

**(1*R*,2*s*,3*S*,6*R*,9*S*)-5,5,10,10-Tetra-
chloro-2-methyltricyclo[7.2.0.0^{3,6}]-
undec-7-ene-4,11-dione**Yoann Coquerel, Aurélien Blanc, Jean-Pierre Deprés,
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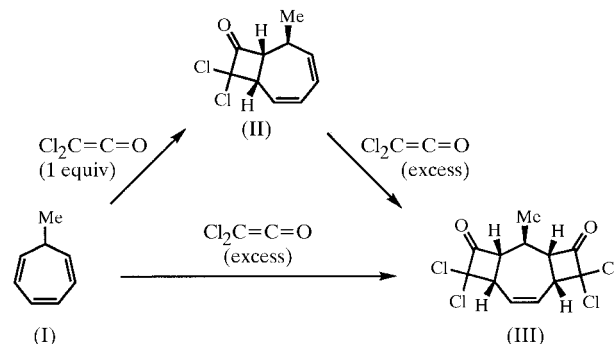
The title compound, C₁₂H₁₀Cl₄O₂, has a pseudoasymmetric centre at the methyl-substituted carbon and, in the solid state, a boat-like conformation.

Comment

In our laboratory, there is ongoing interest in synthetic applications of the 2+2 cycloaddition of dichloroketene with olefins (Brady, 1981; Hyatt & Reynolds, 1994). This reaction is well known to be chemo- (Mehta & Rao, 1985; McMurry & Bosh, 1987; Dowd & Zhang, 1992), regio- (Ghosez *et al.*, 1971; Hassner & Krepski, 1979; Deprés & Greene, 1989) and stereoselective (Hassner *et al.*, 1971; Greene *et al.*, 1985). The resulting α,α -dichlorocyclobutanones can be transformed into a variety of cyclopentanone (Deprés & Greene, 1980; Greene *et al.*, 1983), lactone (Au-Yeung & Fleming, 1977; de Azevedo & Greene, 1995) and lactam (Nebois & Greene, 1996; Delair *et al.*, 1999) natural and non-natural products.

We are currently examining the preparation of bicyclo[5.3.0]decane systems by 2+2 cycloaddition of dichloroketene with 7-substituted cycloheptatrienes, followed by ring expansion. The bicyclo[5.3.0]decane skeleton is frequently encountered in natural products, in particular the guaianolides (Connolly & Hill, 1991), which form one of the largest groups of sesquiterpene lactones (>500 known), many of which are significantly bioactive (Ando *et al.*, 1994). This framework is of course also found in the azulenes (Mochalin & Porshnev, 1977). The reaction of one equivalent of dichloroketene with 7-methylcyclohepta-1,3,5-triene, (I), gives mostly the mono cycloadduct, (II), together with a small amount of the double addition product, (III), in the proportion 9:1. In the presence of excess dichloroketene, however, the starting triene and the mono adduct (II) both undergo regio- and diastereoselective cycloaddition to yield the title compound, (III), in good yield (see Scheme). From the X-ray crystallographic elucidation of this compound (Fig. 1), the structure and stereochemistry of the mono adduct (II) are obvious. Compound (II) should be a

useful intermediate for accessing a number of guaianolides and azulenes. Although double cycloaddition of dichloroketene with polyenes has been reported previously [see, for example, Mehta & Rao (1985)], to the best of our knowledge, this is the first crystallographic determination of a bis- α,α -dichlorocyclobutanone.



The interatomic distances and angles of (III) are in good agreement with those given by Allen *et al.* (1987). Although the molecule potentially exhibits mirror symmetry, in the crystalline state the two α,α -dichlorocyclobutanone units are not perfectly identical. However, the measured bond lengths and angles are extremely close and consequently only mean values will be cited in this discussion.

The cyclobutane rings are fused to the seven-membered ring at C1 and C9 and at C3 and C6, with a C1–C9 (C3–C6) distance of 1.572 (6) Å. C11 (C4) of the carbonyl group [mean C=O 1.189 (2) Å] is bound to C1 (C3) at a distance of 1.530 (2) Å and with a C11–C1–C9 (C4–C3–C6) angle of 88.3 (1)°. Situated 0.310 (2) Å above the plane defined by C11–C1–C9 (C4–C3–C6), the remaining carbon of the cyclobutanone, C10 (C5), is connected to C9 (C6) at a distance of 1.557 (5) Å and to C11 (C4) at a distance of 1.540 (2) Å, with C1–C9–C10 (C3–C6–C5) and C1–C11–C10 (C3–C4–C5) angles of 89.4 (2) and 91.6 (2)°, respectively. The C9–C10–C11 (C6–C5–C4) angle is 88.5 (1)°. Finally, C10 (C5) is connected to the two Cl atoms at a distance of 1.771 (3) Å for the *exo* Cl3 (Cl1) and 1.758 (5) Å for the *endo* Cl4 (Cl2). A difference between these two bond lengths appears to be a general phenomenon, occurring as well in each of the nine α,α -dichlorocyclobutanone structures deposited in the Cambridge Structural Database (CSD; 1999).

It is of interest to compare certain other structural features of (III) with those of the compounds in the CSD. Compound (III) is the first example of an α,α -dichlorocyclobutanone fused to a seven-membered ring, the previously reported examples involving ring fusion with cyclohexanes (Nassimbeni *et al.*, 1977), a cyclopentane (Glen *et al.*, 1982), cyclopentenes (Gordon *et al.*, 1981; Cocuzza & Boswell, 1985; Watson & Nagl, 1987; Dehmlow *et al.*, 1995) and a bicyclo[3.1.0]hexene (Carpino *et al.*, 1981). Notably, the ring-fusion bond length of 1.572 (6) Å in (III) is one of the longest, the others being 1.51 (3) and 1.557 (8) Å (cyclohexanes), 1.57 Å (cyclopentane), 1.55, 1.568 (3), 1.567 (5), 1.570 (3) and 1.575 (4) Å (cyclopentenes), and 1.53 Å (bicyclo[3.1.0]hexene). The dihedral angle in (III) between the previously defined cyclobutanone

plane and the mean plane defined by the two C atoms at the ring fusion and their two non-cyclobutane neighbours [C2 (C2), C1 (C3), C9 (C6) and C8 (C7)] is 66.6 (1)°, whereas in the deposited α,α -dichlorocyclobutanones the values are, respectively, 53.7 (9), 73.3 (4), 65.8, 70.9, 60.1 (1), 69.9 (2), 77.73 (1), 75.2 (2) and 55.5°. Thus, the dihedral angle in (III) is unexceptional and is apparently uninfluenced, somewhat surprisingly, by the size of the seven-membered ring.

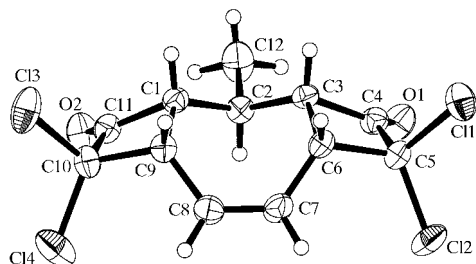


Figure 1
ORTEP (Johnson, 1976) molecular diagram of (III). Displacement ellipsoids are shown at the 40% probability level and H atoms are drawn as small spheres of arbitrary radii.

The crystallographic determination reported in this paper, the first of not only a bis- α,α -dichlorocyclobutanone but also a cycloheptane-containing adduct, nicely complements the few determinations of α,α -dichlorocyclobutanones presently available.

Experimental

Compound (III) and the mono cycloadduct (II) were obtained as a mixture (9:1) by overnight stirring of (I) with trichloroacetyl chloride (3 equivalents) and phosphorus oxychloride (3 equivalents) in ether in the presence of zinc-copper couple, followed by the usual treatment. Compound (III) crystallized as colourless needles (m.p. 379–381 K) from the crude mixture (65% yield). Spectroscopic data, IR (cm⁻¹): 3055, 1804, 1639; ¹H NMR (CDCl₃, 300 MHz, δ , p.p.m.): 1.33 (*d*, *J* = 6.4 Hz, 3H, H12), 2.69 (*m*, 1H, H2), 3.52 (pseudo *t*, *J* = 10.9 Hz, 2H, H1 and H3), 3.77 (pseudo *d*, *J* = 10.5 Hz, 2H, H6 and H9), 6.01 (*s*, 2H, H7 and H8); ¹³C NMR (CDCl₃, 75 MHz, δ , p.p.m.): 17.6 (C12), 32.1 (C2), 48.1 (C6 and C9), 62.3 (C1 and C3), 87.3 (C5 and C10), 125.7 (C7 and C8), 193.4 (C4 and C11); MS (EI) *m/z*, *M*⁺ (isotopic distribution, %): 332 (6), 331 (9), 330 (46), 329 (20), 328 (100), 327 (20), 326 (78).

Crystal data

C ₁₂ H ₁₀ Cl ₄ O ₂	<i>D</i> _x = 1.578 Mg m ⁻³
<i>M</i> _r = 328.02	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> ₂ ₁ / <i>a</i>	Cell parameters from 25 reflections
<i>a</i> = 10.320 (8) Å	θ = 10.3–14.4°
<i>b</i> = 12.390 (4) Å	μ = 0.845 mm ⁻¹
<i>c</i> = 11.219 (2) Å	<i>T</i> = 293 K
β = 105.80 (4)°	Monoclinic prism, colourless
<i>V</i> = 1380 (1) Å ³	0.35 × 0.32 × 0.29 mm
<i>Z</i> = 4	

Data collection

Enraf-Nonius CAD-4 diffractometer	θ_{\max} = 29.96°
ω scans	<i>h</i> = -14 → 14
4160 measured reflections	<i>k</i> = 0 → 17
3971 independent reflections	<i>l</i> = 0 → 15
3675 reflections with <i>I</i> > 0	2 standard reflections
<i>R</i> _{int} = 0.011	every 120 reflections
	intensity decay: 5.54%

Refinement

Refinement on <i>F</i> ²	All H-atom parameters refined
<i>R</i> = 0.066	$w = 1/[\sigma^2(F_o) + 0.00018 F_o ^2]$
<i>wR</i> = 0.050	(Δ/σ) _{max} = 0.037
<i>S</i> = 1.962	$\Delta\rho_{\max}$ = 0.18 e Å ⁻³
3675 reflections	$\Delta\rho_{\min}$ = -0.20 e Å ⁻³
203 parameters	

H atoms were located in difference Fourier syntheses and freely refined, with C–H distances of 0.90 (5)–1.02 (5) Å.

Data collection: CAD-4 Software (Enraf-Nonius, 1989); cell refinement: CAD-4 Software; data reduction: TEXSAN (Molecular Structure Corporation, 1992–1997); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: TEXSAN.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1114). Services for accessing these data are described at the back of the journal.

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