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3,3,5-Triphenyl-1,2-oxathiolane 2,2-Dioxide

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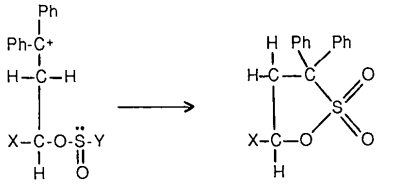
Abstract

The reaction of 1,1,3-triphenyl-1,3-propanediol with thionyl chloride gave an unexpected product, namely, the title compound 3,3,5-triphenyl-1,2-oxathiolane 2,2-dioxide (2), $C_{21}H_{18}O_3S$, which was identified by X-ray analysis.

Comment

The isomerization reaction of phenyl-substituted 2-oxo-1,3,2-dioxathianes (trimethylene sulfites) has been reported (Olsen, Lewis, Mehta & Stack, 1986). The reaction of 1,1,3-triphenyl-1,3-propanediol with thionyl chloride in the presence of pyridine produced compound (1), a triphenylated trimethylene sulfite with the S=O group in an equatorial orientation. IR and ^{1}H NMR spectroscopic data confirmed this structure. The title compound (2), was reportedly produced either by prolonged storage of (1) at room temperature or by refluxing it in acetonitrile. The degradation product of (1) was initially reported to be an isomeric sulfite, a conclusion supported by NMR data but at variance with the IR spectrum.

X-ray analysis was thus undertaken to establish the structure of (2). This showed that degradation of (1) produced 3,3,5-triphenyl-1,2-oxathiolane 2,2-dioxide (2) and not the twist isomer of 4,4,6-triphenyl-1,3,2-dioxathiane 2-oxide. A similar reaction has been noted between 1,1-diphenylpropane-1,3-diol and thionyl chloride which did not give the expected 4,4-diphenyl-1,3,2-dioxathiane 2-oxide but rather 3,3-diphenyl-1,2-oxathiolane 2,2-dioxide (3) (Geise, Lenstra, Petit, Hellier & Phillips, 1980). In the preparation of both (2) and (3), the presence of geminal phenyl groups apparently gives rise to a stable carbonium ion intermediate (4). This allows the SO_2 group to behave as a nucleophile resulting in cyclization to form (2) and (3).



(4)
X = H or Ph
Y = Cl or OH

(3) X = H
(2) X = Ph

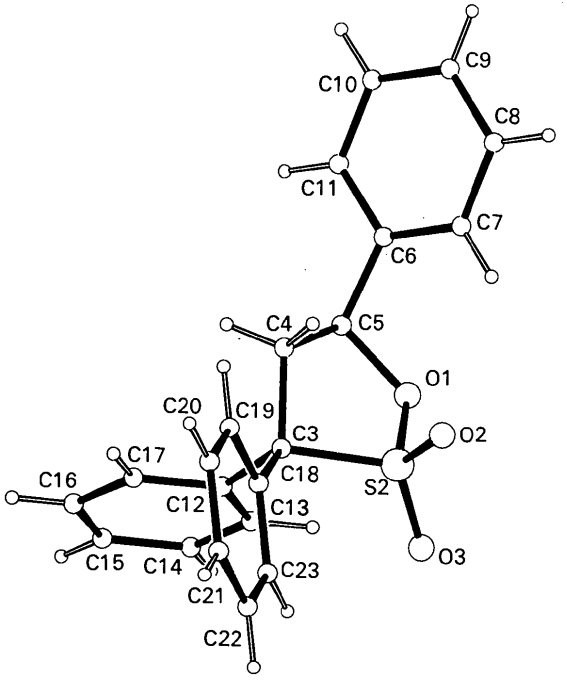


Fig. 1. *PLUTON* (Spek, 1991) drawing of the molecular structure of the title compound.

Experimental

Crystal data

$C_{21}H_{18}O_3S$
M_r = 350.41
Monoclinic
$P2_1/n$
a = 12.614 (4) Å
b = 10.581 (4) Å
c = 12.927 (4) Å
β = 95.62 (2)°
V = 1717.1 (10) Å^3
Z = 4
D_x = 1.356 Mg m^{-3}
D_m = 1.4 Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11–14°
μ = 0.206 mm^{-1}
T = 293 (2) K
Transparent rhombic
0.35 × 0.30 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical
T_{min} = 0.960, T_{max} = 0.980
2562 measured reflections
2381 independent reflections
1679 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0291
θ_{max} = 22.97°
h = 0 → 13
k = 0 → 11
l = −14 → 14
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
$R(F) = 0.0528$
$R(F^2) = 0.1459$
$S = 1.179$
2379 reflections
195 parameters
H atoms were geometrically constrained
$w = 1/[\sigma^2(F_o^2) + (0.1104P)^2$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.453$ e Å^{-3}
$\Delta\rho_{min} = -0.325$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S2	0.0234 (1)	0.1694 (1)	0.7178 (1)	0.045 (1)
O2	0.0878 (2)	0.2108 (2)	0.8075 (2)	0.059 (1)
O1	0.0280 (2)	0.2702 (2)	0.6279 (2)	0.047 (1)
O3	0.0460 (2)	0.0497 (2)	0.6752 (2)	0.064 (1)
C5	−0.0494 (2)	0.3726 (3)	0.6365 (2)	0.039 (1)
C4	−0.1101 (2)	0.3427 (3)	0.7299 (3)	0.040 (1)
C3	−0.1156 (3)	0.1971 (3)	0.7393 (2)	0.038 (1)
C6	0.0054 (2)	0.4980 (1)	0.6461 (2)	0.040 (1)
C7	0.1058 (2)	0.5110 (2)	0.6998 (2)	0.057 (1)
C8	0.1502 (2)	0.6304 (2)	0.7162 (2)	0.068 (1)
C9	0.0943 (2)	0.7368 (2)	0.6788 (2)	0.066 (1)
C10	−0.0061 (2)	0.7238 (2)	0.6251 (2)	0.065 (1)
C11	−0.0505 (2)	0.6044 (2)	0.6088 (2)	0.052 (1)
C12	−0.1972 (1)	0.1442 (2)	0.6541 (1)	0.041 (1)
C13	−0.1723 (2)	0.0931 (2)	0.5605 (2)	0.060 (1)
C14	−0.2532 (2)	0.0580 (3)	0.4852 (1)	0.076 (1)
C15	−0.3591 (2)	0.0741 (3)	0.5036 (2)	0.077 (1)
C16	−0.3841 (1)	0.1252 (2)	0.5972 (2)	0.068 (1)
C17	−0.3031 (2)	0.1603 (2)	0.6725 (2)	0.053 (1)
C18	−0.1334 (2)	0.1474 (2)	0.8461 (1)	0.042 (1)
C19	−0.1593 (2)	0.2285 (2)	0.9244 (2)	0.057 (1)
C20	−0.1745 (2)	0.1808 (2)	1.0220 (2)	0.068 (1)
C21	−0.1638 (2)	0.0520 (2)	1.0413 (1)	0.067 (1)
C22	−0.1380 (2)	−0.0292 (2)	0.9630 (2)	0.062 (1)
C23	−0.1228 (2)	0.0185 (2)	0.8654 (2)	0.050 (1)

Table 2. *Selected geometric parameters* (Å, °)

S2—O2	1.418 (3)	C5—C6	1.496 (3)
S2—O3	1.421 (3)	C5—C4	1.524 (5)
S2—O1	1.583 (2)	C4—C3	1.548 (4)
S2—C3	1.825 (3)	C3—C18	1.514 (3)
O1—C5	1.470 (4)	C3—C12	1.538 (3)
O2—S2—O3	118.1 (2)	C18—C3—C4	115.4 (2)
O2—S2—O1	109.44 (14)	C12—C3—C4	109.7 (2)
O3—S2—O1	107.0 (2)	C18—C3—S2	108.3 (2)
O2—S2—C3	107.9 (2)	C12—C3—S2	114.7 (2)
O3—S2—C3	115.7 (2)	C4—C3—S2	95.5 (2)
O1—S2—C3	96.24 (13)	C7—C6—C5	121.4 (2)
C5—O1—S2	111.6 (2)	C11—C6—C5	118.3 (2)
O1—C5—C6	110.8 (2)	C13—C12—C3	124.9 (2)
O1—C5—C4	107.2 (2)	C17—C12—C3	114.9 (2)
C6—C5—C4	112.5 (2)	C19—C18—C3	121.0 (2)
C5—C4—C3	107.4 (3)	C23—C18—C3	119.0 (2)
C18—C3—C12	112.2 (2)		

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A C_{20} 2:3 Formaldehyde–Cyclohexanone Adduct

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Abstract

The structure of the base-catalyzed condensation product of cyclohexanone and formaldehyde, (±)-(4aα,6β,9aβ,10aβ,14aβ,15a*R**,17*S**)-hexadecahydro-14a,6,9a-(epoxymetheno)benzo[*b*]benzo[2,3]cycloocta-[1,2-*e*]pyran-17-ol, $C_{20}H_{30}O_3$, reported by Plesek & Munk [*Collect. Czech. Chem. Commun.* (1957), **22**, 1596–1602; *Chem. Listy* (1957), **51**, 633–638], is confirmed to be a 2:3 adduct of formaldehyde to cyclohexanone, being formed by a sequence of aldol and Michael reactions followed by intramolecular ketal and hemi-ketal formation.

Comment

Although more than half a dozen different products have been obtained from the condensation of cyclohexanone with formaldehyde, the product depending on the catalyst, reaction conditions and ratio of reactants (Olsen, 1953; Colonge, Dreux & Delplace, 1956; Mounet, Huet & Dreux, 1971), the structure of the most complex product has remained elusive until recently. A crystalline condensation product, formed by heating the reactants with alcoholic NaOH, was reported in 1957 (Plesek & Munk, 1957) and given the empirical formula