Synthesis of diisopropylcyclopropenone and X-ray structure of its dichlorodimethyltin(IV) adduct

Owen J. Curnow,* Glen M. Fern, and Robert J. Pipal

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch
New Zealand
E-mail: owen.curnow@canterbury.ac.nz

Dedicated to Professor James M. Coxon on his 65th birthday

Abstract
Diisopropylcyclopropenone was prepared by a dehydrobromination of 3,5-dibromo-2,6-dimethylheptan-4-one and isolated in 18% yield via an aqueous extraction procedure. It was characterised by an X-ray crystal structure analysis of its complex with dichlorodimethyltin(IV): Dichlorodimethyl(diisopropylcyclopropenone)tin(IV) was found to have a chloro-bridged dimeric structure in the solid state.

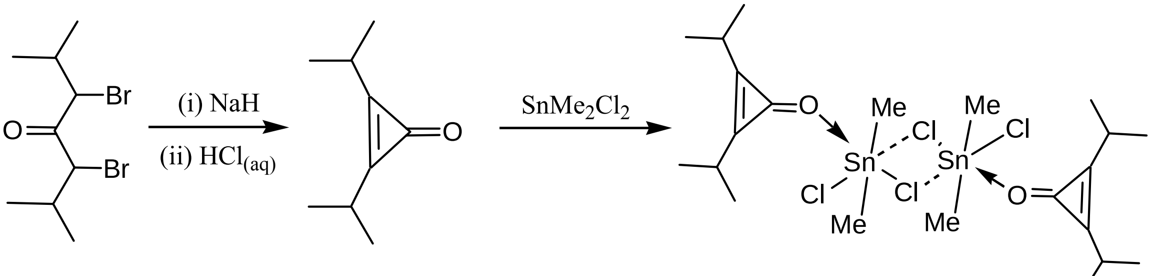
Keywords: Crystal structure, cyclopropenone, tin complex

Introduction

Dialkylcyclopropenones have been studied extensively and are used in the preparation of compounds such as phosphatriafulvenes, vinylcyclopropenes, and cyclopropenium salts.[1] The most versatile route to cyclopropenones involves the dehydrobromination of α,α'-dihaloketones by a modified Favorskii reaction.[2] We had noted that the precursor to prepare the α,α'-dihaloketone for conversion to diisopropylcyclopropenone (**1**), 2,6-dimethyl-4-heptanone, is significantly cheaper than the precursor for the ditertbutyl analogue, 2,2,6,6-tetramethyl-4-heptanone, and since we would expect the diisopropyl analogue **1** to be particularly useful due to the additional stereochemical information that isopropyl groups can provide, we were surprised that the only reference to **1** occurs in a 1969 paper by Ciabattoni and Nathan.[3] This paper states only that it can be prepared by a modified Favorskii reaction of di(bromo-iso-butyl)ketone in a 20% yield and has a boiling point of 70–72 °C at 0.3 mmHg. In this paper we report the preparation, isolation and characterisation of diisopropylcyclopropenone and the structure of its dichlorodimethyltin(IV) complex.

Results and Discussion

Dehydrobromination of 3,5-dibromo-2,6-dimethylheptan-4-one was carried out using sodium hydride in tetrahydrofuran followed by addition of aqueous hydrochloric acid. Typical procedures for the isolation of cyclopropenones involve an extraction of the organics using diethyl ether or petroleum ether. We found that this procedure, however, gave none of the desired product. Collection of the aqueous layer followed by extraction with a more polar organic solvent, such as dichloromethane, did, however, give us our desired cyclopropenone. Apparently, **1** is more soluble in water than in diethyl ether or petroleum ether.



1

2

Scheme 1

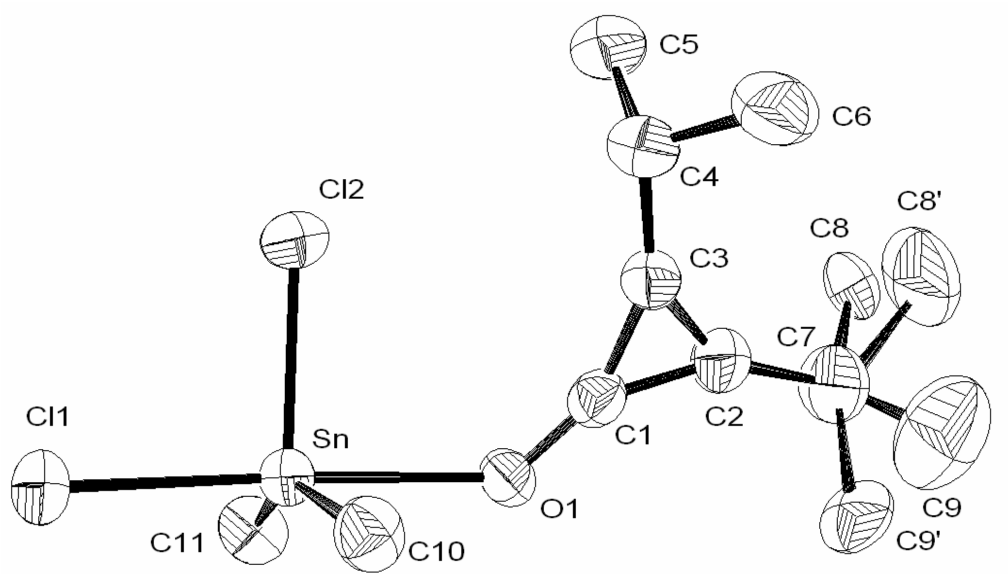


Figure 1. ORTEP of the asymmetric unit of compound **2** (30% probability ellipsoids). Selected bond distances (Å) and angles (°): C(1)–O(1) 1.229(6), C(1)–C(2) 1.379(7), C(2)–C(3) 1.334(8), C(1)–C(3) 1.388(8), C(3)–C(4) 1.491(8), C(2)–C(7) 1.499(6), Sn–O(1) 2.366(4), Sn–Cl(1) 2.4822(16), Sn–Cl(2) 2.3765(14), Sn–C(10) 2.092(6), Sn–C(11) 2.091(5), Sn–Cl(1') 3.5040(16), Sn–O(1)–C(1) 130.5(3), Cl(1)–Sn–Cl(1') 81.82(5), Sn–Cl(1)–Sn' 98.18(5).

^{1}H- and ^{13}C-NMR spectra are consistent with the expected cyclopropenone **1**. There are two diagnostic bands in an infrared spectrum of a cyclopropenone that occur in the ranges of 1890-1800 cm^{-1} and 1660-1600 cm^{-1}.[4] These are due to coupled vibrations of the C=O and C=C double bonds. For **1**, these were observed at 1838 cm^{-1} and 1624 cm^{-1}.

The oily nature of our material hindered us from obtaining a good microanalytical result, so we sought to further confirm the identity of **1** by the synthesis of a coordination compound. Mixing chloroform solutions of **1** and dichlorodimethyltin(IV) produced, upon evaporation of the solvent, large colourless crystals of $Me_2SnCl_2.O{=}CC_2(i\text{-}Pr)_2$ (**2**). The expected 1:1 nature of the complex was confirmed by a single-crystal X-ray diffraction study. As shown in Figure 1, the tin complex exists in the solid state as a weak dimer, with long intermolecular chloro-bridging ligands. The centre of the dimer is a planar Sn_2Cl_2 ring with two long Sn-Cl bonds (ca. 3.50 Å), and two short Sn-Cl bonds (ca. 2.48 Å). A centre of inversion through the Sn_2Cl_2 ring relates each monomeric unit to the other. This dimerisation allows the tin atoms to adopt a conventional octahedral geometry, with the carbonyl oxygen *trans* to the short Sn-Cl bond of the one of the bridging chloro ligands. This structure is similar to that found for the diphenylcyclopropenone analogue.[5]

We have reported the successful preparation and isolation of diisopropylcyclopropenone via an unexpected aqueous-extraction method which will facilitate its use in further chemistry.

Experimental Section

General Procedures. All manipulations and reactions were carried out under an inert atmosphere by use of standard Schlenk line techniques. Reagent grade tetrahydrofuran was distilled prior to use from Na/benzophenone; chloroform was saturated with dinitrogen prior to use. 3,5-Dibromo-2,6-dimethylheptan-4-one was prepared by bromination of 2,6-dimethylheptan-4-one.[6] All other reagents were used as supplied by Aldrich Chemical Company. ^{1}H- and ^{13}C{^{1}H}-NMR data were collected on a Varian XL-300 spectrometer operating at 300 and 75 MHz, respectively. Spectra were measured at ambient temperature with residue solvent peaks as internal standard. EI and FAB mass spectra were collected on a Kratos MS80RFA mass spectrometer. IR spectra were obtained on a Shimadzu FTIR-8201PC spectrophotometer. Elemental analyses were done by Campbell Microanalysis Services at Otago University, Dunedin.

Diisopropylcyclopropenone (1). At –80 °C, NaH (4.606 g of 60% suspension in oil, 115.2 mmol) was added to 3,5-dibromo-2,6-dimethylheptan-4-one (17.191 g, 57.3 mmol) in tetrahydrofuran (120 mL) over a period of three hours. The resulting mixture was stirred overnight at ambient temperature. The mixture was then cooled to –80 °C and 10 mL of 10% $HCl_{(aq)}$ was added drop-wise. The solution was allowed to warm to ambient temperature and the precipitated salts were filtered off and washed with tetrahydrofuran (2 x 20 mL). The washings and filtrate were combined, and the tetrahydrofuran was removed in vacuo. The resulting yellow oil was redissolved in petroleum ether and any residual NaBr filtered off. The cyclopropenone was extracted with portions of water (2 x 100 mL) and then extracted from the water with CH_2Cl_2 (2 x 100 mL). The solvent was removed in vacuo to leave a pale yellow oil (1.46 g, 18%). FT-IR: ν_{max}/cm^{-1} (CH_2Cl_2) 1838 (s), 1624 (s). ^{1}H-NMR ($CDCl_3$): δ 2.76 (septet, ^3J = 7 Hz, 2H, C*H*(CH_3)$_2$), 1.09 (d, ^3J = 7 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C-NMR ($CDCl_3$): δ 163.4 (C=C), 159.3 (C=O), 27.1 (*C*HMe$_2$), 20.2 (CH_3). Mass spectrum *m*/*z* (EI) 138 (20, M^+), 95 (100, $[M – {}^iPr]^+$), 67 (95, $C_5H_7^+$), 55 (40, $C_3H_3O^+$).

Dichlorodimethyl(diisopropylcyclopropenone)tin(IV) (2). Diisopropylcyclopropenone (0.574 g, 4.15 mmol) was added drop-wise to a solution of Me_2SnCl_2 (0.455 g, 2.07 mmol) in chloroform (30 mL). The mixture was stirred for 30 minutes, and the chloroform was then slowly evaporated off to give colourless crystals (0.656 g, yield at least 89%). m.p. 42–46 °C. FT-IR: ν_{max}/cm^{-1} (CH_2Cl_2) 1838 (s), 1585 (s). ^{1}H-NMR ($CDCl_3$): δ 3.02 (septet, ^3J = 7 Hz, 2H, C*H*(CH_3)$_2$), 1.29 (d, ^3J = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.1 (s, 6H, Sn-C*H*$_3$). ^{13}C-NMR ($CDCl_3$): δ 163.5 (C=C), 160.3 (C=O), 27.2 (*C*HMe$_2$), 20.2 (CH(*C*H$_3$)$_2$), 8.8 ($SnCH_3$). Mass spectrum *m*/*z* (FAB) 461 (10, $[SnMe_2Cl({}^iPr_2C_2CO)_2]^+$), 323 (46, $[SnMe_2Cl({}^iPr_2C_2CO)]^+$), 277 (96, $[({}^iPr_2C_3O)_2H]^+$), 139 (100, $[{}^iPr_2C_2COH]^+$). Anal. Calcd for $C_{11}H_{20}Cl_2OSn$: C, 36.92; H, 5.63. Found C, 37.00; H, 5.71.

Crystallography. X-ray crystallographic data for **2** was collected from a single crystal sample (0.7 x 0.7 x 0.35 mm), which was mounted on a glass fibre. Data was collected using a Bruker SMART 1K CCD area detector diffractometer (using the program SMART[7]) and graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Processing was carried out by use of the program SAINT[7] which applied Lorentz and polarisation corrections to three-dimensionally integrated diffraction spots. The program SADABS[8] was utilised for the scaling of diffraction data, the application of a decay correction, and empirical absorption correction based on redundant reflections. The structure for **2** was solved by the direct methods procedure in the SHELXTL program library.[9] The structures were refined by least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as riding contributors at calculated positions, with isotropic thermal parameters based on the attached carbon atom. One isopropyl group is disordered and was modelled as two isopropyls with different site occupancies and with C7 and C7’ constrained to have the same position and thermal parameters.

Crystal data for compound 2. $C_{11}H_{20}Cl_2OSn$, M = 357.86, orthorhombic, a = 12.8756(14), b = 10.5637(11), c = 23.081(2) Å, V = 3139.3(6) Å^3, D_c = 1.514 g cm^{-3}, μ = 1.946 mm^{-1}, $F(000)$ = 1424, T = 293(2) K, space group *P*bca, Z = 8, 10115 reflections measured (θ = 2.37 to 26.38°), 2976 unique (R_{int} = 0.0273), R_1 = 0.0362 ($I > 2\sigma(I)$), wR_2 = 0.11045 (all data), largest difference peak and hole 0.558 and –0.494 e.Å^{-3}. Full crystallographic details were deposited at the Cambridge Crystallographic Data Centre with number CCDC 253372.

References

1. Komatsu, K.; Kitagawa, T. *Chem. Rev.* **2003**, *103*, 1371.
2. Breslow, R.; Posner, J.; Krebs, A. *J. Am. Chem. Soc.* **1963**, *85,* 234.
3. Ciabattoni, J.; Nathan, E.C. *Tetrahedron Lett.* **1969**, *57*, 4997.
4. (a) Briggs, E.M.; Bird C.W.; Harmer, A.F. *Spectrochim. Acta, Part A* **1969**, *25*, 1319; (b) Krebs, A.; Schrader, B. *Liebigs Ann. Chem.* **1967**, *709*, 46; (c) Brown, F.R.; Finseth, D.H.; Miller F.A.; Rhee, K.H. *J. Am. Chem. Soc.* **1975**, *97,* 1011; (d) Krebs, A.; Schrader B.; Höfler, F. *Tetrahedron Lett.* **1968**, 5935.
5. Ng, S.W.; Barnes, C.L.; Hossain, M.B.; Van der Helm, D.; Zuckerman J.J.; Kumar Das, V.G. *J. Am. Chem. Soc.* **1982**, *104,* 5359.
6. Lion, C.; Dubois, J.-E. *Tetrahedron* **1975**, *31*, 1223.
7. *SMART* and *SAINT*. Siemens Analytical, Madison, WI, 1997.
8. *SADABS* version 2.03, G.M. Sheldrick, University of Göttingen, Germany, 2002.
9. *SHELXTL* version 5.1., G.M. Sheldrick, Bruker AXS, Madison, WI, 1998.