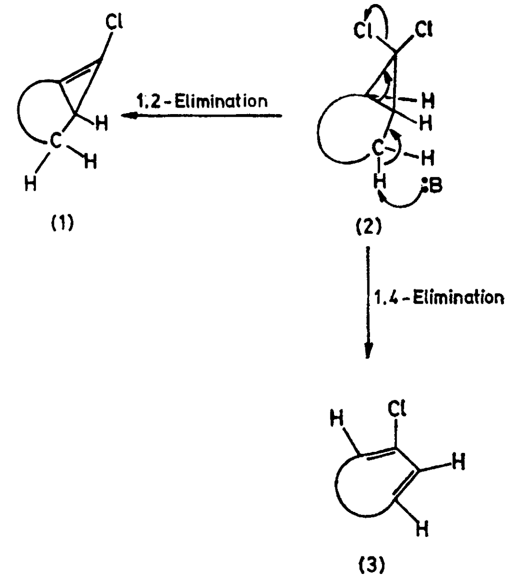
Novel Syntheses of 1,6-Methano[10]annulene and 4-Methylazulene

By Martin G. Banwell* and Con Papamihail

(*Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia,* 5000)

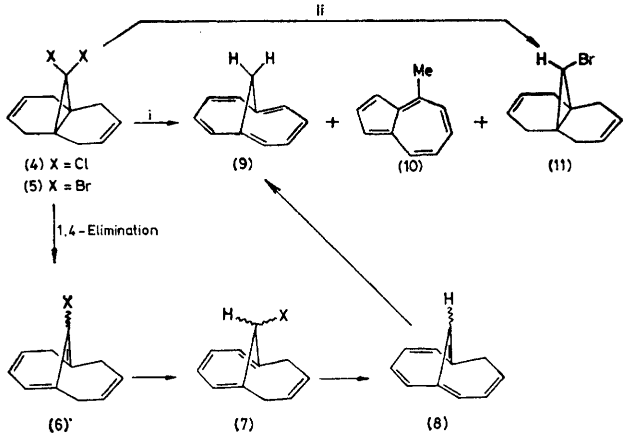
Summary Reaction of 11,11-dichlorotricyclo[4.4.1.$0^{1,6}$]-undeca-3,8-diene (**4**) with potassium t-butoxide in dimethyl sulphoxide affords 1,6-methano[10]annulene (**9**) and 4-methylazulene (**10**); similar treatment of the dibromopropellane (**5**) yields the azulene (**10**), the monobromopropellane (**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 ω-chlorobicyclo[n.1.0]alk-1(ω)-enes (**1**) on treatment with strong base.[1] We have recently reported[2] the base-promoted reactions of tri- and tetra-halogeno-*cis-transoid-cis*-tricyclo$[5.1.0.0^{3,5}]$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 investigation 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.† 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**).



SCHEME 1

Reaction of readily available[3] 11,11-dichlorotricyclo$[4.4.1.0^{1,6}]$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$[4.4.1.0^{1,6}]$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$[4.4.1.0^{1,6}]$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.[3] Comparison of the ^{1}H n.m.r. spectrum of the azulene (**10**) with the published[4] 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.[5]



SCHEME 2. *Reagents:* i, Bu^{t}OK, Me$_2$SO; ii, Bu$^n_3$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.[6]] 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.[7] Also, in view of the recent efforts[8] 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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† 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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