π Participation in Addition Reactions of *endo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene

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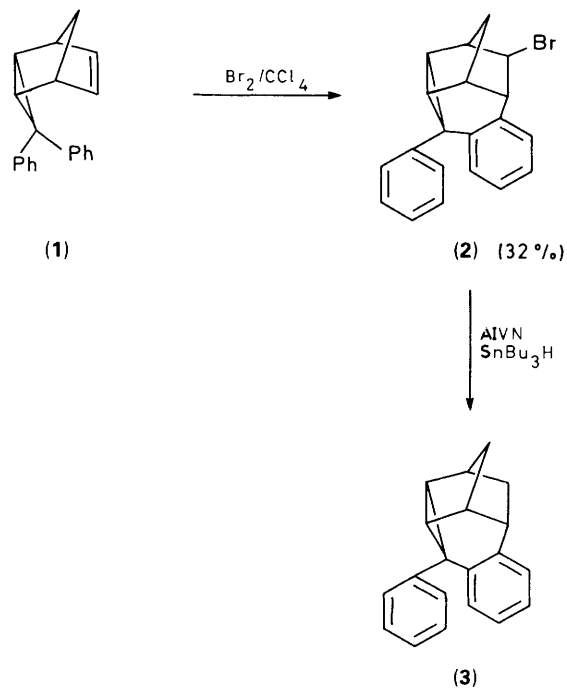
Radical initiated LRAMERO (long range aryl migration coupled with electrophilic ring opening) is one example of π participation occurring from the *syn* phenyl ring of (**1**) in both electrophilic and radical addition reactions.

Neighbouring group participation in addition reactions to carbon–carbon double bonds has been extensively studied.[1] It is known that π participation by aryl groups affects the stereospecificity of additions to strained systems such as norbornenes[2] and can cause the LRAMERO rearrangement (long range aryl migration coupled with electrocyclic ring opening) under both addition[3] and solvolytic conditions.[4] We report here evidence of π participation in additions to the strained *endo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**1**)[5] and the first observation of LRAMERO under radical conditions. As expected, similar additions with the *exo* counterpart (**4**) showed no evidence of π participation.

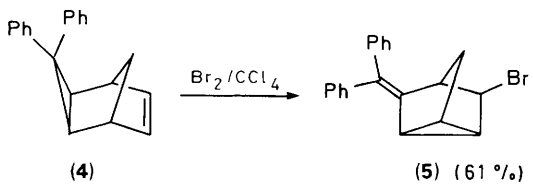
Bromination of (**1**) took place readily giving rise to a complex mixture of six products. The major product (**2**), (m.p. 115—116.5 °C) isolated in 32% yield, eluted on TLC after (**1**). The structure‡ of the monobromo product (**2**) was based on the presence of three quaternary aromatic carbons, an *ortho* aromatic proton significantly shielded[6] by the adjacent aryl ring, and the reduction of (**2**) to a tetracyclic benzo-hydrocarbon (**3**) (see Scheme 1) which was identical to that isolated from the solvolysis of a related tosylate;[7] its formation presumably involves an $Ar_{2,6}$ mechanism.



(**1**) (**2**) (32%) (**3**)

AIVN = azobisisovaleronitrile

Scheme 1

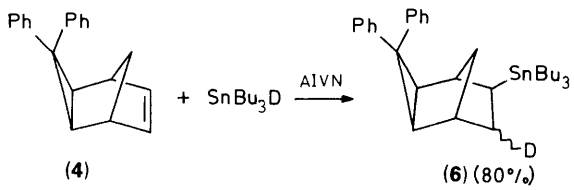


(**4**) (**5**) (61%) (**1**)

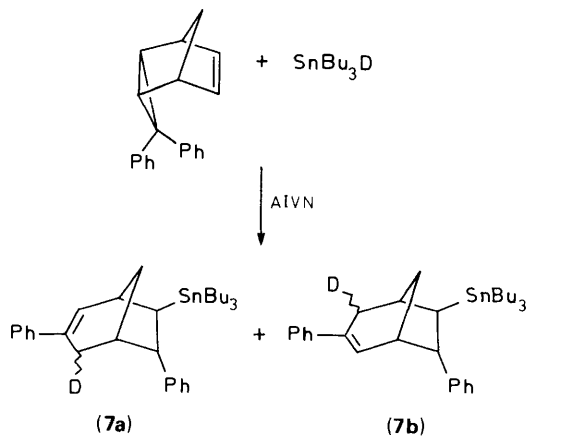
Bromination of the *exo* hydrocarbon (**4**) was reported earlier[8] to give the cyclopropyl ring opened§ product (**5**) in 61% yield, as shown in equation (1), in which no π participation could occur.

Radical initiated addition of tri-n-butyltin deuteride to (**4**) gave the expected reduction product (**6**) as a clear viscous oil in 80% yield as shown in equation (2). The analytical data as well as the proton and carbon NMR spectra supported the presence of a geminal diphenyl cyclopropyl group and the tri-n-butyltin moiety.

In contrast, addition of tri-n-butyltin deuteride to *endo*-(**1**) gave a 75% yield of a clear viscous oil which was shown by ^{1}H NMR to be a 3.5:1 mixture of phenyl migrated ring opened allylic isomers (**7a**) and (**7b**) (equation 3). This structural assignment is based on the analytical data, the presence of the tri-n-butyltin moiety, the loss of the geminal diphenyl cyclopropyl structure, the presence of two styryl proton doublets at δ 5.97 (rel. integral 3.5) and 6.63 (rel. integral 1), and the presence of two benzylic proton signals at δ 3.55 (rel. integral 3.5) and 3.47 (rel. integral 1). The



(**4**) (**6**) (80%) (2)



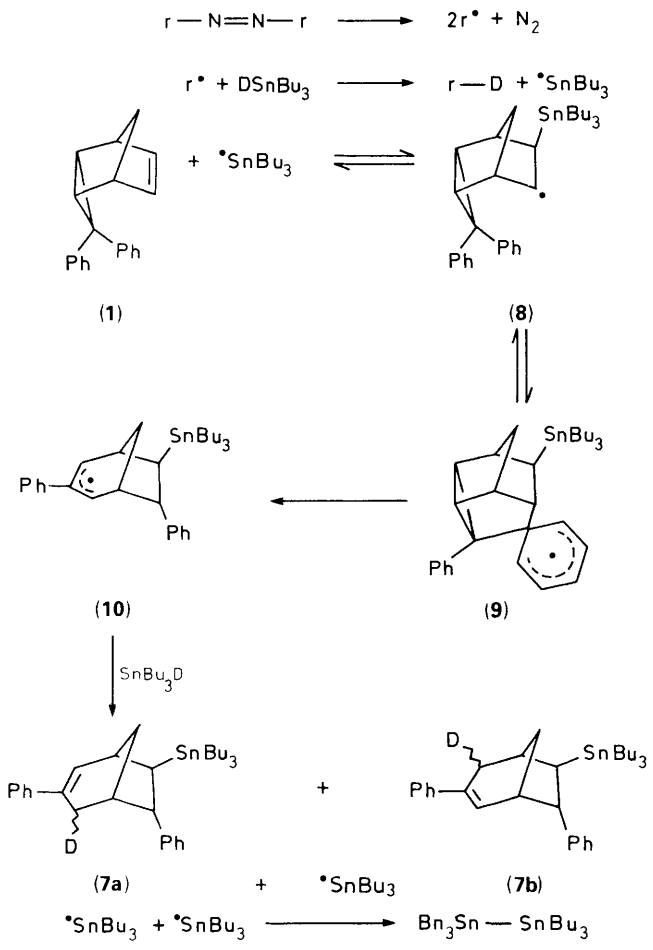
(**7a**) (**7b**) (3)

(**7a**) + (**7b**) = 75%

† Deceased 13th May 1987.

‡ All new compounds were characterized by elemental analysis and spectroscopic techniques on samples purified by rotational TLC. The reported yields are the best from a series of trials.

§ Addition of 2,4-dinitrobenzenesulphenyl chloride (2,4-DNS) resulted in a product of similar structure. In contrast, the addition of 2,4-DNS reagent to (**1**) gave a mixture of at least six products (TLC).



Scheme 2

assignment of the double bond position in the two isomers is based on an examination of models to ascertain the effect of the C-7 phenyl group on the proton chemical shifts of the vinyl protons at C-2. In the minor isomer (**7b**), the vinyl signal is deshielded by the freely rotating C-7 phenyl group. In the major isomer (**7a**) the vinyl proton is at somewhat higher chemical shift since it is on the other side of the molecule and is unaffected by the phenyl ring.

Relative rate studies performed in individual NMR tubes indicated that the radical addition to *exo*-(**4**) was approximately 2.1 times faster than the addition to *endo*-(**1**). Part of this difference is due to the longer chain length observed for the reaction on (**4**) through variation of the initial concentration of initiator. However, competitive studies on mixtures of (**1**) and (**4**) showed exclusive reaction of (**1**) while (**4**) remained almost unreacted. This reactivity difference can be explained if the initial addition of the tin radical to (**4**) to produce the radical precursor to (**6**) is reversible,[9] whereas the addition to *endo*-(**1**) to produce radical (**8**) is less reversible because it rearranges *via* an $Ar_{1,5}$ transition state (**9**) to a more stable allylic radical (**10**) (see Scheme 2). The allylic radical then abstracts a deuterium from another tri-n-butyltin deuteride on either side in the observed 3.5 : 1 ratio.

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