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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1164). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(*E*)-But-2-enoxy-1,2-benzisothiazole 1,1-Dioxide: Unusual C—O—C Ether Bond Lengths and Reactivity

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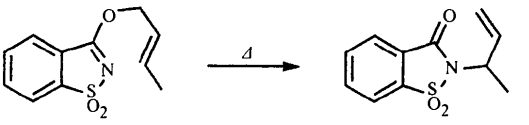
Abstract

Ethers such as the title compound, $C_{11}H_{11}NO_3S$, (1), rearrange thermally to give *N*-allyl isomers, (2), in high yield. The X-ray structure determination of the title ether shows a central C—O—C linkage which has one very short (notional) C—O single bond and one exceptionally long single C—O bond. The thermal migration of allyl from the O to the N atom involves the breaking of one of the ether bonds in (1) and a shortening of the other as it becomes a formal carbonyl group in the product (2). The rearrangement is thus considerably assisted by the ground-state structure of the starting ether, in which the bond to be broken is already stretched and the one that is to form a carbonyl group is already a substantial partial double bond.

Comment

Compounds bearing an allylic alcohol function are often vital structural units of biologically active systems. In addition, allylic alcohols have attracted widespread attention as key intermediates for the synthesis of various types of compounds (Kumar & Dittmer, 1994; Adam, Peters & Renz, 1994; Evans, Holmes & Russell, 1994; Bergmeier & Stanchina, 1995; Fujii, Habashita, Akaji, Nakai, Ibuka, Fujiwara, Tamamura & Yamamoto, 1996).

The title compound, (1), can be prepared readily from 3-chloro-1,2-benzisothiazole 1,1-dioxide (pseudosaccharyl chloride) and crotyl alcohol in the presence of base. It undergoes easy thermal rearrangement to the *N*-allyl isomer [(2); see scheme below]. Formally, this [3,3] rearrangement is similar to that reported for 5-allyloxy-1-phenyltetrazoles (Cristiano, 1994; Cristiano, Johnstone & Price, 1996). Under some conditions, [1,3] migration may also occur. Recent investigations concerning the structure and reactivity of aryloxytetrazoles and aryloxypseudosaccharins towards catalytic hydrogenolysis and cross-coupling have shown that much of the reactivity of these ethers can be ascribed to unusual bond lengths in the central C—O—C ether bonds caused by a usually powerful electronegative effect from the tetrazole or pseudosaccharyl ring system (Brigas & Johnstone, 1996; Alves, Brigas & Johnstone, 1996; Alves, 1996). For example, aryloxypseudosaccharins (3-aryloxy-1,2-benzisothiazole 1,1-dioxides) are characterized by having an ether linkage in which one C—O bond is long and the other is short. The effect of the benzisothiazole 1,1-dioxide ring system is to lengthen the aryl C—O bond from a typical value of 1.36 Å in a phenol to about 1.44 Å in the ether. At the same time, the link from the ether oxygen to the pseudosaccharyl system is very short (1.32 Å) for a C—O single bond, *viz.* it is a partial double bond. The net result of these electronic changes on converting a phenol into its pseudosaccharyl ether is to provide a molecular structure that lies close to the supposed transition-state structure for the migration shown below, in which an originally strong phenolic C—O bond becomes easily cleavable catalytically in the ether.



(1) (2)

Because of the ease of rearrangement of allyloxypseudosaccharins such as compound (1) (see scheme above), it was of interest to discover whether or not the electronegative pseudosaccharyl system was exerting a strong electronic influence on the allyloxy group,

thereby making the rearrangement easier than it would be without its influence.

There are two molecules in the asymmetric unit of (1) (Fig. 1). Except where otherwise stated, the following discussion concerns one of these molecules [C(1)–C(11)]. As with the aryloxypseudosaccharins, the C—O bonds in the central C—O—C ether linkage of the title compound are unequal in length. Compared with aryloxypseudosaccharins, allyloxypseudosaccharin (1) possesses a central C—O—C linkage in which one C—O bond is shorter [1.314 (7) *versus* 1.32–1.34 Å] and one that is much longer [1.488 (7) *versus* 1.42–1.44 Å] than normal values. Indeed, the long single C—O bond in ether (1) is significantly longer than even a normal aliphatic C—O single bond, which is typically 1.43 Å (Handbook of Chemistry and Physics, 1993–94), and has a bond order (Pauling, 1947, 1960) of only 0.9. Similarly, the short C—O bond to the pseudosaccharyl ring has a partial double-bond character of 1.59.

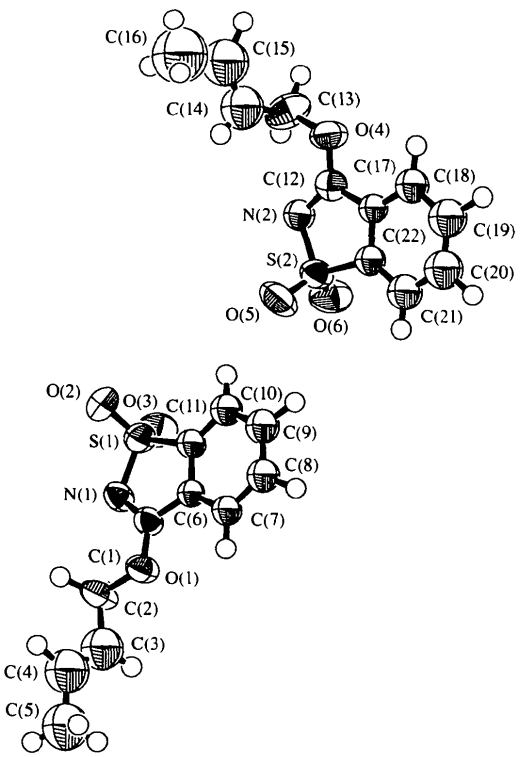
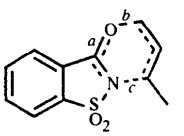


Fig. 1. A perspective view of the two independent molecules of the title compound showing 50% probability displacement ellipsoids. The atomic numbering system does not follow normal rules of chemical nomenclature. H atoms have been assigned arbitrary radii.

The powerful electronegative effect of the pseudosaccharyl group extends even into the allyl group itself. The single C(2)—C(3) bond of the allyl group is thus shorter at 1.477 (9) Å than a 'standard' single bond (1.53 Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987; Handbook of Chemistry and Physics, 1993–94). The C(3)—C(4) double bond is slightly shorter [1.278 (9) Å] than that of a 'standard' double bond (1.29 Å).

As well as the strong conjugation between the ether oxygen and the pseudosaccharyl ring system, evident from the very short C—O bond length, the ether C—O—C bond angle is close to 116°, indicating a considerable degree of sp^2 character at the O atom. This is again similar to the corresponding linkage in aryloxypseudosaccharins (Brigas & Johnstone, 1996; Alves, Brigas & Johnstone, 1996). Furthermore, the torsion angle N(1)—C(1)—O(1)—C(2) is 0.0 (8)°, consistent with sp^2 hybridization at the oxygen and the consequent drive for maximum overlap between the *p* orbital on oxygen and the π system in the pseudosaccharin rings. In a further interesting comparison with some 70 diaryl ethers, aryl tetrazolyl ethers and aryl pseudosaccharyl ethers, for which the sum of the two C—O bond lengths of the ether linkages is 2.78±0.02 Å (Alves, 1996), the corresponding sum for compound (1) is very similar at 2.803 (13) Å.

The rearrangement of the allyloxy compound (1) to its *N*-allyl isomer [(2); see scheme above] in which an N—C bond is formed [*c* in structure (3)] requires that the short ether C—O bond [*a* in structure (3)] should shorten more as it moves towards being a C—O double bond and that the long C—O bond [*b* in structure (3)] should stretch more as it breaks. The structure of the starting allyloxypseudosaccharin (1) is thus geometrically well advanced along the reaction coordinate and must be quite similar to the likely structure of the transition state. The proximity of the transition state and starting structures implies an early transition state, with a small activation energy of reaction (Leffler, 1953; Hammond, 1955). It has been pointed out that bond distance and energy are particularly important because they provide good reasons for the sensitivity of the activation energy of bond breaking to small changes in ground-state geometry (Bürgi & Dunitz, 1987). The migration is thus made easier than it would have been if there had been no inequality in the C—O bonds of the central ether linkage. This structure determination provides at least a partial explanation for the ease of rearrangement observed in the reaction scheme above.



(3)

If the two independent molecules in the asymmetric unit are compared, it is found that for their benzisothiazole 1,1-dioxide sections and for the central C—O—

C bonds, the bond lengths and angles are very similar within error limits and the above discussion is applicable to either molecule. In contrast, comparison of the C2—C3 and C4—C5 bond lengths in the allylic section of one molecule with the corresponding C13—C14 and C14—C15 lengths in the other shows that for these specific bonds there are significant differences; C2—C3 is 0.032 (12) Å longer than C13—C14, and C4—C5 is 0.058 (13) Å shorter than C14—C15. Efforts are being made to determine whether or not these two differences are real or perhaps due to random noise in the data, even though all other lengths and angles are consistent between the two molecules.

Experimental

3-Chloro-1,2-benzisothiazole 1,1-dioxide (pseudosaccharyl chloride; 2.71 g, 13.46 mmol) was added to a mixture of (*E*)-but-2-enol (crotyl alcohol; 1.25 ml, 1.06 g, 14.7 mmol) and triethylamine (5 ml) in toluene (30 ml). The solution was stirred at 313 K until all of the starting material had disappeared (TLC; about 1 h). The precipitate of triethylamine hydrochloride was filtered off and the filtrate was evaporated to give a yellow solid, which was recrystallized from ethanol (2.2 g, 69.1% yield; m.p. 397–398 K). Analysis: found C 55.6, H 4.7, N 5.9%; $C_{11}H_{11}NO_3S$ requires C 55.7, H 4.7, N 5.9%. ^{1}H NMR ($CDCl_3$): δ 1.75 (3H, *d*, J = 5.7 Hz), 4.95 (2H, *d*, J = 6.7 Hz), 5.8 (1H, *m*), 6.0 (1H, *m*), 7.73 (3H, *m*), 7.88 (1H, *d*, J = 6 Hz).

Crystal data

$C_{11}H_{11}NO_3S$
M_r = 237.27
Monoclinic
$P2_1/n$
a = 8.145 (4) Å
b = 16.375 (5) Å
c = 17.274 (4) Å
β = 92.26 (3)°
V = 2302 (1) Å^3
Z = 8
D_x = 1.369 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 3.7–6.7°
μ = 0.259 mm^{-1}
T = 153 K
Needle
0.40 × 0.15 × 0.15 mm
Colourless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4168 measured reflections
3855 independent reflections
2048 reflections with $I > 3\sigma(I)$

R_{int} = 0.03311
θ_{max} = 25°
h = 0 → 10
k = 0 → 19
l = −21 → 21
3 standard reflections
every 150 reflections
intensity decay: 0.10%

Refinement

Refinement on F
R = 0.0569
wR = 0.0623
S = 1.810
2048 reflections
199 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$

$(\Delta/\sigma)_{max}$ = 0.0585
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O(1)—C(1)	1.314 (7)	C(3)—C(4)	1.278 (9)
O(1)—C(2)	1.488 (7)	C(4)—C(5)	1.51 (1)
O(4)—C(12)	1.317 (7)	C(13)—C(14)	1.445 (9)
O(4)—C(13)	1.483 (8)	C(14)—C(15)	1.336 (9)
C(2)—C(3)	1.477 (9)	C(15)—C(16)	1.52 (1)
C(1)—O(1)—C(2)	115.9 (4)	C(3)—C(4)—C(5)	125.8 (7)
C(12)—O(4)—C(13)	117.4 (4)	O(4)—C(13)—C(14)	110.3 (5)
O(1)—C(2)—C(3)	107.1 (5)	C(13)—C(14)—C(15)	119.3 (7)
C(2)—C(3)—C(4)	122.0 (7)	C(14)—C(15)—C(16)	123.3 (7)

N(1)—C(1)—O(1)—C(2)	0.0 (8)
N(2)—C(12)—O(4)—C(13)	−1.3 (8)
C(1)—O(1)—C(2)—C(3)	174.1 (5)
C(2)—O(1)—C(1)—C(6)	179.7 (5)
C(12)—O(4)—C(13)—C(14)	85.1 (6)
C(13)—O(4)—C(12)—C(17)	178.1 (5)

H atoms were included in calculated positions and allowed to ride with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

The authors thank Dr Alexander J. Blake for perspicacious comments on the alkene bond lengths, one of the referees for his cautionary remarks on the effects of random noise in the data and Dr Marjorie M. Harding for her encouragement. The authors also gratefully acknowledge generous financial assistance from JNICT (Portugal) and the Eschenmoser Trust (UK).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(1α,4aβ,9aβ)-4a-Acetoxy-9a-chloro-1-methoxy-3-trimethylsiloxy-1,4,4a,9,9a,10-hexahydroanthracene-9,10-dione

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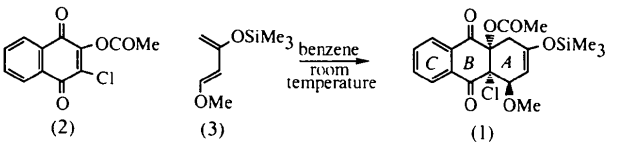
Abstract

The structure of the title compound, (1α,4aβ,9aβ)-9a-chloro-1-methoxy-9,10-dioxo-3-trimethylsiloxy-1,4,4a,9,-9a,10-hexahydro-4a-anthracenyl acetate, $C_{20}H_{23}ClO_6Si$, was determined in order to ascertain the regiochemistry of the Diels–Alder reaction between acetoxychloronaphthoquinone and a 1,3-dioxybutadiene.

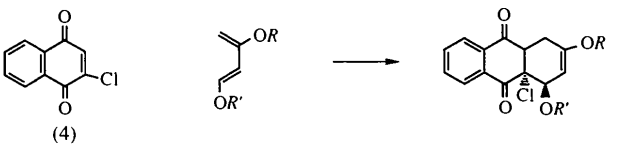
Comment

The title compound, (1), was the sole product obtained from the Diels–Alder cycloaddition reaction between acetoxychloronaphthoquinone (2) (Fries & Ochwat, 1923) and 1-methoxy-3-(trimethylsilyloxy)butadiene, (3) (Scheme I). The present structure analysis establishes that the regiochemistry of cycloaddition is such that the nucleophilic methylene terminus of the diene has attacked *ipso* to the acetoxy group; this is the same orientation with respect to the chloro group as for additions involving monochloro quinones, *e.g.* compound (4) (see Scheme II) (Cameron, Feutrill & Keep, 1989).



(2) (3) (1)

Scheme I



(4)

Scheme II

Compound (1) is a linear tricycle with a *cis* junction between rings *A* and *B*. Both rings *A* and *B* exist in slightly distorted half-chair conformations with approximate local axes of symmetry bisecting the C1—C6 and C3—C4 bonds for ring *A*, and the C1—C6 and C8—C13 bonds for ring *B*. The methoxy substituent occupies a pseudo-axial position [O6—C5—C4—C3 −98.7 (5)°] and is antiperiplanar to the chloro substituent [O6—C5—C6—Cl −163.6 (3)°]. The chloro substituent is pseudo-equatorial with respect to ring *B* and pseudo-axial with respect to ring *A*, while the acetoxy substituent is pseudo-axial with respect to ring *B* and pseudo-equatorial with respect to ring *A*.

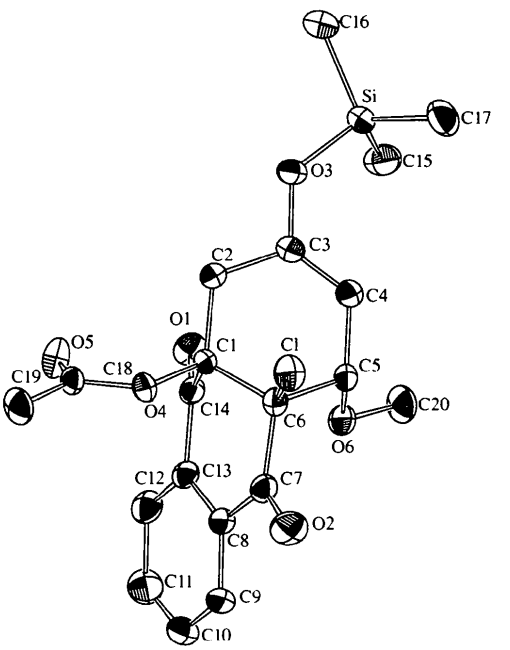


Fig. 1. *ZORTEP* (Zsolnai, 1994) diagram of (1). Displacement ellipsoids are plotted at the 30% probability level.