

A New Diene permitting Evaluation of Facial Selectivity in Diels–Alder Additions and Preparation of a Norbornadienone

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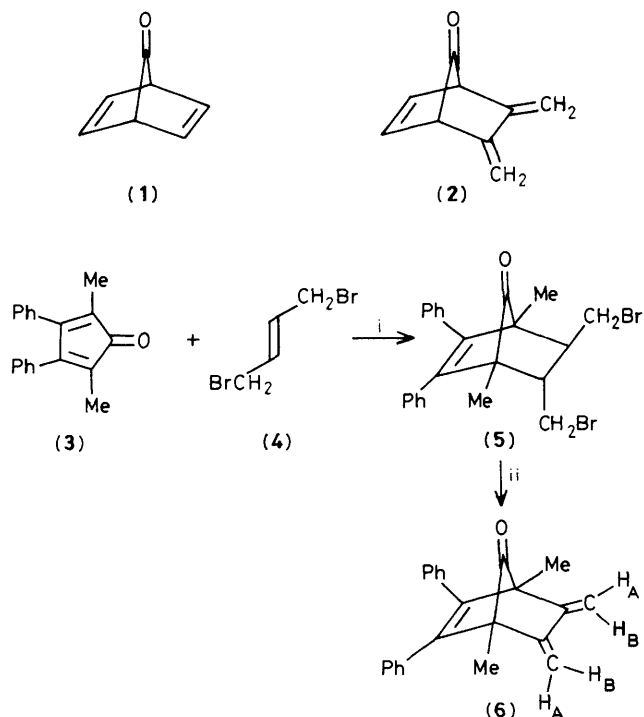
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The reaction of 5,6-dimethylene-1,4-dimethyl-2,3-diphenylnorborn-2-en-7-one (**6**) with dienophiles, is used as a probe for π -facial selectivity in Diels–Alder reactions and is shown to proceed through norbornadien-7-ones, one of which exhibits moderate stability.

Several approaches to the synthesis of norbornadien-7-one (**1**) have been reported,¹ but none has been successful. All attempts have been frustrated by the ready loss of carbon monoxide from such systems and the concomitant formation of a benzenoid hydrocarbon.^{1,2} Where stable derivatives of norbornadien-7-one have been reported they involve systems where anchimeric assistance of the π -bond towards decarbonylation has been reduced, *i.e.* where each of the π -bonds has been incorporated into aromatic rings,³ or part of a π -bonded metal carbonyl complex.⁴ Previous claims to have formed simple derivatives of (**1**) have been reported but these do not stand close inspection.^{1†}

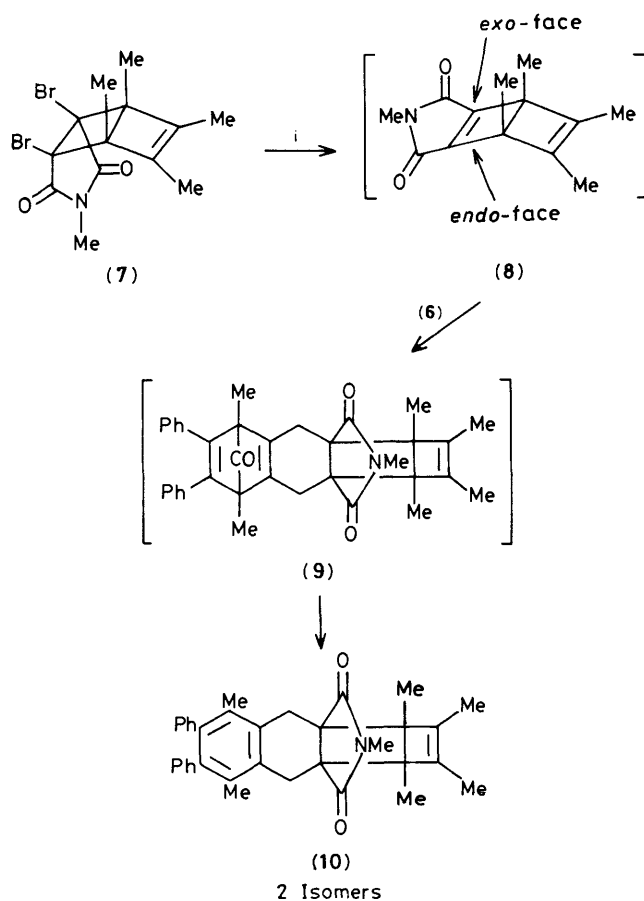
We reasoned that advantage could be taken of the facility of the above-mentioned decarbonylation to develop a diene which would be useful as a kinetic trapping agent to evaluate the π -facial selectivity⁵ of dienophilic species. Thus reaction of a diene of type (**2**) with a dienophile should lead first to a norbornadien-7-one, which could be expected to decarbonyl-

ate to the aromatic product much faster than it would revert to starting materials. Two advantages accrue from such a reaction: (a) the aromatic product is thermally stable and analysis of the product(s) would directly indicate the π -facial selectivity; (b) any complication owing to stereoselectivity in the initial step is avoided as both stereoisomers yield the same aromatic product upon decarbonylation.[‡] Such Diels–Alder reactivity of a 5,6-dimethylenenorborn-2-en-7-one is unexplored, since the parent compound (**2**)⁶ although available, has not been so studied. We chose to study a derivative of (**2**) since it was readily prepared by the two step process outlined



Scheme 1. Reagents: i, C₆H₆, 105°C, 36 h; ii, KF, dimethylformamide, 80°C, 24 h.

† The latest report is that of Khattab and coworkers (S. A. Khattab, N. A. Khalifa, and S. A. Mahgoub, *Indian J. Chem., Sect. B.*, 1977, **15**, 432). These workers appear to confuse their purported norbornadien-7-one with impure starting material; other aspects of this paper are incorrect.



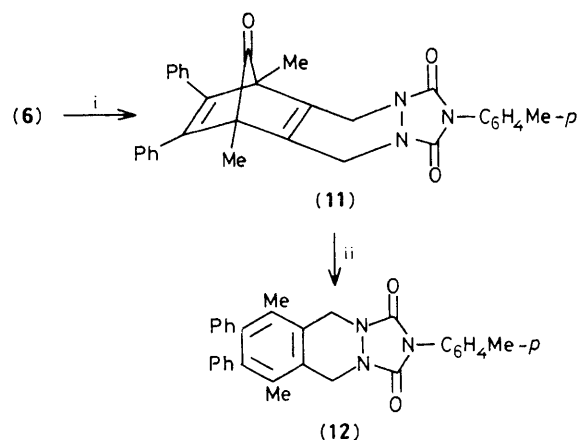
Scheme 2. Reagents: i, Zn/Ag couple, tetrahydrofuran, heat. *Added in proof:* Nuclear Overhauser enhancement studies indicate that the major isomer of (**10**) is that derived from attack of (**6**) at the *exo*-face of (**8**).

‡ *o*-Xylylenes offer features similar to (**6**) but are themselves too unstable for normal handling; the related Dewar species is available but synthetic entry to such a system is difficult.

in Scheme 1.⁷ Diene (6)[§] is only the second example of this ring system to be reported and our method appears to have general application. Model reactions between diene (6) and simple dienophiles like *N*-methylmaleimide confirmed the activity of the diene and the ready loss of carbon monoxide from the adduct.

The ability of diene (6) to trap transient species was evaluated by its reaction with the Dewar benzene (8) (Scheme 2). This dienophilic species was generated from the known dibromo-derivative (7)⁸ by treatment with a Zn/Ag couple in tetrahydrofuran at reflux in the presence of (6) to yield a mixture (7:1) of two isomeric aromatic products (10). These products are logically derived by decarbonylation of the first-formed adducts (9) and since both isomers (10) retain vinyl methyl resonances in their ¹H n.m.r. spectra it follows that they result from cycloadditions occurring at either face of the maleimide π -bond in (8).[¶]

More interestingly, reaction of diene (6) with *N*-*p*-tolyltriazolinedione occurred at low temperature (-40°C) to yield a bridge carbonyl containing product (Scheme 3). ¹³C N.m.r. spectral data (-40°C) of this labile species are fully in accord with the norbornadien-7-one derivative (11) (*inter alia* carbonyl resonance at δ 187.4 and bridgehead quaternary carbon at δ 61.6).^{||} Conversion of (11) into the aromatic hydrocarbon (12) occurred upon warming to room tempera-



Scheme 3. Reagents: i, *N*-*p*-tolyltriazolinedione, CDCl_3 , -40°C , 5 min; ii, 20°C , 5 min.

ture ($t_{1/2} < 1$ min at 20°C). This is the first authenticated example of a simple norbornadien-7-one, in which the π -bonds are not part of an aromatic ring, which is sufficiently stable for spectral identification.

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[§] Physical data for diene (6): m.p. 160 – 161°C ; ¹H n.m.r. (CDCl_3) δ 1.32 (6H, s, CH_3), 5.03 (2H, s, $\text{C}=\text{CH}_A\text{H}_B$), 5.54 (2H, s, $\text{C}=\text{CH}_A\text{H}_B$), 6.9–7.3 (10H, m, aromatics); ¹³C n.m.r. (CDCl_3) δ 8.5, 59.4, 101.9, 127.4, 127.9, 129.0, 134.1, 143.6, 147.1, 204.5.

[¶] Furan, traditionally used in this trapping role, yields a single 1:1-adduct upon reaction with (8), while 2,5-dimethylfuran yields two 1:1-adducts. These data are difficult to interpret. The furan result would indicate 100% selectivity from the one face: the dimethyl furan result could support this (*i.e.* two stereoisomers from the same face) or be in conflict (*i.e.* one stereoisomer from each face). These results are typical of such experiments and where definitive structural assignments are unavailable (here the tetra-substituted dienophile precludes use of vicinal coupling constants to assign stereochemistry) decisions regarding the facial selectivity cannot be made.

^{||} The high-field carbonyl resonance of (11) is close to that observed in *endo*-tricyclo[5.2.1.0^{2,4}]oct-6-en-8-one (R. Bicker, H. Kessler, A. Steigel, and G. Zimmerman, *Chem. Ber.*, 1978, **111**, 3215) and reflects cross conjugation of the carbonyl group with the two double bonds.