

THE PREPARATION OF 7-METHYLENEBENZONORBORNADIENE, AND ITS USE IN THE  
SYNTHESIS OF ISOBENZOFULVENE: COPING WITH LITTLE FRAGMENTATION!

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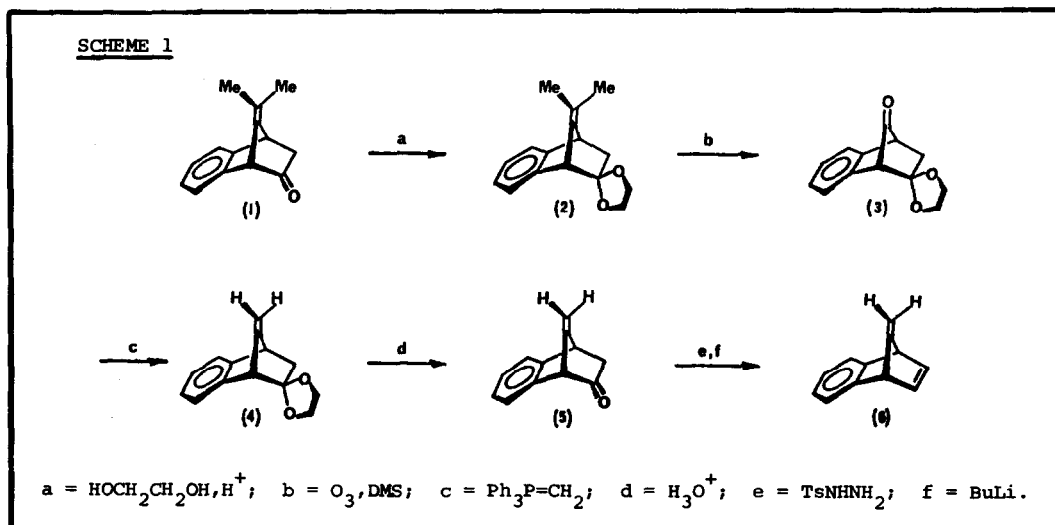
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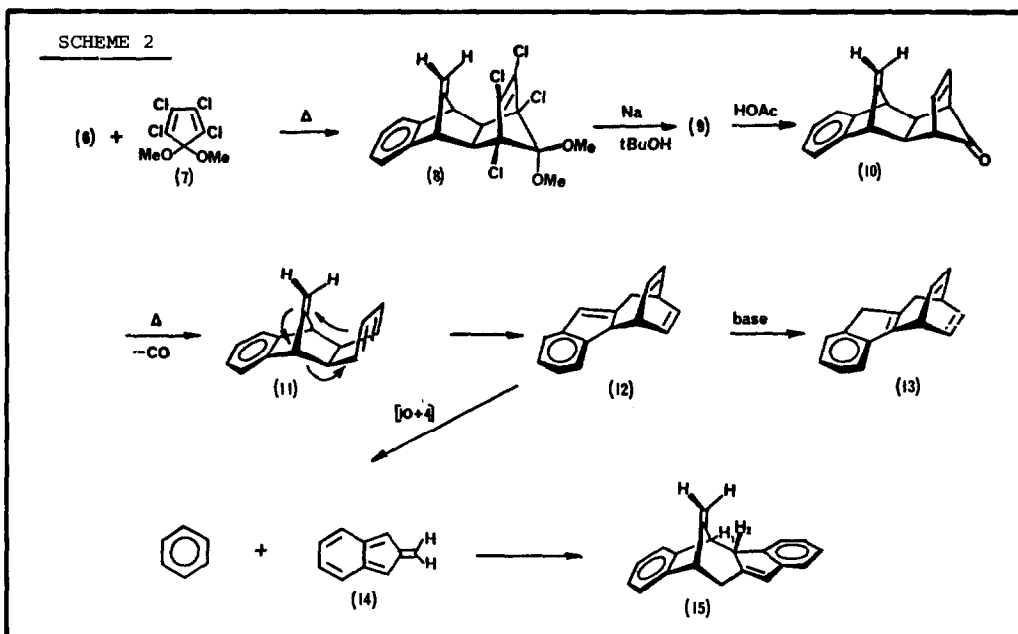
The isobenzofulvene (IBF) nucleus has proved to be extremely versatile in the modes of electrocyclic addition which it undergoes. Our initial studies, which employed 8,8-dimethylisobenzofulvene have demonstrated that [8+2] addition occurs with standard  $2\pi$ -dienophiles<sup>1</sup>, [8+6] addition with tropone<sup>2</sup>, and [10+8] addition in its self dimerisation reaction.<sup>3</sup> The feature of these reactions is their complete perispecificity with each class of reagent, and the fact that each mode of cycloaddition is in complete accord with P.M.O. prediction.<sup>4</sup>

In order to further study the specificities of the IBF nucleus, we have sought to generate the parent member of the series. In this way both substituent perturbations on the IBF molecular orbitals are removed and potential steric (non-bonding) interactions are eliminated in bimolecular reactions. We have previously reported that the parent IBF can be generated and trapped in adduct form, but on that occasion the method was not conducive to reliable intermolecular cycloadditions.<sup>6</sup> The present communication concerns an alternative route directed at the production of the parent isobenzofulvene.

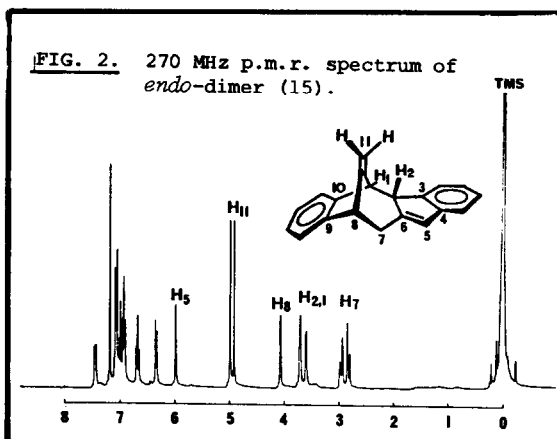
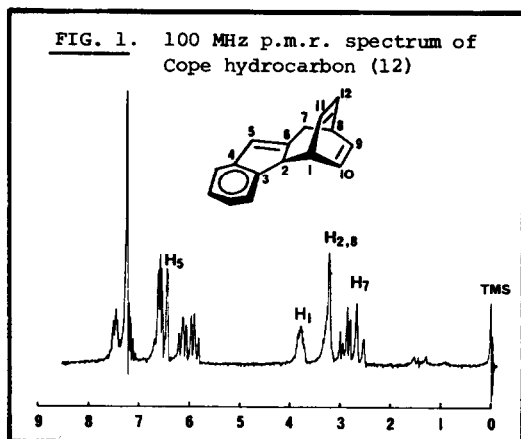
The starting material for the present investigation was 7-methylenenorbornadiene (6).<sup>5</sup> Whilst this can be prepared by the addition of benzyne to fulvene<sup>6</sup>, the latter is difficult to prepare in quantity, and the longer multistep route (SCHEME 1) proved advantageous.



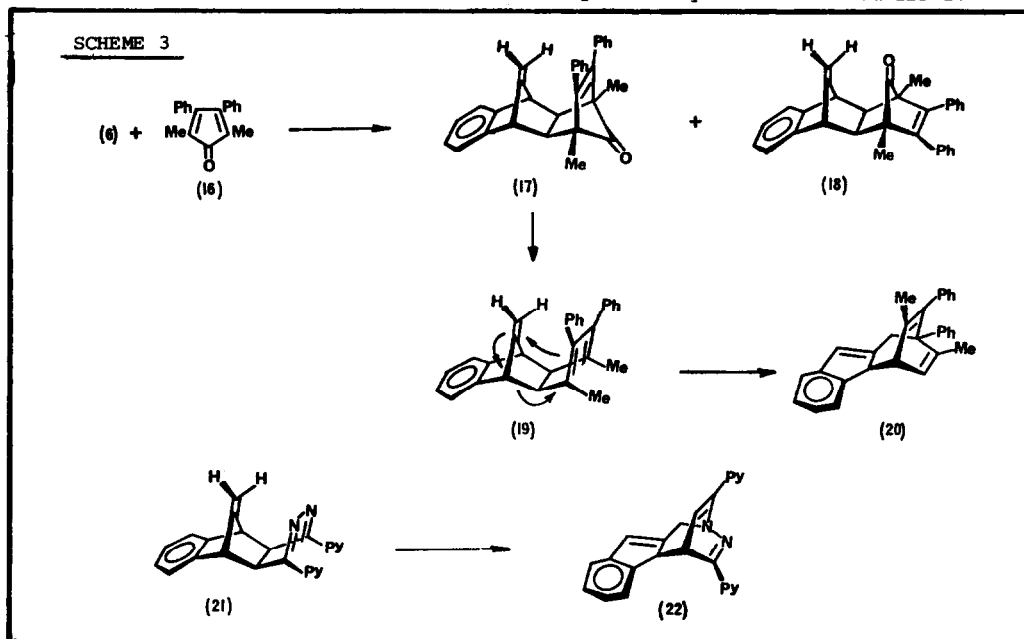
We have used several approaches for the conversion of 7-methylenebenzonorbornadiene to IBF. In the first of these the sequence outlined in SCHEME 2 was investigated. Here the ketone (10) was a key intermediate which was obtained in crystalline form, m.p. 105°C (dec). The p.m.r. spectrum of (10)<sup>7</sup> [CDCl<sub>3</sub>, δ ppm: 2.36 (m,H2,7); 3.20 (m,H1,8); 3.56 (s,H3,6); 4.42 (s,H13); 6.68 (t,H9,10); 7.1-7.4 (m, Aromatics)] was fully consistent with the *exo,endo*-stereochemical assignment shown in (10), which follows logically from its mode of synthesis. Thermal decarboxylation of this ketone was achieved under mild conditions, since the chelotropic elimination of



the carbonyl bridge is facilitated by relief of steric compression in compounds of this type.<sup>8</sup> The major product obtained in this reaction was not the cyclohexadiene (11), nor a fragmentation product derived therefrom, but the hydrocarbon (12), subsequently established to arise from a facile [3.3] sigmatropic Cope rearrangement of the intermediate diene (11)<sup>8</sup>. The structure of the Cope product (12)<sup>7</sup> rested on its p.m.r. spectrum (FIG. 1) and the symmetry of the bond-shift isomer (13), formed from (12) on treatment with base. Attempts to induce isomer (12) to act as a precursor to the desired isobenzofulvene, *via* a [10+4] cycloreversion reaction were not encouraging; only small amounts of benzene (*ca* 10%) and the dimeric products derived from the IBF could be obtained. The predominant dimer, also obtained from thermolysis of (10), was isolated by p.l.c. and recrystallized from methanol, m.p. 98-100°C. The 270 MHz spectrum of this dimer (15)<sup>7</sup> is shown in FIG. 2. A feature of this spectrum is the coupling between the bridgehead proton H1 and the vicinal indenyl proton H2. This is indicative of *endo*-stereochemistry since the related *endo*-8,8-dimethyl isobenzofulvene dimer, but not the *exo*-isomer, shows a similar coupling. The structures in this latter series have been determined by X-ray and chemical means.<sup>3,10,11</sup>



The stereoselectivity of the dimerisation of (14) can not be explained by PMO theory since both the *exo*- and *endo*-transition states for this reaction gain some stabilisation *via* secondary orbital overlap.<sup>12</sup> The absence of substituents at the 8-position of the IBF nucleus rules out steric dominance which accounts for some of the *endo*-specificity in substituted IBF's.<sup>13</sup>



The competition between the Cope rearrangement and fragmentation in compounds of type (11) may be more widespread than initially appreciated. Thus reaction of 7-methylenebenzornbornadiene with the dienone (16) leads to the formation of the Cope product (20), presumably *via* (17)  $\rightarrow$  (19)  $\rightarrow$  (20), together with the stable 1:1-adduct (18).<sup>14</sup> In addition, preliminary investigations indicate that the diaza-analogue (21), formed from (6) and 3,6-di(2'-pyridyl)-*s*-tetrazine, forms a Cope-rearrangement product (22), but spectral support is less clear in this case, and the assignment must be considered tentative.

Since numerous 7-mono- and 7,7-disubstituted methylenebenzornbornadienes all readily undergo fragmentation after treatment with the above-mentioned *s*-tetrazine,<sup>15</sup> there is good

evidence to suggest that steric factors play a large part in determining the mode of reaction of the intermediate 4,5-diaza-9,10-benzotricyclo[6,2,1,0<sup>2,7</sup>]undeca-3,5,9-trienes and their carbocyclic analogues. It is fortunate, then, that small steric perturbations at the 11-methylidene position favour fragmentation so that even 8-monomethylisobenzofulvene can be generated in quantitative yield from the corresponding dihydropyridazine intermediate, thus confirming that the *s*-tetrazine route is a versatile entry into isobenzofulvenes<sup>1,10,15,16</sup> except in the case of the parent molecule.

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#### REFERENCES AND FOOTNOTES

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3. M.N. Paddon-Row, P.L. Watson and R.N. Warrener, *Tetrahedron Lett.*, 1973, 1033.
4. M.N. Paddon-Row, *Aust. J. Chem.*, 1974, 27, 299.
5. An interesting aromatisation reaction was uncovered in the course of investigating a carbene (iii) insertion route to (6). Thus treatment of the tosylhydrazone (i) with the hindered base (ii) yielded significant amounts of naphthalene, according to the following sequence:
 

The diagram shows a chemical reaction sequence. On the left is structure (i), a bicyclic tosylhydrazone with a TsHN=HC group. An arrow with a delta symbol (heat) and a structure (ii) of a hindered base below it points to structure (iii), a carbene intermediate with an :HC group. From (iii), a vertical arrow with a crossed-out circle points down to structure (6). A horizontal arrow points from (iii) to the products: naphthalene and acetylene (HC≡CH).
6. R.N. Warrener, G.J. Collin, G.I. Hutchison and M.N. Paddon-Row, *J.C.S. Chem. Comm.*, 1976, 373.
7. The complete names of these compounds are: (10) 12-methylidene-4,5-benzotetracyclo[6.2.1.1.0<sup>2,7</sup>]dodeca-4,9-dien-11-one; (12) 3,4-benzotricyclo[6.2.2.0<sup>2,6</sup>]dodeca-3,5,9,11-tetraene; (15) 11-methylidene-3,4:9,10-dibenzotricyclo[6.2.1.0<sup>2,6</sup>]undeca-3,5,9-triene.
8. R.K. McCulloch, A.R. Rye and D. Wege, *Aust. J. Chem.*, 1974, 27, 1929.
9. Cope rearrangement has ample precedent in this field where the diene olefin is stereochemically aligned with the *exo*-cyclic double bond.<sup>2,10</sup>
10. H. Tanida, T. Irie and K. Tori, *Bull. Chem. Soc. Japan*, 1972, 45, 1999.
11. P. Leveritt, personal communication.
12. M.N. Paddon-Row, unpublished results.
13. K.I. Gell, B.Sc. Honours Thesis, A.N.U. 1973.
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