J Chem Crystallogr (2011) 41:1053–1059
DOI 10.1007/s10870-011-0045-3

ORIGINAL PAPER

Dichloroenol Ethers X-ray Analysis in the Mechanistic Elucidation of Ynol Ethers Formation

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Received: 20 November 2009 / Accepted: 7 March 2011 / Published online: 23 March 2011

Abstract X-ray crystallographic data are provided for dichloroenol ethers (*S*,*E*)-2-(1-(1,2-dichlorovinyloxy)ethyl)-1,3,5-triisopropylbenzene (**2**) and (*S*,*E*)-2-(1-(1,2-dichloroprop-1-enyloxy)ethyl)-1,3,5-triisopropylbenzene (**3**). The former forms colorless crystals (orthorhombic, $P2_12_12_1$ space group) and exhibits the following cell parameters: $a = 10.212(5)$ Å; $b = 10.359(8)$ Å; $c = 18.217(6)$ Å. The latter also affords colorless crystals (monoclinic, $P2_1$ space group) with $a = 13.558(2)$ Å; $b = 10.891(1)$ Å; $c = 15.260(2)$ Å; $\beta = 115.65(1)°$. The data complement those recently reported for two other dichloroenol ethers, ((1*R*,2*S*)-2-((*E*)-1,2-dichlorovinyloxy)cyclohexyl)benzene (**5**) and ((1*R*,2*S*)-2-((*E*)-1,2-dichloroprop-1-enyloxy)cyclohexyl) benzene (**6**). The X-ray analyses of these dichloroenol ethers, the only reported to date, establish unambiguously the *trans* stereochemistry of the chlorides in these and, by extension, similarly prepared enol ethers. This information was required for the complete mechanistic understanding of ynol ethers formation from dichloroenol ethers. Structural comparison of these dichloroenol ethers with some carbon (dichloroalkene) and nitrogen (dichloroenamine) analogues is also presented.

Keywords Dichloroenol ethers · Ynol ethers · Crystal structure · Mechanism · Stereochemistry

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Introduction

Ynol ethers have long been employed in synthesis, in particular for the formation of enol ethers [1, 2]. The most useful method for their preparation begins from dichloroenol ethers **II** (Scheme 1) [3–5]. These ethers are easily prepared through the reaction of a potassium alkoxide with trichloroethylene. Subsequent addition of excess *n*-butyllithium, followed by an electrophile, then affords the corresponding ynol ethers **VI**. Although used for decades, this transformation remained mechanistically ambiguous until our recent study that successfully defined the reaction pathway [6]. We were able to show that *n*-butyllithium initially effects deprotonation of **II** at −78 °C to give **III** (the addition of one equivalent of *n*-butyllithium, followed by methyl iodide, leads to **IV**), which then upon warming suffers *syn* β-elimination, and not rearrangement, to generate isolable **V**. This complete elucidation, however, required unequivocal knowledge of the stereochemistry of the dichloroenol ethers, which was absent in the literature [7, 8]; no dichloroenol ether crystal structure had been reported.[1]

Dichloroenol ethers **2** [9] and **5** were prepared from (*S*)-1-(2,4,6-triisopropylphenyl)ethanol (**1**) and (*S*)-*trans*-2-phenylcyclohexanol (**4**), respectively (Scheme 2). Fortunately, on slow evaporation of the solvent (diethyl ether for **2** and ethyl acetate for **5**), each afforded colorless prisms suitable for single crystal X-ray analysis. The resulting structures established the previously assumed *trans* assignment for these enol ethers. Moreover, the dichloroenol ethers **3** and **6**, formed from **2** and **5**, respectively, by deprotonation, followed by lithio carbenoid trapping with methyl iodide, also produced colorless prisms suitable

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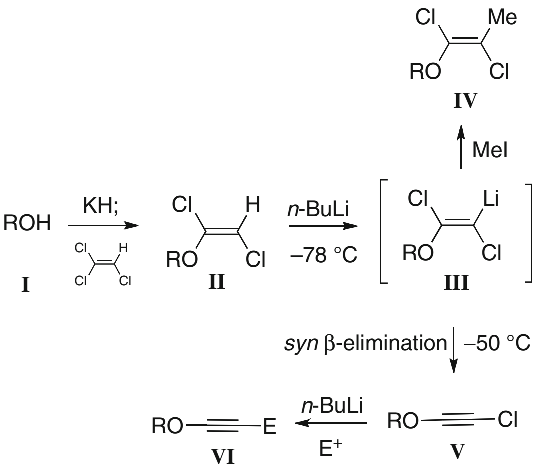
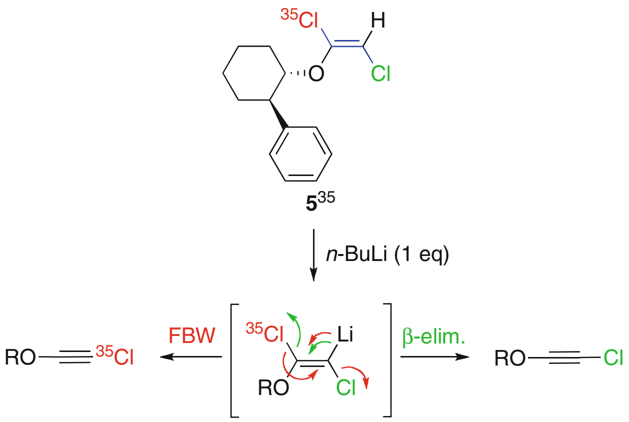
[1] The structures of dichloroenol ethers **5** and **6**, reported without detailed discussion in ref 3, represented the first examples.



Scheme 1 Mechanism of formation of ynol ethers **VI** from dichloroenol ethers **II**

for single crystal X-ray analysis on slow, controlled evaporation of ethyl acetate solutions. The structures of these derivatives provided unambiguous proof that the *trans* relationship of the chlorines is retained in the products, indicating a low-temperature configurational stability for the intermediate lithio carbenoids **III**. Upon warming, however, these carbenoids are converted into the chloro acetylenic ethers **V** and thence, by reaction with an additional equivalent of *n*-butyllithium and an electrophile, into the acetylenic ethers **VI**.

A final experiment was required to determine which of two potential mechanisms (or in what combination) was operative for the formation of the chloro acetylenic ethers **V** from the now established transient lithio carbenoids **III**: a well-known Fristch–Buttenberg–Wiechell (FBW) rearrangement [10–14] or a relatively uncommon *syn* (as opposed to *anti*) *β*-elimination. For this purpose, a chlorine-35 labeled dichloroenol ether $\mathbf{5}^{35}$ was prepared, which would provide, depending on the mechanism, either a labeled chloro acetylenic ether (FBW rearrangement) or one with natural abundance (*syn β*-elimination) (Scheme 3). The labeled compound $\mathbf{5}^{35}$ was obtained from the corresponding chloro acetylenic ether by reaction with H^{35}Cl. On deprotonation with one equivalent of *n*-butyllithium, *only* the natural abundance chloro acetylenic ether was produced, as evidenced by ESI mass spectrometry (triple quadrupole analyzer) of the derived chloroacetate, thus proving an exclusive *syn β*-elimination pathway. Metadynamics ab initio calculations were fully concordant with this result: the *syn β*-elimination was found to be 5 kcal/mol more favorable than the FBW rearrangement [6].

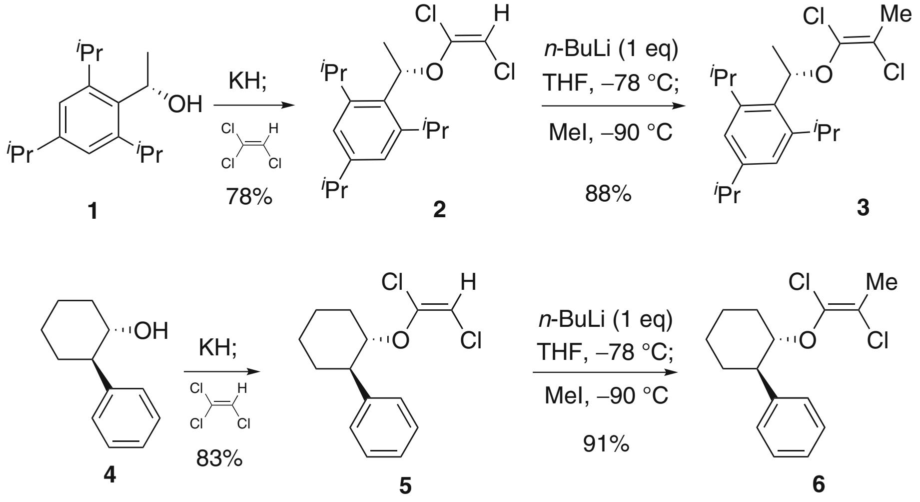


Scheme 3 Labeling experiment

Experimental

(*S*,*E*)-2-(1-(1,2-Dichlorovinyloxy)ethyl)-1,3,5-triisopropylbenzene (**2**)

An argon-flushed flask was charged with potassium hydride (30% suspension in mineral oil, 14.3 g, 107 mmol). The mineral oil was removed by washing with pentane



Scheme 2 Synthesis of dichloroenol ethers **2**, **3**, **5**, and **6**

(3×10 mL), and anhydrous THF (60 mL) was then added. A solution of (*S*)-1-(2,4,6-triisopropylphenyl)ethanol (**1**) (12.0 g, 48.3 mmol) in anhydrous THF (40 mL) was added dropwise at 0 °C. The mixture was stirred for 2 h at 20 °C, cooled to −50 °C, and treated dropwise with a solution of trichloroethylene (4.80 mL, 53.4 mmol) in anhydrous THF (20 mL). The reaction mixture was allowed to warm to 0 °C and stirred until TLC (eluent pentane) showed complete disappearance of starting material, at which time the mixture was carefully treated with methanol and water. The crude product was extracted with pentane in the usual way and the combined extracts were washed with water, dried over Na_2SO_4, filtered, and concentrated under vacuum at 0 °C. The residue was purified by flash chromatography on silica gel (pretreated with 2.5% of triethylamine v/v, eluent pentane) to afford 13.0 g (78%) of dichloroenol ether **2** as a white solid, which was recrystallized by slow evaporation of a diethyl ether solution to afford colorless crystals: mp 38–41 °C; $[\alpha]^{20}_{\mathrm{D}}$ −16.2 (*c* 1.0, $CHCl_3$); IR (film) υ (cm^{-1}) 3086, 1623, 1609, 1078, 1040; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.00 (q, $J = 6.9$ Hz, 1H), 5.60 (s, 1H), 3.75–3.15 (br s, 2H), 2.90 (sept, $J = 6.9$ Hz, 1H), 1.70 (d, $J = 6.9$ Hz, 3H), 1.35–1.20 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5 (C_q), 142.9 (C_q), 131.2 (C_q), 122.1 (CH), 98.3 (CH), 76.4 (CH), 34.1 (CH), 29.4 (CH), 24.7 (CH_3), 24.5 (CH_3), 23.9 (CH_3), 20.3 (CH_3); MS (EI$^+$) *m/z* 343 and 341 (M$^+$), 248, 231 (100%); Anal. Calcd. for $C_{19}H_{28}ClO$: C, 66.47; H, 8.22. Found: C, 66.63; H, 8.36.

(*S*,*E*)-2-(1-(1,2-Dichloroprop-1-enyloxy)ethyl)-1,3,5-triisopropylbenzene (**3**)

To a solution of dichloroenol ether **2** (841 mg, 2.45 mmol) in anhydrous THF (11 mL) at −78 °C was added dropwise *n*-BuLi (2.5 M in hexanes, 1.08 mL, 2.7 mmol). After 5 min, the mixture was cooled to −90 °C and MeI (0.31 mL, 4.98 mmol, prefiltered through a pad of basic alumina) and distilled HMPA (2.5 mL) were added. The solution was allowed to warm to −50 °C over 1 h and then at 20 °C before being treated with water. The crude product was isolated with pentane in the usual manner and purified by flash chromatography on silica gel (pretreated with 2.5% of triethylamine v/v, eluent pentane) to afford 770 mg (88%) of dichloroenol ether **3** as a white solid, which was recrystallized by slow evaporation of an ethyl acetate solution to afford colorless crystals: mp 40.5–41 °C; $[\alpha]^{20}_{\mathrm{D}}$ −26.9 (*c* 1.0, $CHCl_3$); IR (film) υ (cm^{-1}) 2961, 2359, 1659, 1459, 1379, 1169, 1050; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.02 (s, 2H), 5.85 (q, $J = 6.8$ Hz, 1H), 4.20–2.98 (m, 2H), 2.87 (sept, $J = 6.9$ Hz, 1H), 2.17 (s, 3H), 1.64 (d, $J = 6.8$ Hz, 3H), 1.35–1.19 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.2, 146.7, 138.5, 131.8, 122.1, 111.1, 76.3, 34.1, 29.4, 24.7, 24.5, 23.9, 21.6, 20.8; MS (EI$^+$) *m/z* 381.4 (M + Na)$^+$, 359.3 (M + H)$^+$, 231.2; Anal. calcd. for $C_{20}H_{30}Cl_2O$: C, 67.23; H, 8.47. Found: C, 67.51; H, 8.50.

((1*R*,2*S*)-2-((*E*)-1,2-Dichlorovinyloxy)cyclohexyl)benzene (**5**)

The procedure for **2** was used to obtain **5**: (+)-*trans*-2-phenylcyclohexanol (**4**) (2.40 g, 13.6 mmol), potassium hydride (30% wt in oil, 4.00 g, 30.0 mmol), and THF (20 mL) afforded 3.08 g (83%) of dichloroenol ether **5** as a white solid, which was recrystallized by slow evaporation of an ethyl acetate solution to give colorless crystals: mp 57–57.5 °C; $[\alpha]^{20}_{\mathrm{D}}$ +95.3 (*c* 1.0, $CHCl_3$); IR (neat) υ (cm^{-1}) 3104, 3031, 2941, 2854, 1629, 1452, 1278, 1087; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33–7.18 (m, 5H), 5.32 (s, 1H), 4.42 (dt, $J = 10.6$, 4.4 Hz, 1H), 2.84–2.75 (m, 1H), 2.26–2.18 (m, 1H), 1.99–1.88 (m, 2H), 1.80–1.73 (m, 1H), 1.61–1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 142.8, 142.4, 128.2, 127.7, 126.5, 97.9, 83.2, 49.7, 34.4, 31.6, 25.6, 24.6; MS (ESI) *m/z* 293.0 (M + Na)$^+$.

((1*R*,2*S*)-2-((*E*)-1,2-Dichloroprop-1-enyloxy)cyclohexyl)benzene (**6**)

The procedure for **3** was used to obtain **6**: dichloroenol ether **5** (262 mg, 0.97 mmol), *n*-BuLi (2.5 M in hexanes, 0.425 mL, 1.1 mmol), and MeI (0.120 mL, 1.93 mmol) gave 252 mg (91%) of dichloroenol ether **6** as a white solid, which was recrystallized by slow evaporation of an ethyl acetate solution to provide colorless crystals: mp 43–43.5 °C; $[\alpha]^{20}_{\mathrm{D}}$ +76.8 (c 1.0, $CHCl_3$); IR (neat) υ (cm^{-1}) 3028, 2930, 2858, 1658, 1448, 1181, 1000; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32–7.16 (m, 5H), 4.33 (dt, $J = 10.6$, 4.3 Hz, 1H), 2.81–2.72 (m, 1H), 2.22–2.13 (m, 1H), 1.98 (s, 3H), 1.96–1.86 (m, 2H), 1.79–1.71 (m, 1H), 1.61–1.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.1, 137.5, 128.1, 127.6, 126.3, 110.7, 82.5, 49.7, 34.5, 31.4, 25.7, 24.6, 21.3; MS (ESI) *m/z* 291.0 (M + Li)$^+$; Anal. calcd. for $C_{15}H_{18}Cl_2O$: C, 63.17; H 6.37. Found: C 63.55; H 6.49.

For compound **2**, a prismatic colorless crystal was chosen of 0.34* 0.23* 0.17 mm^3 dimensions, which was mounted on a glass fiber using paraffin. The crystal was then centred on a Bruker-AXS-Enraf–Nonius Kappa-CCD diffractometer, working at 150°K and at the monochromated (graphite) MoKα radiation $\lambda = 0.71073$ Å. Data reduction, cell determination, and refinement were performed using Eval-CCD. 22204 reflections measured from φ and ω scans were recorded for $1.12 < \theta < 30.0°$ and merged into 5625 unique reflections, including Friedel-pairs. Even though the Flack parameter is too small, it nicely corroborates the chemically known *S* configuration at C-6.

For compound **3**, a monocrystalline block of 0.38* 0.36* 22 mm^3 dimensions was mounted on a glass fiber and centered on a Bruker-AXS-Enraf–Nonius Kappa-CCD diffractometer, working at 200°K and at the monochromated (graphite) MoKα radiation $\lambda = 0.71073$ Å. Data reduction, cell determination, and refinement were performed using EvalCCD. 43784 reflections measured from φ and ω scans were recorded for $1.48 < \theta < 27.5°$ and merged into 10103 unique reflections, including Friedel-pairs. For this compound, the Flack parameter (0.00(2)) unambiguously allowed to establish the *S* configuration at C-7, in agreement with the chemically known configuration [15, 16].

For compounds **5** and **6**, see ref. [6].

In all cases, the data were corrected for the Lorentz and polarization effects.

Structure Determination and Refinement

The structures were solved using SIR-92 [17] and refined using TeXsan [18]. Cl, C, N, and O atoms were refined anisotropically by the full matrix least-squares method. H atoms were set geometrically and recalculated before the last refinement cycle. Figures were created using ORTEP [19]. Crystal data are summarized in Table 1.

Results and Discussion

All four compounds display four molecules inside the cell and whereas **2**, **5** and **6** display one molecule in the asymmetric unit, **3** display two molecules (**3a**, **b**) in the asymmetric unit. Compounds **2** and **5** crystallize in the orthorhombic $P2_12_12_1$ space group, while **3** and **6** crystallize in monoclinic systems ($P2_1$ and $C2$ space groups, respectively). Since there is no hydrogen bonding, the secondary structures may come from phenyl-group π-stacking Fig. 1.

From a structural point of view, the alkyl substituent on the oxygen atom (2,4,6-triisopropylphenylethyl in **2** and **3a**, **b**, and *trans*-2-phenylcyclohexyl in **5** and **6**) has little

Table 1 Crystal data and structure refinement

Compound	**2**	**3**
Name	(*S*,*E*)-2-(1-(1,2-dichlorovinyloxy)ethyl)-1,3,5-triisopropylbenzene	(*S*,*E*)-2-(1-(1,2-dichloroprop-1-enyloxy)ethyl)-1,3,5-triisopropylbenzene
CCDC deposit no. or code	742825	742824
Color/shape	Colorless/block	Colorless/platelet
Chemical formula	$C_{19}H_{28}Cl_2O$	$C_{20}H_{30}Cl_2O$
Formula weight (g.mol^{-1})	343.34	357.36
Temperature (K)	150	200
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit-cell dimensions	$a = 10.212(5)$ Å $b = 10.359(5)$ Å $c = 18.217(6)$ Å	$a = 13.558(2)$ Å $b = 10.891(1)$ Å $c = 15.260(2)$ Å $\beta = 115.65(1)°$
Unit-cell volume (Å^3)	1927.2(8)	2031.3(5)
Z	4	4
Density (calculated) (g/cm^3)	1.183	1.168
Absorption coefficient (mm^{-1})	0.337	0.322
Diffractometer/scans	Bruker–Enraf–Nonius Kappa CCD/phi and omega	Bruker–Enraf–Nonius Kappa CCD/phi and omega
Wavelength (Å)	0.71073	0.71073
θ range for data collection (°)	1.12–30.00	1.48–27.50
Reflections measured	22204	43784
Independent/observed reflections	5625 (Rint = 0.114)/4424 [$I > 2\sigma(I)$]	10103 (Rint 0.104)/8512 [$I > 1.5\sigma(I)$]
Data/restraints/parameters	4424/0/199	8512/0/415
Goodness of fit on *F*	0.933	1.908
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0501$, w$R2 = 0.0773$	$R1 = 0.0509$, w$R2 = 0.0686$
R indices (all data)	$R1 = 0.0683$, w$R2 = 0.0864$	$R1 = 0.0585$, w$R2 = 0.0706$

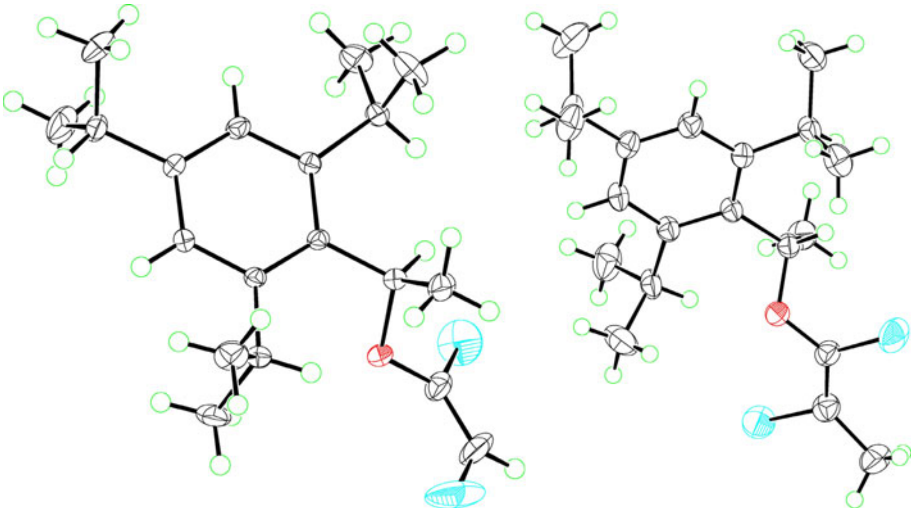


Fig. 1 Ortep drawing of compounds **2** and **3a**

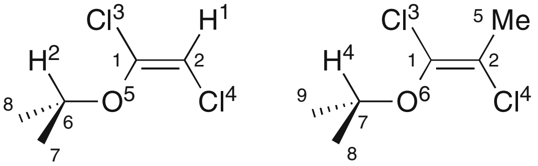


Fig. 2 Numbering for the dichloroenol ethers

influence on the pendant dichlorovinyloxyl or dichloropropenyloxyl portion of the molecule: the distances and angles are very similar, and not different from those expected [20].

As seen in Fig. 2 and Table 2, the six atoms of the dichlorovinyloxyl and dichloropropenyloxyl groups are nearly in the same plane. In the methylated dichloroenol ethers **3a**, **b** and **6**, the out of plane deformation is slightly greater than in **2** and **5**, but small.

Overall, compounds **2**, **5** and **3a**, **b**, **6** have very similar C_{sp3}–O bond distances and dihedral angles (see Table 3). Methylation of **2** and **5** to produce **3** and **6,** respectively, is attended by a small shortening of the C_{sp3}–O bonds. Interestingly, the conformation of the *O*-alkyl dichloroenol ethers is similar in all four compounds: The α-hydrogen of the alkyl groups (H^2 or H^4) is located in nearly the same plane as the chlorine atom (Cl^3) (Table 3, last column), most probably to minimize steric interactions due to 1,3-allylic strain [21, 22]. Two related enol ethers with reported crystallographic structures show similar solid-state conformations, with the corresponding α-hydrogen of the secondary alkyl groups sitting nearly in the same plane as the double bond (dihedral angles of 8.61 and 5.46°) [23, 24].

While the dichlorovinyloxyl and dichloropropenyloxyl groups display roughly comparable distances and angles, when the oxygen atom is replaced by a nitrogen atom [25, 26] or a carbon atom [27, 28], noticeable differences are found (Table 4). However, it should be noted that there are exceedingly few reported structures of such derivatives and therefore generalizations are somewhat perilous.

2 and **3** are enantiopure, and their absolute configurations could be assigned by X-ray crystallography [15, 16]. Additionally, the absolute configurations of **2**, **3**, **5** and **6** follow from those of the starting materials, which are known.

Conclusion

Through X-ray analysis, the *trans* relationship of the chlorines in dichloroenol ethers prepared by a popular

Table 2 Table of Least-squares planes

Compound	**2**	**3a**	**3b**	**5**	**6**
Atoms defining planes	Distance to plane (Å)				
Cl^3	−0.0016	0.0175(10)	−0.0132(10)	−0.0168	−0.0175(10)
Cl^4	0.0036	0.0171(10)	−0.0167(9)	−0.0246	−0.0153(9)
O^5 (**2**, **5**) or O^6 (**3**, **6**)	−0.0191	−0.0484(16)	0.0379(15)	0.0398	0.0447(13)
C^1	0.0296	0.0389(24)	−0.0308(23)	−0.0377	−0.0252(18)
C^2	0.0033	−0.0176(26)	0.0056(25)	−0.0008	0.0280(19)
H^1 (**2**, **5**) or C^5 (**3**, **6**)	−0.0157	−0.1588(31)	0.1282	0.0402	0.1874(28)
Mean deviation from plane (Å)	0.0121	0.0497	0.0387	0.0266	0.0530

Table 3 Distances and dihedral angles of the C_{sp3}-O bond

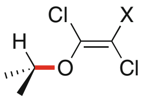
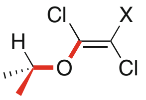
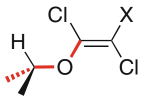
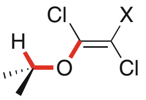
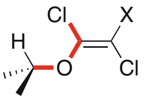
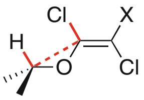
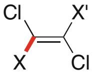
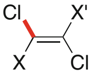
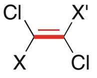
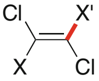
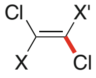
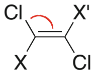
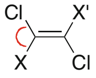
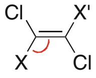
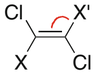
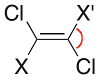
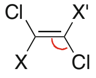
Compound	C–O distance (Å)	Dihedral angle (°)				
(X = H/Me)						
2 (X = H)	1.475(2)	−154.4(2)	79.2(2)	−38	70.0(2)	22.94
3a (X = Me)	1.463(3)	−165.9(2)	67.5(3)	−51	58.1(2)	2.86
3b (X = Me)	1.466(3)	−166.7(2)	66.7(2)	−51	64.3(2)	7.62
5 (X = H)	1.472(6)	−157.7(4)	79.1(5)	−40	67.2(5)	19.68
6 (X = Me)	1.460(2)	−161.8(1)	76.1(2)	−44	61.6(2)	12.67

Table 4 Angles and distances of dichlorovinyl derivatives

Structures	X	X′											
			Distances in Å				Angles in °						
FEHRIT	C	H	1.54(2)	1.7546	1.30(2)	0.96	1.72(3)	116(2)	124.66	119.89	120.10	120.33	120(2)
MCVCHO	C	H	1.5091	1.7625	1.3178	1.09	1.7113	112.97	117.99	128.93	118.66	118.57	122.74
AGUXAB	N	H	1.373(6)	1.937(7)	1.097(9)	0.93	1.859(10)	105.7(7)	112.1(5)	142.1(9)	125.8(6)	125.8(6)	108.3(7)
RAGKUG	N	H	1.4081(17)	1.7341(15)	1.323(2)	0.95	1.7096(17)	119.76(11)	115.62(10)	124.62(14)	119.02	112.02	121.96(12)
2 (742825)	O	H	1.340(2)	1.737(2)	1.322(3)	0.95	1.724(4)	118.3(2)	115.8(1)	125.7(2)	120.2	120.2	119.6(2)
EGOREY (**5**)	O	H	1.325(6)	1.741(6)	1.316(8)	0.95	1.681(7)	118.3(5)	116.1(4)	125.3(6)	119.4	119.4	121.2(5)
3a (742824)	O	C	1.341(3)	1.732(3)	1.326(3)	1.479(4)	1.730(3)	119.7(2)	115.9(2)	124.0(2)	127.3(3)	115.7(2)	117.0(2)
3b (742824)	O	C	1.334(3)	1.738(3)	1.322(3)	1.471(4)	1.737(3)	118.9(2)	115.2(2)	125.6(2)	128.6(3)	115.0(2)	116.3(2)
EGORIC (**6**)	O	C	1.339(2)	1.748(2)	1.318(3)	1.477(3)	1.728(2)	118.8(1)	115.1(1)	125.8(2)	128.1(2)	114.8(2)	117.0(1)

procedure has been unambiguously proven. This information has been used in fully delineating the mechanism of the formation of ynol ethers from dichloroenol ethers.

Supplementary Material

Crystallographic data (CIF) for (*S*,*E*)-2-(1-(1,2-dichlorovinyloxy)ethyl)-1,3,5-triisopropylbenzene, (*S*,*E*)-2-(1-(1,2-dichloroprop-1-enyloxy)ethyl)-1,3,5-triisopropylbenzene, ((1*R*,2*S*)-2-((*E*)-1,2-dichlorovinyloxy)cyclohexyl)benzene, and ((1*R*,2*S*)-2-((*E*)-1,2-dichloroprop-1-enyloxy)cyclohexyl)benzene have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-742825, CCDC-742824, CCDC-EGOREY, and CCDC-EGORIC. This material is available free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1223-336033. E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments We thank Prof. P. Dumy (UJF) for his interest in our work and the French Ministry of Education, Research and Technology (MENRT) for a fellowship (to B.D.).

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