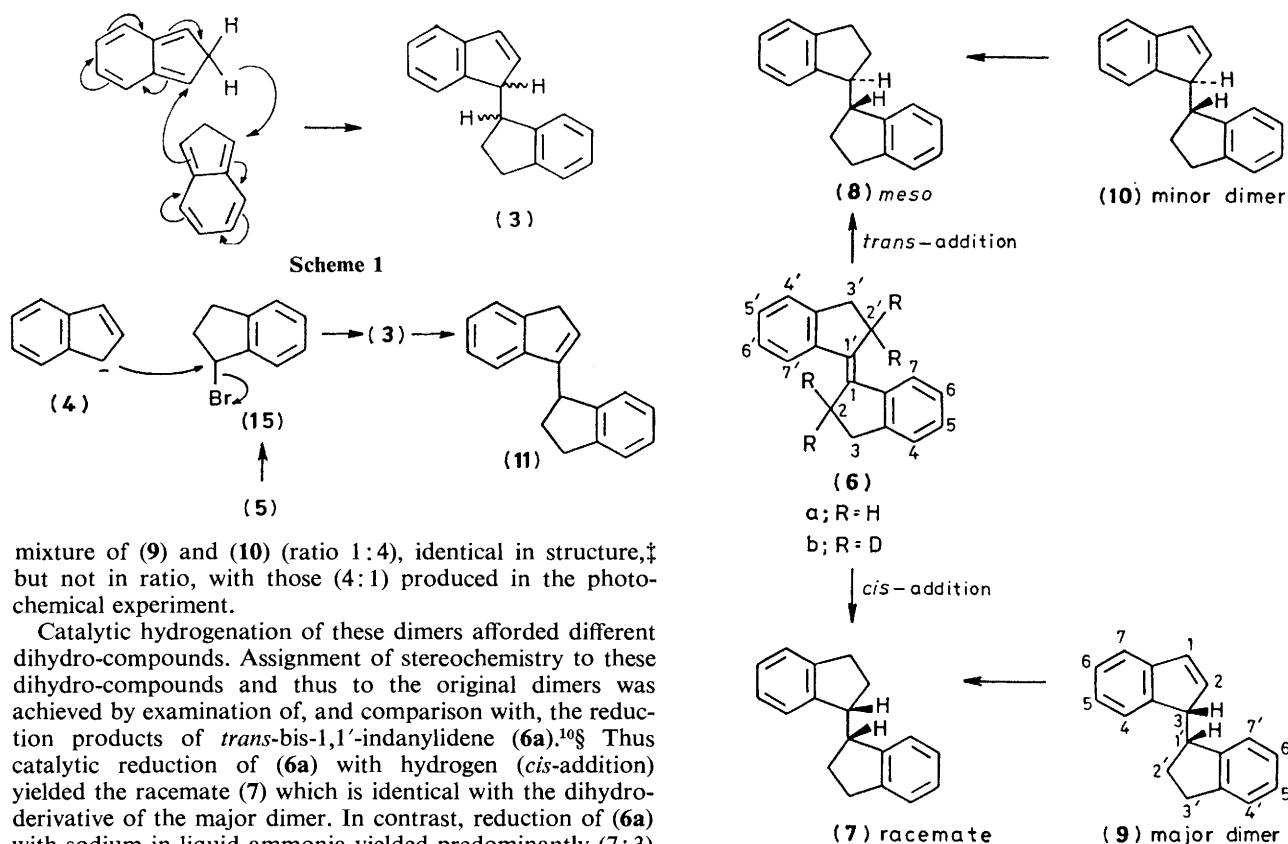
Despite these advances in isoindene chemistry, the parent, isoindene, has defied observation in the free form. Earlier attempts in this laboratory to generate isoindene *via* the photobisdecarbonylation route were unsuccessful leading only to indene even at 0°C .⁸

In the present study we report the results of the photolysis (medium-pressure Hg lamp, Pyrex filter) of the α -diketone substrate (**1**) at -60°C . Under these conditions indene was not observed and two dimeric ($\text{C}_{18}\text{H}_{16}$) hydrocarbons were isolated. These compounds can be considered to be dimeric combinations of either or both indene and isoindene. Photolysis of (**1**) in the presence of $[^2\text{H}_3]$ indene resulted in no

deuterium incorporation into the dimer fraction, thus ruling out the participation of indene in the dimerisation process. We therefore consider the two hydrocarbons to be derived from isoindene. Separation of the two dimers was achieved by h.p.l.c.† and in each case ^{13}C n.m.r. spectroscopy† revealed the presence of only four sp^3 -carbons, thus ruling out cyclo-addition products, including the $[8\pi + 6\pi]$ structure favoured by F.M.O. calculations.⁹ Furthermore the existence of twelve aromatic and two olefinic carbon resonances in each dimer suggests that they are derived by an ene-type $[8\pi + 8\pi + 2\sigma]$ -reaction (see Scheme 1) and should be assigned the gross structure (**3**). This proposal was confirmed by the synthesis of (**3**). Thus treatment of the sodium salt of indene (**4**) in liquid ammonia with 1-bromoindane (**5**) gave a diastereomeric



† Chromatography was performed on μ -Porasil using hexane as eluant with (**9**) having the longer retention time. Compound (**9**) ^1H n.m.r. (CDCl_3) δ 0.9–1.1 and 1.6–1.8 (2H, m, 2'-H), 2.74 (2H, t, J 7.0 Hz, 3'-H), 4.0–4.1 (2H, m, 1-H, 1'-H), 6.08 (1H, dd, J 5.5, 1.1 Hz, 2-H), 6.81 (1H, dd, J 5.5, 0.6 Hz, 3-H), and 7.1–7.5 (8H, m, arom.); ^{13}C {H} n.m.r. δ 25.58 (t, J 129 Hz, 2'-C), 31.76 (t, J 130 Hz 3'-C), 45.83 (d, J 132 Hz, 1'-C), 54.21 (d, J 126 Hz, 1-C), 121.02, 122.74, 123.65, 124.80, 126.23, 126.61, 126.74, 126.92, 132.50 (d, J 165 Hz, 2-C), 136.48 (d, J 168 Hz, 3-C), 144.32 (s), 145.04 (s), 145.79 (s), and 146.58 p.p.m. (s). Compound (**10**) ^1H n.m.r. (CDCl_3) δ 1.3–1.5 and 2.0–2.2 (2H, m, 2'-H), 2.5–2.8 (2H, m, 3'-H), 3.9–4.0 (2H, m, 1-H, 1'-H), 6.49 (1H, dd, J 5.5, 1.2 Hz, 2-H), 6.81 (1H, dd, J 5.5, 0.9 Hz, 3-H), 6.76 (d, J 7.5 Hz), and 6.9–7.4 (8H, m, arom.); ^{13}C {H} n.m.r. δ 27.23 (2'-C), 31.74 (3'-C), 45.77 (1'-C), 54.26 (1-C), 120.89, 123.64, 124.01, 124.54, 126.01, 126.60, 126.61, 126.76, 131.77, 138.08, 144.60, 144.97, 145.45, and 145.50 p.p.m.



mixture of (9) and (10) (ratio 1:4), identical in structure,[‡] but not in ratio, with those (4:1) produced in the photochemical experiment.

Catalytic hydrogenation of these dimers afforded different dihydro-compounds. Assignment of stereochemistry to these dihydro-compounds and thus to the original dimers was achieved by examination of, and comparison with, the reduction products of *trans*-bis-1,1'-indanylidene (6a).¹⁰ Thus catalytic reduction of (6a) with hydrogen (*cis*-addition) yielded the racemate (7) which is identical with the dihydro-derivative of the major dimer. In contrast, reduction of (6a) with sodium in liquid ammonia yielded predominantly (7:3) the *meso*-compound (8) (*trans*-addition) which proved to be identical with the minor dihydro-dimer.[¶] Accordingly the major and minor dimers of isoindene were assigned structures (9) and (10), respectively.

Dimerisation of isoindenes by this ene-type mechanism can only occur if a hydrogen is present at the 2-position and this, coupled with the lower migratory aptitude of alkyl groups,¹¹ accounts for the fact that 2,2-dialkylisoindenes can be isolated at close to ambient temperature. Our results clearly show that suppression of the [1,5]-sigmatropic rearrangement of isoindene is not in itself sufficient to enable the monomeric

hydrocarbon to be isolated under these conditions. The dimers (9) and (10) represent a new mode of reaction for isoindene and further broaden the already diverse range of dimerisation reactions exhibited by molecules containing the *o*-xylylene moiety.

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[‡] Ready rearrangement to (11) occurs upon treatment of (3) with base. Indeed (11) can become the major product if (4) and (5) are added together to a solution of sodium in liquid NH₃. ¹H N.m.r. for (11) (CDCl₃) δ 2.1–2.3 and 2.5–2.7 (2H, m, 2'-H), 3.0–3.1 (2H, m, 3'-H), 3.34 (2H, s, 3-H), 4.46 (1H, t, *J* 7.7 Hz, 1'-H), 6.11 (1H, s, 2-H), and 7.1–7.5 (8H, m, arom.).

[§] The *trans*-stereochemistry for (6a), which is critical to the stereochemical assignments made to (7) and (8), has been confirmed by nuclear Overhauser studies. Thus irradiation of the unresolved 2-H and 3-H signals (δ 3.10) in the ¹H n.m.r. spectrum of (6a) results in a 36% enhancement of the 7'-H signal (δ 7.5). The corresponding 2,2,2',2'-tetra-deuteriated compound (6b) [$>95\%$ D] was examined. A similar irradiation revealed only a 6% enhancement of 7'-H which appears to be derived from a ⁵J coupling (0.44 Hz) between 7'-H and 3'-H. Such results can only be accommodated by the *trans*-disposition of the indane rings, and are in agreement with the earlier assignment (ref. 10).

[¶] Contrary to a previous report (E. Marechal, J. J. Barselier, and P. Sigwalt, *Bull. Soc. Chim. Fr.*, 1964, 1740) we find that radical coupling of indenyl magnesium bromide affords a mixture of the diastereomeric 1,1'-bi-indenyls separable by h.p.l.c. The sole product reported previously m.p. 99–100 °C can be assigned the racemic structure since hydrogenation proceeds *via* (9) to afford (7). *Added in proof*: Heimer *et al.* have confirmed this assignment by an X-ray structure determination of *rac*-3,3'-bi-indan-1-one derived from the crystalline 1,1'-bi-indenyl (N. E. Heimer, M. Hojatie, and C. A. Panetta, *J. Org. Chem.*, 1982, **47**, 2593).

References

- 1 K. Alder, F. Pascher, and H. Vagt, *Chem. Ber.*, 1942, **75**, 1501; K. Mackenzie, *J. Chem. Soc.*, 1960, 473.
- 2 W. P. Lay, K. Mackenzie, and J. R. Telford, *J. Chem. Soc. C*, 1971, 3199.
- 3 W. R. Roth and J. D. Meier, *Tetrahedron Lett.*, 1967, 2053.
- 4 W. R. Roth, *Tetrahedron Lett.*, 1964, 1009; N. S. Isaacs, *Can. J. Chem.*, 1966, **44**, 415.
- 5 K. Alder and M. Fremery, *Tetrahedron*, 1961, **14**, 190.
- 6 F. J. Palensky and H. A. Morrison, *J. Am. Chem. Soc.*, 1977, **99**, 3507; D. Giachero and H. A. Morrison, *ibid.*, 1978, **100**, 7109; W. R. Dolbier, K. Matsui, J. Michl, and D. V. Horak, *ibid.*, 1977, **99**, 3876; W. R. Dolbier, K. Matsui, H. J. Dewey, D. V. Horak, and J. Michl, *ibid.*, 1979, **101**, 2136.
- 7 R. N. Warrener, P. A. Harrison, and R. A. Russell, *J. Chem. Soc., Chem. Commun.*, 1982, preceding paper.
- 8 R. N. Warrener, R. A. Russell, and T. S. Lee, *Tetrahedron Lett.*, 1977, 49; R. N. Warrener, R. A. Russell, and P. A. Harrison, *ibid.*, p. 2031.
- 9 R. N. Warrener, M. N. Paddon-Row, R. A. Russell, and P. L. Watson, *Aust. J. Chem.*, 1981, **34**, 397; P. A. Harrison and M. N. Paddon-Row, unpublished results.
- 10 D. Lenoir and P. Lemmen, *Chem. Ber.*, 1980, **113**, 3112.
- 11 C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.