94. Stereo and Face Selectivity in Cycloadditions of 1,2,3-Trichloro-3-fluorocyclopropenes to Acyclic Dienes and Furans

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Dedicated to Prof. *Kurt Schaffner* on the occasion of his 60th birthday

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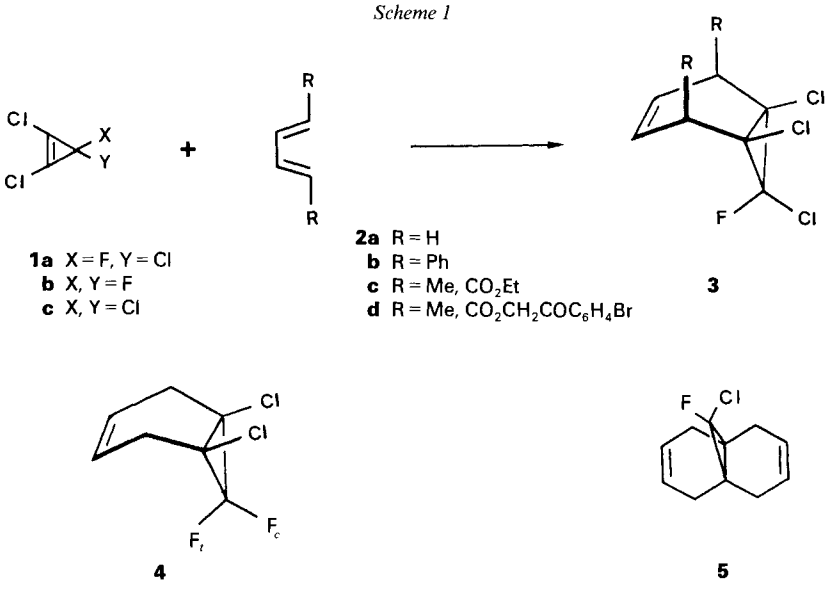
The stereo and face selectivities of the cycloaddition of 1,2,3-trichloro-3-fluorocyclopropene (**1a**) with acyclic dienes and furans has been re-investigated by X-ray determination and correlation of ^{19}F-NMR data. The isolated adducts of dienes exclusively have *exo*-configuration, and *exo*-configuration predominates with furans. The Cl substituents of the resulting cyclopropane ring are *cis*-oriented. The face selectivity of the reaction with both types of substrates is attributed to electrostatic interactions between the F and the bridgehead Cl substituents, which destabilize the F-*cis*-transition state (**13** (F-*cis*)) over **13** (F-*trans*).

Introduction. – The *Diels-Alder* reaction is one of the most important methods for the synthesis of six-membered rings. Synthetic and mechanistic interest in this reaction is due to its high regio- and stereoselectivity, which have been exploited in natural-product synthesis [1] and interpreted by theoretical models [2]. According to the nature of the substituents on dienes and dienophiles, the cycloaddition of furans and 1,3-dienes to cyclopropenes may be classified as a *Diels-Alder* reaction with normal or reverse electron demand [3]. Until recently, the information about the stereochemistry of the *Diels-Alder* reaction of substituted cyclopropenes was incomplete and, in part, contradictory. Several examples of this reactions with 1,2-di- and tetrahalogenocyclopropenes have recently been re-examined by X-ray crystallography and modern NMR techniques [4] [5], and as a consequence of these investigations, some of the reported configurations of the adducts had to be revised. The following empirical guidelines for predicting the configuration of the (kinetic) products in cycloadditions of cyclopropenes have been formulated by *Apeloig et al.* [5]: 'The parent cyclopropene and 1,2-disubstituted cyclopropenes are expected to yield *endo*-adducts, exclusively or predominantly. 3,3-gem-Disubstituted cyclopropenes are predicted to yield *exo*-adducts with open-chain dienes, or with cyclic dienes where the bridging unit introduces in the *exo*-transition state relatively small additional steric interactions (*e.g.*, furan). With cyclic dienes where the bridging unit is more sterically demanding (*e.g.*, cyclopentadiene), *endo*-products are expected.' These rules apply also when the 3,3-gem-substituents are halogens, *i.e.*, F or Cl.

In the case of 1,2,3-trichloro-3-fluorocyclopropene (**1a**, *Scheme 1*), the stereochemical outcome of the reaction is still further complicated, since the addition may not only be *exo* or *endo*, but for each of these modes the reaction can take place on either of the two faces of the cyclopropene, so that four stereoisomers may be formed. Although it was recognized early, that the reaction of **1a** with butadiene exhibits exclusive face selectivity,

Scheme 1



1a X = F, Y = Cl
b X, Y = F
c X, Y = Cl

2a R = H
b R = Ph
c R = Me, CO_2Et
d R = Me, $CO_2CH_2COC_6H_4Br$

3

4

5

and that with furan exclusive stereo and some face selectivity [6], the structures of the adducts were not determined unambiguously, and were in part attributed on the grounds of questionable assumptions, which later proved incorrect. We have, therefore, re-examined the stereochemistry of these reactions by the determination of the structure of two adducts of **1a** by X-ray diffraction methods.

Results and Discussion. – a) *Addition of 1,2,3-Trichloro-3-fluorocyclopropene* (**1a**) *to 1,3-Dienes.* The cycloadditions of **1a** to buta-1,3-diene (**2a**) [6] and (1*E*,4*E*)-1,4-diphenylbuta-1,4-diene (**2b**) [7] have been already reported. While the adduct of **1a** to **2a** is a liquid (**3a**), the reaction between **2b** and **1a** provides a solid product **3b** in low yield, but the crystals proved to be unsuitable for X-ray analysis. The formation of **3b** is accompanied by a small amount (< 5%) of an unidentified secondary product which exhibits a *triplet* at 36.2 ppm ($J = 1.5$ Hz) in the ^{19}F-NMR spectrum. The reaction between **1a** and ethyl sorbate (**2c**) (3 d, 110°) afforded a 95:5 mixture of unseparable liquids in 57% yield. The F substituent of the major component **3c** resonates as a *singlet* at 22.18 and that of the minor product at 39.05 ppm (downfield from C_6F_6). Attempts to prepare crystalline derivatives by hydrolysis, catalytic hydrogenation, or bromination of **3c** resulted either in decomposition of starting material or in formation of products in the liquid state. A crystalline compound was, however, obtained when **1a** was added to the *p*-bromophenacyl sorbate (**1d**) [18]. Reaction at 110° in $CHCl_3$ for 5 d resulted in recovery of 50% of unreacted **1d** and 25% of a 95:5 mixture of adducts. The ^{19}F-NMR spectrum of the crude reaction mixture revealed a situation similar to that in the addition of **1a** to **2c**: the major component **3d** resonantes at 22.4 and the unidentified secondary product at 39.1 ppm. Pure **3d** (m.p. 110–111°) was obtained by column chromatography during which the secondary product decomposed.

Table 1. *^{19}F-NMR Data of Adducts* **3a–d** *of* **1a** *to Acyclic Dienes*[a])

Compound	δ[a])	J(H,F) [Hz]
3a	18.6	1.5 ([6]: 0)
3b	18.2[b])	0[b])
3c	22.2	0
3d	22.4	0

[a]) Downfield from C_6F_6. [b]) [7].

The structure of **3a** has been deduced by *Law* and *Tobey* [6] by comparison of its ^{19}F-NMR spectra with those of other adducts of halogenocyclopropenes in particular of 1,2-dichloro-3,3-difluorocyclopropene (**1b**). Typically, the F substituent *anti* to the double bond (*cis* to the bridgehead Cl substituents) in **4** (F_c) usually couples with the CH_2 protons by 3–4 Hz, while the F substituent *syn* to the double bond and *trans* to the bridgehead halogens (F_t) shows no such coupling. The ^{19}F-NMR spectra of **3a–d** are summarized in *Table 1*. The resonance lines fall in a relatively narrow range of 18.2–22.4 ppm. For comparison, the ^{19}F shift of the chlorofluorocarbene adduct **5** of isotetraline [9], where the F-atom is in a similar environment except for replacement of the *trans*-Cl substituents, which are replaced by the second cyclohexene ring is 17.0 ppm. This, together with the very weak or totally absent H,F coupling with the allylic protons suggests identical configuration for all compounds.

Final proof of the structure of **3d** (*Fig. 1*) was obtained by X-ray crystallography (*Fig. 1*). The compound crystallized in a non-solvated (**3d**) or solvated (**3d′**) form from EtOH and MeOH solutions, respectively. In both cases, the conformations of the molecules can be considered as identical. Details of the structure determinations are given

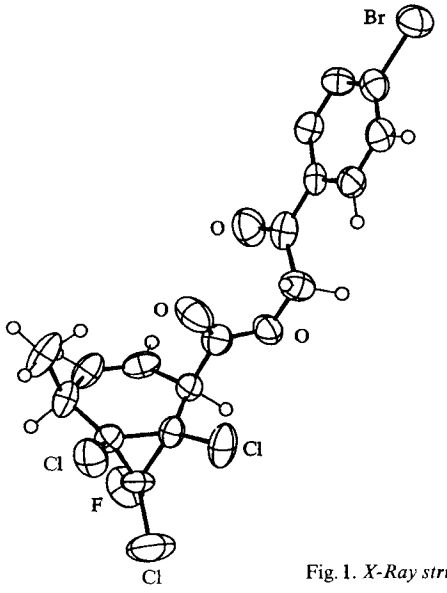


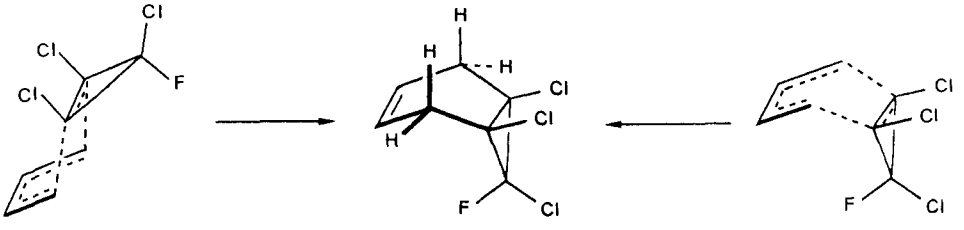
Fig. 1. *X-Ray structure of* **3d**

in the *Exper. Part* (*cf. Table 2*). The cyclohexene moiety of **3d** is nearly planar as in the adduct of phenylbutadiene to **1c** [4] and not puckered as previously assumed [6].

As *Fig. 1* shows, the bridgehead Cl substituents of **3d** are oriented *cis* to the Me and carboxy groups of the diene moiety, and the flagpole F-atom lies *trans* to the bridgehead halogens and *syn* to the C=C bond. This is the result of an *exo*-addition of the diene to the cyclopropene. Accordingly, the stereoselectivity of the cycloaddition of **1a** to open-chain dienes is identical to that of tetrachlorocyclopropene (**1c**) [4], which contradicts the view of *Law* and *Tobey* [6], that the cycloadditions of tetrahalogenocyclopropenes to all dienes should be *endo*.

The question of stereoselectivity of the *Diels-Alder* reaction between **1a** and **2a** is irrelevant because of the lack of substituents at the termini of the diene. If the appropriate face selectivity is respected, both an *exo*- (**6**-*exo*) and *endo*-transition state (**6**-*endo*) may lead to the correct structure (*Scheme 2*). With 1,4-disubstituted dienes, however, only the *exo*-transition state will lead to the correct product with the correct configuration. The

Scheme 2

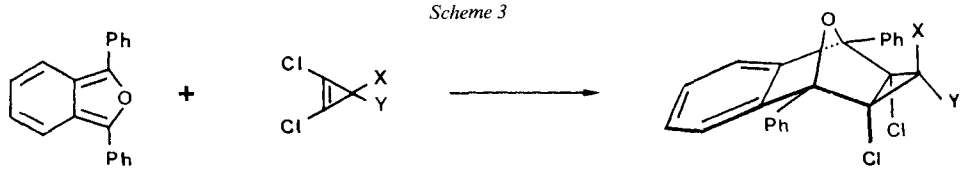


6-*exo* **3a** **6**-*endo*

analogy between the reactions of butadiene (**2a**) and its substitution products **2b–d** suggests that the *Diels-Alder* reaction of **1a** with **2a** proceeds in the same way as that of the substituted dienes, *i.e.*, *via* the *exo*-transition state (**6**-*exo*). The factors determining the face selectivity in the addition of **2a** should be identical to those operating in the reaction with the substituted dienes **2b–d**, which *must* proceed *via* an *exo*-transition state.

b) *Addition of 1,2,3-Trichloro-3-fluorocyclopropene* (**1a**) *to Furans.* The reaction of **1a** with 1,3-diphenylisobenzofuran (**7**) at room temperature resulted in formation of a single adduct **8a** (*Scheme 3*), which was isolated in 86% yield (after recrystallization). Compound **8a** exhibits a *singlet* in the ^{19}F-NMR spectrum at 30.1 ppm (downfield from C_6F_6).

Scheme 3



7

1a X = F, Y = Cl
b X, Y = F
c X, Y = Cl

8a X = F, Y = Cl
b X, Y = F
c X, Y = Cl

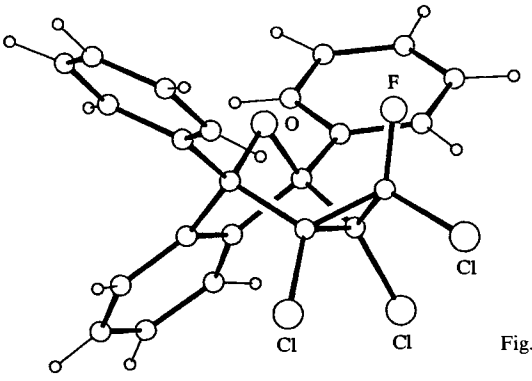
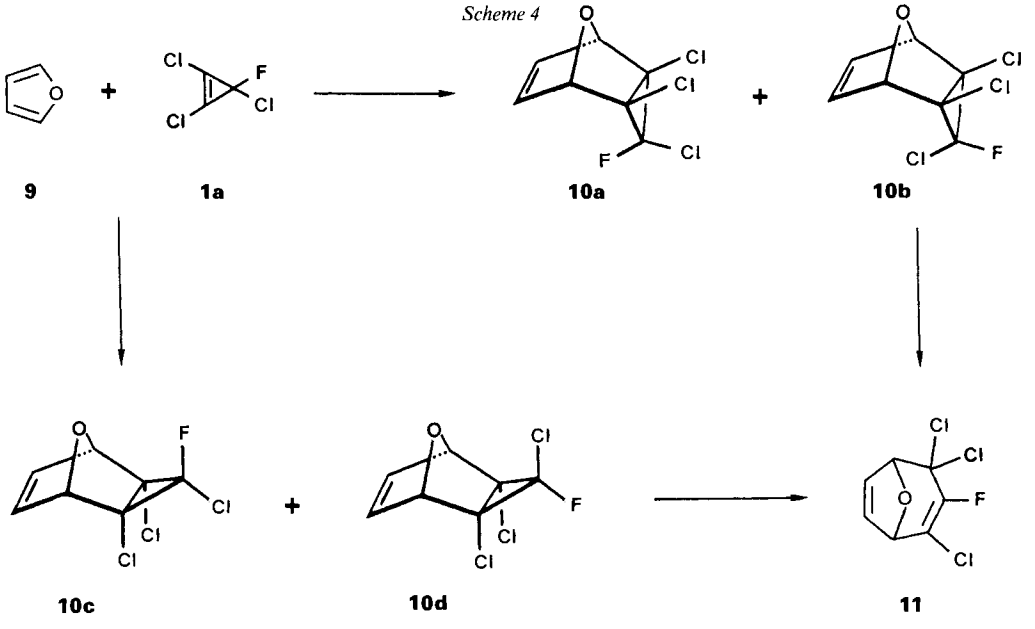


Fig. 2. *X-Ray structure of* **8a**

The crude reaction mixture contained, in addition, a small amount (< 5%) of a second, unidentified product with a ^{19}F *singlet* at 56.3 ppm. The structure of the major component **8a** was established by X-ray crystallography (*Fig. 2*; see also *Exper. Part, Table 2*). The adduct has *exo*-configuration, like the adduct **8b** [4] and **8c** [10] of **7** with **1b** and **1c**, respectively. The F substituent of **8a** lies *syn* to the O bridge, and *trans* to the vicinal Cl-atoms as is the case with the acyclic dienes.

The cycloaddition of furan (**9**) to **1a** has been investigated some years ago by *Law* and *Tobey* [6]. Contrary to the reaction between **1a** and **2a**, which exhibits very high face selectivity and results in a single adduct, that of **1a** with **9** leads to a mixture of two products in a ration of 1.5:1, to which the structures **10a** and **11** were assigned (*Scheme 4*). It was argued, that *endo*-addition would be preferred in this reaction, because of unfavorable steric interactions between the O-atom of the furan and the geminal flagpole

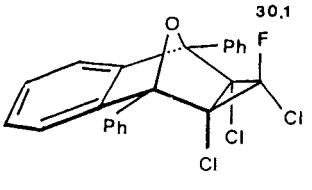
Scheme 4



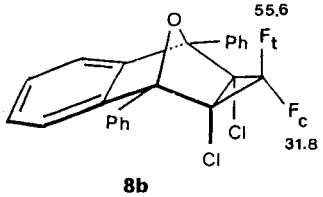
halogen atoms of the cyclopropene in the *exo*-transition state. Compound **10a** would be expected from the *endo*-addition of the cyclopropene, with the F substituent *syn* with respect to the C=C bond. The formation of **11** was explained by a thermal disrotatory ring opening of the stereoisomeric *endo*-adduct **10b**, which has the Cl substituent at the flagpole *syn* to the C=C bond. The mechanism of formation of **11**, according to *Law* and *Tobey* [6], involves outward rotation of the halogen atoms at the bridgehead, accompanied by ionization of the halogen atom at C(3) *trans* to the bridgehead halogen atom and *syn* to the C=C bond [11]. The incipient allylic carbenium ion is then intercepted by the halide leaving group. Contrary to **10b**, the isomeric **10a** is stable under the reaction conditions (80°). The electrocyclic process cannot occur owing to the unfavorable orientation of the Cl substituent at C(3). Electrocyclic ring opening of **10a** with departure of the properly oriented F does not take place because of the high strength of the C–F bond.

The interpretation of *Law* and *Tobey* is based on the assumption of *endo*-addition of **1a** to **9**, but experimental proof for this assumption was not given. Clearly, an analogous argument can be made, if the adducts have *exo*-configuration. In this case, the isomer **10c** which has the F substituent *syn* to the O bridge should be the stable product, while **10d** will undergo the electrocyclic rearrangement to **11**.

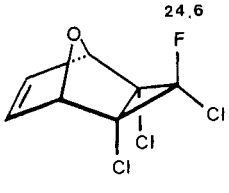
The tricyclic product of the reaction between **1a** and **9** is a liquid at room temperature, so that its structure cannot be obtained by conventional X-ray crystallography. However, comparison of its ^{19}F-NMR data with that of **8a** indicates that it should have *exo*-configuration **10c**, which is consistent with the configuration of all other known adducts of tetrahalogenocyclopropenes to furans. The compound isolated by *Law* and *Tobey* exhibits a *triplet* at 138.4 ppm upfield from Cl_3CF which corresponds to 24.6 ppm downfield from C_6F_6 [12]. In **8a**, the *syn*-orientation of the F substituent with respect to the O bridge is established by X-ray. This F-atom resonates at 30.1 ppm, *i.e.*, in the same range as the F-atom of the compound isolated by *Law* and *Tobey*, to which structure **10a** was attributed. In the model compound **8b**, the F substituent *syn* to the O-atom, but *trans* to the bridgehead Cl-atoms (F_t) resonates at 55.6 ppm [4]. Thus, replacement of the *cis* (with respect to bridgehead Cl-atoms) F-atom (F_c) by the Cl-atom produces an upfield shift of



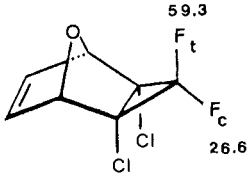
8a



8b



10c



12

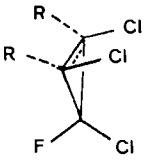
25.5 ppm on the resonance line of F_c in going from **8b** to **8a**. In the series of furan adducts, for comparison, the difluoro derivative **12** exhibits a ^{19}F resonance at 59.3 ppm [6] for F_t and the upfield shift in going from **12** to the chlorofluoro derivative **10c** is 35 ppm. The *cis*-F-atom (F_c) in **12** resonates at 26.6 ppm. If the structure of the adduct were **10d**, then one would expect to find an analogous upfield shift upon replacement of F_t by the Cl-atom, which would bring the line in the range around 0 ppm, which is clearly not the case. Finally, if the furan adduct had *endo*-configuration (**10a**) the ^{19}F resonance should be in the range of that observed for the adducts of open chain dienes.

Law and *Tobey* [6] have interpreted the (partial) face selectivity in the reaction of **1a** with furan (**9**) with a steric effect operating in an *endo*-transition state. The smaller size of the F as compared to the Cl substituent was believed to favor the transition state leading to **10a** over the one leading to **10b**. Since the furan adducts have in reality *exo*-configuration, this reasoning cannot apply. No explanation was given, however, for the remarkable face selectivity in the addition of **1a** with butadiene (**2a**), but an *endo*-transition state was assumed implicitly equally for this reaction.

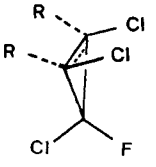
The relative orientation of the F and Cl substituents in the adducts of **1a** to furans and open-chain dienes is the same, and, therefore, we believe that the underlying reasons for the face selectivity with both types of substrates should also be the same. The relative rate of reaction of furan with the cyclopropenes have been determined [6], and they show a clear decrease of reactivity upon replacing Cl by F at the CH_2 position of the cyclopropene. The decrease of the reaction rate upon replacement of Cl by F is the opposite of that expected for a steric effect and, furthermore, it is irreconcilable with the view, that the F substituent should stabilize the transition state of the reaction, for example by interaction with the emerging double bond in the reaction with dienes or by interaction of the O-atom upon reaction with furans.

This trend may, however, be readily understood, if it is assumed, that the cycloadditions of tetrahalogenocyclopropenes to dienes and furans have the characteristics of *Diels-Alder* reactions with inverse electron demand [3]. The high electronegativity of F decreases the electron density of the cyclopropene C=C bond, thereby rendering the latter less reactive.

Since the F substituent decreases the reactivity of cyclopropenes in *Diels-Alder* reactions, we believe that the face selectivity observed in cycloadditions with **1a** should be attributed to a destabilizing effect of this substituent. In the transition state leading to **13** (F-*trans*), the all-*cis*-Cl-atoms are aligned in the same direction, while the C–F bond points in the opposite direction. This arrangement should be electrostatically more favorable than that in the transition state leading to **13**(F-*cis*) where the C–F bond is aligned with the C–Cl bonds. The importance of electrostatic effects for determining face selectivity of *Diels-Alder* reactions has recently been demonstrated [13], and preliminary model



13 (F-*trans*)



13 (F-*cis*)

calculations confirm that of the four possible transition states for *Diels-Alder* reactions with **1a**, the one leading to **13**(F-*trans*) is energetically the most favorable [14] one.

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Experimental Part

General. See [15].

Synthesis of Cycloadducts. The preparation of **3a** [6] and **3b** [7] has been reported in the literature.

p-*Bromophenacyl* c-*1*,c-*6*,c-*7-Trichloro*-t-*7-fluoro*-c-*5-methylbicyclo[4.1.0]hept-3-ene*-r-*1-carboxylate* (**3d**). A mixture of **2d** (0.5 g, 1.6 mmol) and **1a** (1.0 g, 5.7 mmol) [7] [16] in $CHCl_3$ (4.0 ml) was heated 5 d to 110° in a sealed tube in presence of K_2CO_3 (100 mg). After cooling and filtration, the mixture was evaporated to dryness. Flash chromatography of the residue (SiO_2, $CHCl_3/CCl_4$ 1:2) afforded 190 mg (25%) of **3d**, contaminated with *ca.* 10 mg of an unknown (^{19}F-NMR: 39.1, *s*), and 250 mg (50%) of unreacted **2d**. The product was further purified by slow column chromatography during which the unknown decomposed. M.p. 110–111° (EtOH). ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.75 (*d*, 2 H); 7.62 (*d*, 2 H); 5.90 (*m*, 1 H); 5.68 (*m*, 1 H); 5.35 (*d*, 2 H); 4.10 (*m*, 1 H); 3.02 (*m*, 1 H); 1.45 (*d*, 3 H). ^{19}F-NMR ($CDCl_3$, 188 MHz): 22.40 (*s*).

The same procedure, starting with *ethyl (2*E,*4*E*)-hexa-2,4-dienoate* (**2c**) and **1a** afforded **3c** in 57% yield. ^{1}H-NMR ($CDCl_3$, 200 MHz): 5.80 (*m*, 1 H); 5.54 (*m*, 1 H); 4.20 (*q*, ^3J = 7, 2 H); 3.90 (*m*, 1 H); 3.00 (*m*, 1 H); 1.50 (*d*, *J* = 7.3, 3 H); 1.25 (*t*, ^3J = 7, 3 H). ^{19}F-NMR ($CDCl_3$, 188 MHz): 22.18 (*s*).

c-*1*,r-*1a*,c-*7a-Trichloro-2,7-epoxy*-t-*1-fluoro-1a,2,7,7a-tetrahydro*-c-*2*,c-*7-diphenyl-1*H-*cyclopropa[*b*]naphthalene* (**8a**). To **1a** (0.55 mmol) in $CHCl_3$ (2.0 ml) was added *1,3-diphenylisobenzofuran* (**7**) (65 mg, 0.55 mmol), and the soln. was stirred 1 h at r.t. After evaporation, the residue was recrystallized (CH_2Cl_2) to give **8a** (205 mg, 86%). M.p. 182°. IR ($CHCl_3$): 3060*w*, 3010*m*, 1500*m*, 1460*m*, 1450*s*, 1350*m*, 1300*s*, 1210*m*, 1090*s*, 1045*m*, 980*s*, 905*s*. MS ($C_{23}H_{14}Cl_3FO$): 436, 434, 430 ($M^{+\cdot}$, absent), 105 (100), 77 (52), 51 (17).

Crystallographic Data for Compounds **3d**, **3d′**, *and* **8a**. Cell parameters and reflections intensities were measured at r.t. on a *Philips PW1 100* (**3d**, **8a**) and *Nonius CAD4* (**3d′**) diffractometers with monochromated Mo*K*α radiation. A summary of crystal data, intensity measurements, and structure refinement is given in *Table 2*. The

Table 2. *Summary of Crystal Data, Intensity Measurement, and Structure Refinement for Compounds* **3d**, **3d′**, *and* **8a**

	3d	**3d′**	**8a**
Formula	$C_{17}H_{13}O_3FCl_3Br$	$C_{17}H_{13}O_3FCl_3Br$ $(CH_3OH)_{0.25}$	$C_{23}H_{14}OFCl_3$
Mol. wt.	470.5	478.5	431.7
Solvent of crystallization	EtOH	MeOH	CH_2Cl_2/hexane
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space Group	$P\bar{1}$	$P2_1/c$	*Pnma*
a [Å]	7.894(1)	10.939(1)	16.151(4)
b [Å]	10.393(2)	24.004(2)	15.345(2)
c [Å]	12.995(3)	7.6185(8)	7.927(1)
α [°]	105.48(1)	90	90
β [°]	102.76(1)	100.58(1)	90
γ [°]	102.22(1)	90	90
V [Å^3]	959.7(3)	1966.5(3)	1964.6(6)
Z	2	4	4
F_{000}	468	950	880
D_c [gr·cm^{-3}]	1.63	1.61	1.46
μ(Mo*K*α) [mm^{-1}]	2.563	2.503	0.487
*A** min. and max.	1.439, 1.938	1.633, 1.714	–
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.53	0.55	0.58
Temp. [K]	298	298	298
No. measured reflc.	2360	2957	3689

Table 2 (cont.)

	3d	**3d′**	**8a**
No. observed reflc.	1594	2037	1106
Criterion for observed	$\|F_o\| > 4\sigma(F_o)$	$\|F_o\| > 4\sigma(F_o)$	$\|F_o\| > 4\sigma(F_o)$
Refinement (on F)	Full matrix	Full matrix	Full matrix
No. parameters	226	236	154
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Max. and average Δ/σ	3.4×10^{-4}, 4×10^{-5}	0.67, 0.022	0.015, 0.008
Max. and min. $\Delta\rho$ [e·Å^{-3}]	1.27, −0.91 (near Br)	0.97, −0.77 (near Br)	0.47, −0.51
S	3.72	2.00	1.44
R, wR [%]	7.6, 3.2	7.0, 4.1	4.6, 2.7

structures were solved by direct methods (MULTAN-87) [17] and refined by least-squares analysis with the XTAL3.0 program [18]. Atomic scattering factors and anomalous dispersion terms are taken from [19]. All coordinates of the H-atoms were calculated for **3d** and **3d′** and observed and refined with a fixed value of isotropic atomic displacement parameters for **8a**. Absorption corrections from *Gaussian* grid integration have been applied for compounds **3d** and **3d′**. The molecule of compound **8a** is located on a mirror plane with atoms C1(1), O, F, and C(1) in special positions **4c**. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, England.

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