

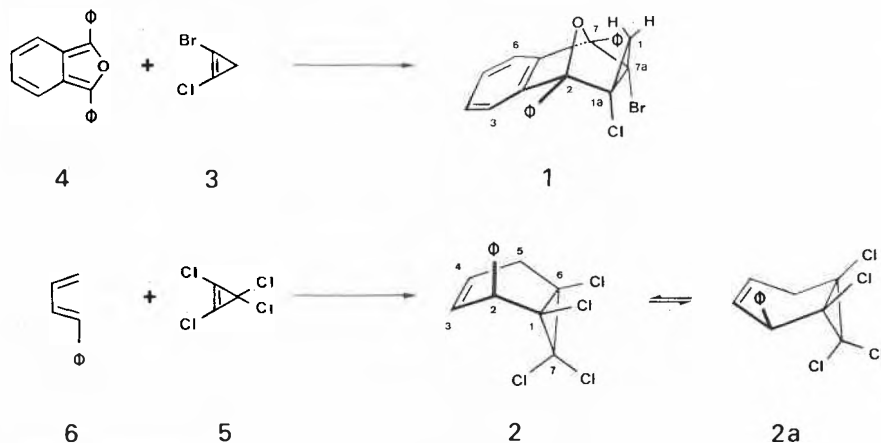
Stereochemistry of the Diels-Alder Addition of Halogenated Cyclopropenes**

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Abstract: The structures of two cycloadducts (**1** and **2**) of cyclopropenes to 1,3-diphenylisobenzofuran and *trans*-1-phenylbutadiene are established by X-ray crystallography. Both are *exo* adducts. In **2** the phenyl substituent occupies a *pseudo*-axial position; the ring-flipped conformation (**2a**) with the phenyl ring *pseudo*-equatorial is not observed.

Diels-Alder additions of dienes to cyclopropenes are well known^[1], but the stereochemistry of these reactions does not necessarily follow the normal course. For example, with cyclopentadiene, cyclopropenes usually afford *endo* adducts exclusively^[2], but additions to furans are often specifically *exo*^[3]. In some cases mixtures of *exo* and *endo* compounds are produced^[4]. Tetrahalogenated cyclopropenes add *endo* to cyclopentadiene^[5] and the same mode is assumed for addition to furans, although in the latter case the structures of the adducts are not definitely established. Addition to acyclic dienes is believed to be *endo*^[5,6].

We have now obtained X-ray crystallographic evidence for two Diels-Alder adducts (**1** and **2**) prepared by addition of 1-bromo-2-chlorocyclopropene (**3**) to 1,3-diphenylisobenzofuran (**4**)^[7] and, respectively, tetrachlorocyclopropene (**5**) to *trans*-1-phenylbutadiene (**6**)^[8]. Both adducts have *exo* configuration.



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Fig. 1. Stereoscopic view of **1** (*r*-1a-bromo-*c*-7a-chloro-1a,2,7,7a-tetrahydro-*c*-2,7-diphenyl-2,7-epoxy-1*H*-cyclopropa[*b*]naphthalene).

Adduct **1** was obtained as racemic mixture in 85% yield upon reaction of equimolar amounts of **3** and **4** at -25°C (30 min) followed by work-up at room temperature^[7]. **1** crystallizes from EtOH (*m.p.* 149–150 $^{\circ}\text{C}$) as hexagonal prisms in the space group $P2_1/c$; $a = 10.232(3)$, $b = 8.907(2)$, $c = 20.638(9)$ Å, $\beta = 101.78^{\circ}$; $Z = 4$; $\rho_c = 1.529\text{ g}\cdot\text{cm}^{-3}$ ($\rho_{\text{exp}} = 1.528$)^[9]. The final *R* factor, based on 1269 observed reflec-

tions ($|F_o| > 4\sigma(F_o)$ and $|F_o| > 8$), was 0.062. Since the enantiomers of **1** are equitably distributed over the same crystallographic site a disorder occurs with respect to the position of the chloro and bromo substituents at C(1a) and C(7a), respectively. These disordered halogen atoms

have been refined with isotropic atomic displacement parameters. The structure (Fig. 1) of **1** confirms the NMR-based criterion for *exo* adducts of cyclopropenes to furans^[4]. H–C(1) *syn* to the oxygen bridge is strongly deshielded by the latter and resonates at $\delta = 3.20$, while H–C(1) *anti* shows a signal at $\delta = 2.18$ ($^2J_{\text{HH}} = 7\text{ Hz}$). In the corresponding *endo* adduct the cyclopropane hydrogens are expected to resonate at $\delta \approx 2$ ^[4].

The adduct of tetrachlorocyclopropene (**5**) to *trans*-1-phenyl-1,3-butadiene (**6**) was obtained upon heating a 2:1 mixture of the educts in CCl_4 to 100 $^{\circ}\text{C}$ (**3d**) in presence of hydroquinone and NaHCO_3 . Chromatography on SiO_2 with CH_2Cl_2 afforded colorless crystals of **2** (*m.p.* 122–123 $^{\circ}\text{C}$) with the following characteristics: Orthorhombic, space group $Pbca$; $a = 7.2286(13)$, $b = 15.986(4)$, $c = 22.750(7)$ Å; $Z = 8$; $\rho_c = 1.556\text{ g}\cdot\text{cm}^{-3}$,

$\mu = 8.78\text{ cm}^{-1}$ ^[9]. The final *R* factor, based on 1042 observed reflections ($|F_o| > 4\sigma(F_o)$ and $|F_o| > 8$), was 0.052. The structure is shown in Fig. 2.

The cyclohexene ring of **2** adopts an almost planar boat configuration with an angle of 166.9 $^{\circ}$ between the planes containing C(2)–C(3)–C(4)–C(5) and C(2)–C(1)–C(6)–C(5), respectively. The latter plane forms an angle of 109.9 $^{\circ}$ with that of the cyclopropane ring. The phenyl ring is *cis* to the chloro substituents at C(1) and C(6).

The stereochemistry of Diels-Alder reactions with cyclic dienes is described with respect to the bridges in the bicyclic adduct. By analogy, *endo* addition in acyclic dienes implies that the bulkier substituents of the dienophile (CCl_2 in **5**) are oriented towards the central bond of the cisoid diene, and this orientation leads to a product where the 1-*trans* phenyl substituent of the diene ends up *cis* to the dichlorocyclopropane. This is the mode of addition we and others^[6] have assumed for addition of tetrahalogenocyclopropenes to *trans,trans*-1,4-diphenylbutadiene. The structure of **2** suggests that our hypothesis may well be wrong. Unfortunately, we were unable so far to obtain a crystal structure of an adduct with 1,4-diphenylbutadiene owing to possibly twinned crystals.

Cycloadducts of butadiene to **5** can adopt two conformations analogous to **2** and **2a**. It has been suggested^[5] that the

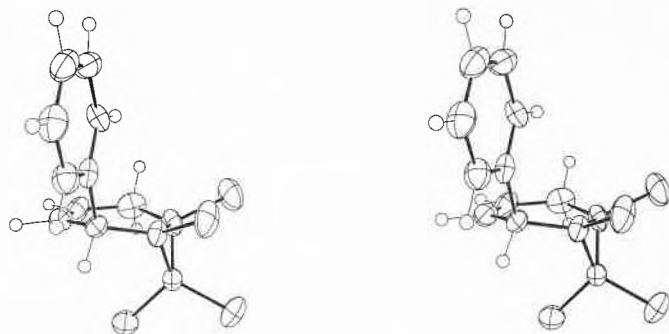


Fig. 2. Stereoscopic view of **2** (*r*-1,*c*-6,7,7-tetrachloro-*c*-2-phenylbicyclo[4.1.0]hept-3-ene).

ring-flipped conformation **2a** should be preferred, **2** being destabilized by dipole interactions between the double bond and the *syn*-C(7) chloro substituent. The crystal structure of **2** contradicts this argument. The preference for the phenyl substituent in the *pseudo*-axial position is surprising and might indicate an unfavorable steric interaction between the *pseudo*-axial hydrogens at C(2,5) and the *syn* chloro substituent at C(7) in **2a**. It is expected, however, that these conformational preferences will be different for adducts with 1,4-disubstituted butadienes (provided that

they are also *exo*) where transannular interactions between the *pseudo*-axial substituents destabilize conformations corresponding to **2**.

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