

Synthesis of Cycloproparenes from Furans: 2,7-Diphenyl-1*H*-cyclopropa[*b*]-naphthalene**

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Abstract: 2,7-Diphenyl-1*H*-cyclopropa[*b*]naphthalene (**1b**) is synthesized in 72% overall yield via cycloaddition of 1,3-diphenylisobenzofuran (**2b**) to 1-bromo-2-chlorocyclopropene (**3a**) followed by aromatization of the adduct **4b** with low-valent titanium.

A considerable variety of synthetic methods have been developed for cycloproparenes^[1]. While they are usually convenient for the preparation of the parent compounds, their adaptation to synthesis of substituted derivatives is not always straightforward, in particular if the required precursor must first be obtained by multistep synthesis. For example, 1,1-dichloro-2,7-diphenyl-1*H*-cyclopropa[*b*]naphthalene (**1c**) is available through a sequence of nine steps, seven of which are needed for the preparation of the starting compound *trans*-1,2-diphenyl-1,2-dihydrocyclobutabenzene from phthalic anhydride^[2]. In connection with other work we needed a sample of 2,7-diphenyl-1*H*-cyclopropa[*b*]naphthalene (**1b**). We considered the possibility of obtaining **1b** by reduction of the dichloro derivative **1c** by a method developed some time ago^[3], but in view of the nine steps needed for **1c** it was decided to try an independent approach which at the same time would extend the methodology for the synthesis of substituted cycloproparenes.

Diels-Alder addition of furans and isobenzofurans to halogenated cyclopropenes are well known^[4], but to our knowledge aromatization of the adducts to yield cycloproparenes has not yet been reported. We now report that this transformation can be achieved by low-valent titanium^[5] (Scheme 1).

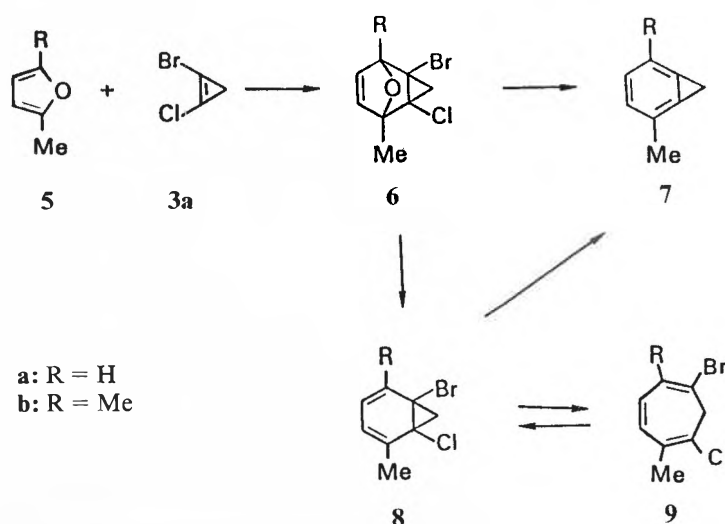
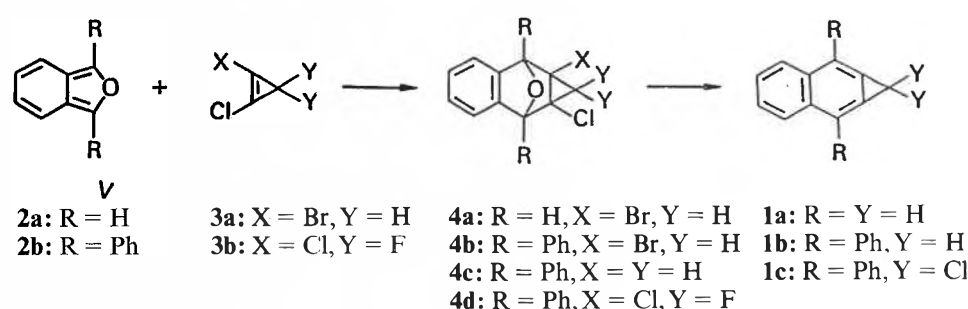
When 1,3-diphenylisobenzofuran (**2b**) is allowed to react with 1-bromo-2-chlorocyclopropene (**3a**)^[6], the adduct **4b** forms in ca. 85% yield. The stereochemistry of **4b** is not known, but comparison of the spectral data with those of analogous compounds suggests that it should be the *exo*-adduct^[7]. Treatment of **4b** with *n*-BuLi results in reduction of the bromo substituent and affords **4c** (30%). However, treatment of **4b** with TiCl₃/LiAlH₄ affords 2,7-diphe-

nyl-1*H*-cyclopropa[*b*]naphthalene (**1b**), *m.p.* 131°C (d), in 72% yield. The structure is consistent with the spectral data. The ¹H-NMR spectrum (Fig. 1) shows the proton signals of the cyclopropene moiety at $\delta = 3.55$. The AA'BB' system of the naphthalene protons (H-C(3)-H-C(6)) is centered at $\delta = 7.44$ and 8.17 while the protons of the adjacent phenyl rings exhibit complex multiplets at $\delta = 7.4-7.6$ (*m* and *p*) and 7.65-7.75 (*o*). The characteristic IR frequency of cycloproparenes is found at $\nu = 1675$ cm⁻¹. The mass spectrum of **1b** shows the peak of the parent ion at *m/z* 292 and fragments due to loss of H and C₆H₅.

Extension of the approach to other cyclopropa[*b*]naphthalenes and cyclopropabenzene is in principle possible, but some problems in the aromatization step have yet to be overcome. Thus the cycloadduct **4a**^[8] obtained from isobenzofuran and dienophile **3a** leads with TiCl₃/LiAlH₄ to a 2:1 mixture of 2-methylnaphthalene and parent cyclopropa[*b*]naphthalene (**1a**) (60% combined yield). The ratio changes to 1:3 when the reaction is carried out with TiCl₃/BuLi. Since **1a** is stable under the reaction conditions, the ring-opened product should not be formed via over-reduction of **1a**. The cycloadduct **4d** (from diphenylisobenzofuran (**2b**) and 1,2-dichloro-3,3-difluorocyclopropene (**3b**) affords no identifiable product upon reaction with TiCl₃/LiAlH₄.

Another complication arises upon reaction of cycloadducts obtained from 2-

Scheme 1



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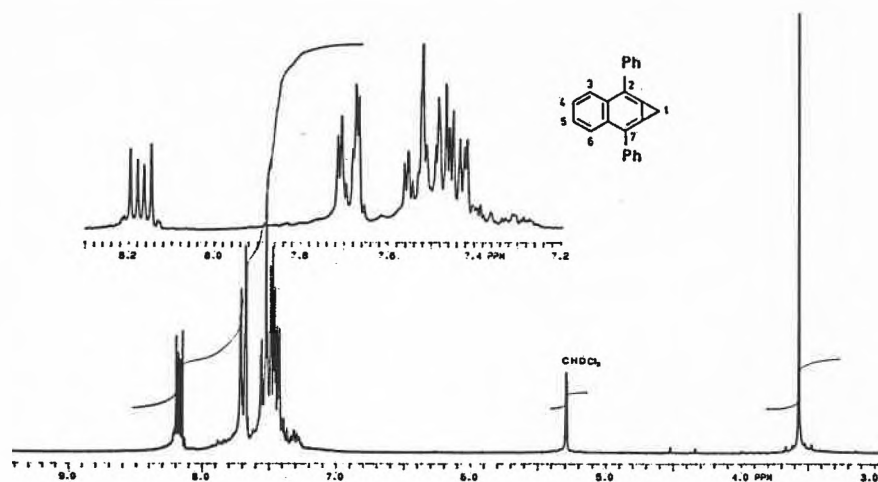


Fig. 1. ¹H-NMR spectrum of 2,7-diphenyl-1H-cyclopropa[b]naphthalene **1b** (CD₂Cl₂, 200 MHz).

methyl- or 2,5-dimethylfuran (**5a** or **5b**) and **3a** with TiCl₃/LiAlH₄: The mono-substituted adduct **6a** affords a ca. 1:1 mixture of 2-methyl-1H-cyclopropabenzene (**7a**) and 1-bromo-6-chloro-2-methylcyclohepta-1,3,5-triene (**9a**) together with the 5-methyl isomer. In the case of the dimethyl derivative **6b** only cycloheptatriene **9b** is

formed (30%). Preliminary experiments show that conversion of **9a** to **7a** (via norcadiene **8a**) is slow with TiCl₃/LiAlH₄, which suggests that two competitive pathways are operative. One must involve attack on oxygen and lead to the norcadiene **8a**; precedent for such a reaction path exists in the literature^[9]. The other

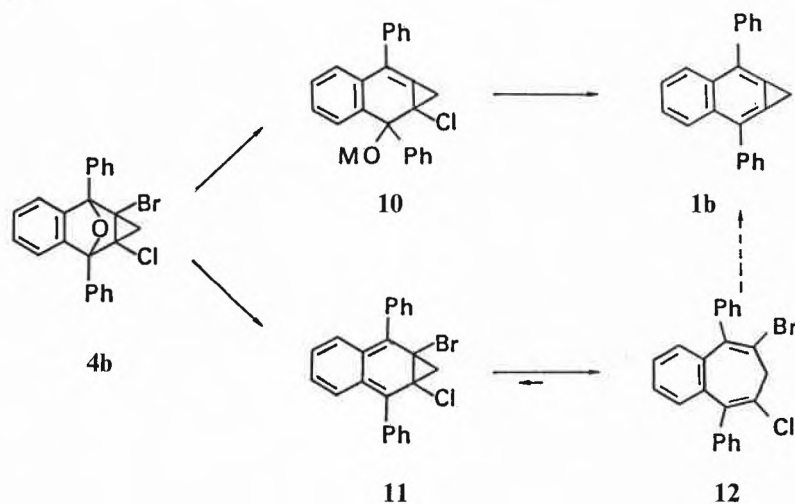
one should involve attack at the halogen substituent, whereby the formation of the norcadiene structure can be avoided. It is interesting to note, however, that conversion of **9a** to **7a** is possible under appropriate conditions^[10].

These observations are of interest with respect to the formation of cyclopropa[b]-naphthalenes **1a** and **1b** (Scheme 2): Aromatization via **10** should proceed in the same way as with the furan adducts **6**. However, the pathway involving formation of a diene (**8**) from initial attack on oxygen^[9] should be greatly disfavored, because in the naphthalene series it requires an energetically unfavorable *o*-naphthoquinodimethane intermediate **11**. The latter is expected to undergo electrocyclic ring opening to **12**, rather than further reduction to **1b**.

The cycloheptatriene **12**, once formed, would probably not be amenable to further reduction so that its absence from the reaction products lends support to the hypothesis that **1b** is formed from **10**.

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Scheme 2



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