

## Novel Syntheses of 1,6-Methano[10]annulene and 4-Methylazulene

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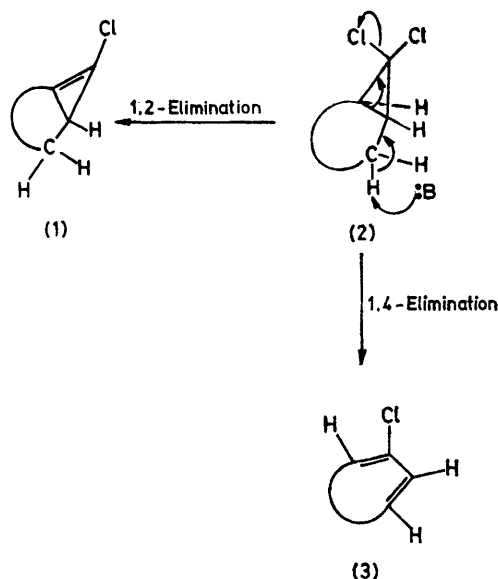
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*Summary* Reaction of 11,11-dichlorotricyclo[4.4.1.0<sup>1,6</sup>]-undeca-3,8-diene (**4**) with potassium t-butoxide in dimethyl sulphoxide affords 1,6-methano[10]annulene (**9**) and 4-methylazulene (**10**); similar treatment of the dibromopropellane (**5**) yields the azulene (**10**), the mono-

bromopropellane (**11**), but diminished yields of the annulene (**9**).

DIHALOGENOCARBENE adducts (**2**) of medium- and large-ring cycloalkenes are believed to undergo initial 1,2-elimination

to give  $\omega$ -chlorobicyclo[*n*.1.0]alk-1( $\omega$ )-enes (**1**) on treatment with strong base.<sup>1</sup> We have recently reported<sup>2</sup> the base-promoted reactions of tri- and tetra-halogeno-*cis-transoid-cis*-tricyclo[5.1.0.0<sup>3,5</sup>]octanes. In spite of the possibilities for 1,2-elimination in these systems, evidence was presented for 1,4-elimination with cleavage of the cyclopropyl moiety and formation of a cyclic diene (**3**) (Scheme 1). An in-

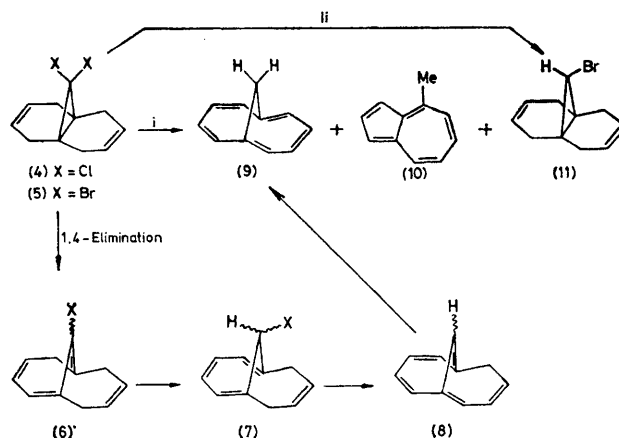


SCHEME 1

vestigation of the reactions of *gem*-dihalogeno[*n.m*.1]propellanes in strongly basic media, where possible competition from 1,2-elimination reactions is avoided, would be of interest.<sup>†</sup> Herein we report the preliminary results of such a study which demonstrate novel and simple syntheses of 1,6-methano[10]annulene (**9**) and 4-methylazulene (**10**).

Reaction of readily available<sup>3</sup> 11,11-dichlorotricyclo[4.4.1.0<sup>1,6</sup>]undeca-3,8-diene (**4**) with 5 mol. equiv. of potassium *t*-butoxide (in the form of its *t*-butyl alcohol monosolvate) in oxygen-free dimethyl sulphoxide at room temperature for 16 h afforded, after extractive work-up and t.l.c., 1,6-methano[10]annulene (**9**) (13%), and the deep blue 4-methylazulene (**10**) (10%). Similar treatment of 11,11-dibromotricyclo[4.4.1.0<sup>1,6</sup>]undeca-3,8-diene (**5**) afforded 4-methylazulene (**10**) (10%), diminished quantities (1%) of 1,6-methano[10]annulene (**9**), and a small amount (4%) of 11-bromotricyclo[4.4.1.0<sup>1,6</sup>]undeca-3,8-diene (**11**). The annulene (**9**) obtained in these reactions was identical in all respects with an authentic sample prepared by the method of Vogel and his co-workers.<sup>3</sup> Comparison of the <sup>1</sup>H n.m.r. spectrum of the azulene (**10**) with the published<sup>4</sup> spectra of

the five possible methylazulenes allowed its unequivocal assignment as the 4-methyl isomer. All additional spectroscopic data are consistent with this regioisomer. The monobromopropellane (**11**) was identical in all respects with an authentic sample prepared by half-reduction of the dibromo-compound (**5**) with tri-*n*-butyltin hydride.<sup>5</sup>

SCHEME 2. Reagents: i, Bu<sup>4</sup>OK, Me<sub>2</sub>SO; ii, Bu<sub>3</sub>SnH, benzene.

A plausible mechanism for the conversion of the propellanes (**4**) and (**5**) into compound (**9**) is illustrated in Scheme 2. Initial 1,4-elimination would afford the bridgehead dienes (**6**). [Species closely related to compound (**6**) have been proposed to explain apparent retention of configuration in bimolecular nucleophilic substitution at a cyclopropyl carbon atom.<sup>6</sup>] Base-promoted prototropic rearrangement of the tetraenes (**6**), to give the tetraenes (**7**), followed by dehydrohalogenation would give rise to the pentaene (**8**). Further prototropic rearrangement would yield the aromatic annulene (**9**). The mechanism for azulene formation is less obvious. The annulene (**9**) is inert to treatment with potassium *t*-butoxide in dimethyl sulphoxide and is thus precluded as a precursor to 4-methylazulene (**10**).

The supposition that the tetraenes (**6**) are intermediates *en route* to 1,6-methano[10]annulene suggests that base-promoted 1,4-eliminations in halogeno[*n.m*.1]propellanes may provide a useful route to bridgehead dienes, which are species of considerable current interest.<sup>7</sup> Also, in view of the recent efforts<sup>8</sup> devoted to azulene syntheses, the application of strategies based on the above observations may be of some synthetic utility for the preparation of such compounds.

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<sup>†</sup> To the best of our knowledge only one study of base-promoted reactions of halogeno[*n.m*.1]propellanes has been reported; L. A. M. Turkenburg, J. W. Van Straten, W. H. De Wolf, and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1980, **102**, 3256 and references cited therein.

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