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## Crystal and Molecular Structure of a Covalent Perchloric Acid Ester: *p*-Tolylsulfonylmethyl Perchlorate

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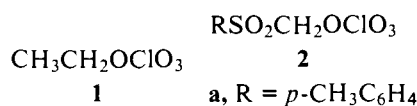
Contribution from the Department of Organic Chemistry and Department of Structural Chemistry, The University, Zernikelaan, Groningen, The Netherlands. Received June 9, 1977

**Abstract:** The crystal and molecular structure of *p*-tolylsulfonylmethyl perchlorate (**2a**) has been analyzed by x-ray diffraction methods. The crystals are monoclinic, the space group is  $P2_1/c$ ;  $a = 11.796$  (3),  $b = 5.242$  (2),  $c = 20.320$  (5) Å,  $\beta = 114.28$  (2)°. The structure has been refined to an  $R$  factor of 0.072 on 1723 reflections with  $|F_o| > 3\sigma_c(F_o)$ . The bond lengths and angles around the central methylene carbon (C(8)) unequivocally demonstrate the covalent bonding between C(8) and O(3) of the perchlorate group. Important molecular parameters are as follows: C(8)–S(1) = 1.805 (4), C(8)–O(3) = 1.423 (5), Cl(1)–O(3) = 1.641 (4), Cl(1)–O(4) = 1.397 (5), Cl(1)–O(5) = 1.379 (5), and Cl(1)–O(6) = 1.407 (6) Å. The reduced  $\pi$  character of the Cl(1)–O(3) bond is reflected in the marked increase in bond length relative to the other Cl(1)–O bonds. Short intermolecular C–H...O distances (H(82)...O(2) = 2.184 (3) Å) indicate strong intermolecular hydrogen bonding between the methylene protons and a sulfonyl oxygen atom of an adjacent molecule.

Ever since the preparation of ethyl perchlorate (**1**) by Hare and Boye<sup>1</sup> in 1841, it has been recognized that most neat perchlorate esters, in which the  $ClO_4$  function is covalently bound to carbon, are extremely hazardous compounds, being sensitive to heat, shock, and friction.<sup>2</sup> Their strong explosive violence has not encouraged structural<sup>3</sup> and chemical investigation<sup>4,5</sup> despite the obvious theoretical interest<sup>6</sup> and easy synthetic accessibility<sup>7</sup> of these types of compounds.

Recently, crystalline and relatively stable alkyl- and aryl-

sulfonylmethyl perchlorates (**2**) were prepared from the reaction of  $\alpha$ -diazosulfones with perchloric acid.<sup>8</sup>



Employing appropriate safety precautions, handling of small (ca. 0.1 g) quantities of these compounds involves little hazard

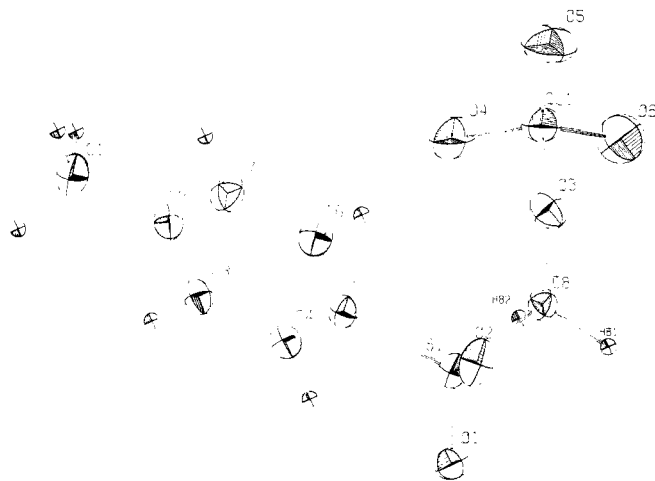


Figure 1. A view of the molecule **2a** showing 50% probability ellipsoids and the atomic numbering scheme.

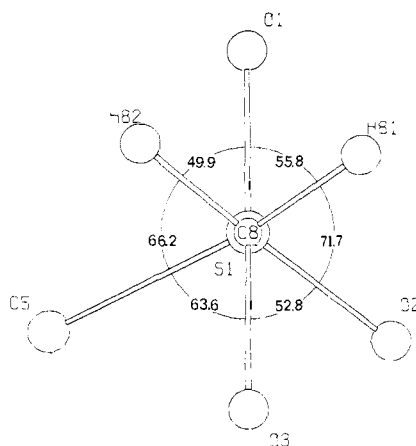
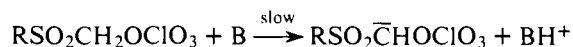


Figure 2. Newman projection along the C(8)-S(1) bond with torsion angles, showing the gauche conformation of the aryl and perchlorate functions.

and even correct combustion analyses could be obtained.<sup>8</sup> The nonionic nature of the esters **2** was mainly deduced from spectral properties and from the substantial solubility in nonpolar solvents. Interestingly, nucleophilic displacement of the perchlorate group in **2** has not been accomplished despite the excellent properties of the perchlorate anion as a leaving group. Even in the presence of weakly basic nucleophiles, the compounds preferentially undergo general-base-catalyzed solvolysis<sup>8b,9</sup> which demonstrates the high kinetic acidity of the central methylene protons.



B = Brønsted base

Herein we report the first single-crystal x-ray diffraction study of a covalent perchlorate ester (**2a**, R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sup>8,10</sup> which offers definite proof that the perchlorate moiety is covalently linked to the rest of the molecule.

### Experimental Section

Crystal data: C<sub>8</sub>H<sub>9</sub>SClO<sub>6</sub>; mol wt 268.5; monoclinic; space group P2<sub>1</sub>/c; *a* = 11.796 (3), *b* = 5.242 (2), *c* = 20.320 (5) Å; β = 114.28 (2)°; Z = 4; V = 1145.35 Å<sup>3</sup>; *d* = 1.52 (*d*<sub>c</sub> = 1.56) g cm<sup>-3</sup>, λ(Mo Kα)

Table I. Final Coordinates for **2a**. Hydrogen Atoms Are Numbered According to the Carbon Atoms to Which They Are Linked

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.3167 (6)	0.0848 (14)	0.2270 (3)
C(2)	0.2566 (5)	0.1433 (10)	0.2777 (2)
C(3)	0.1596 (4)	-0.0064 (10)	0.2776 (2)
C(4)	0.1021 (4)	0.0445 (10)	0.3233 (2)
C(5)	0.1415 (4)	0.2518 (9)	0.3694 (2)
C(6)	0.2377 (5)	0.4055 (10)	0.3707 (3)
C(7)	0.2940 (5)	0.3473 (11)	0.3244 (3)
C(8)	0.1523 (4)	0.1597 (9)	0.5100 (2)
S(1)	0.0663 (1)	0.3231 (2)	0.4259 (1)
Cl(1)	0.3855 (1)	0.0483 (3)	0.5658 (1)
O(1)	-0.0543 (2)	0.2073 (7)	0.3982 (2)
O(2)	0.0771 (4)	0.5915 (6)	0.4411 (2)
O(3)	0.2746 (3)	0.2632 (7)	0.5414 (2)
O(4)	0.3681 (4)	-0.0804 (10)	0.5021 (2)
O(5)	0.4898 (4)	0.2010 (11)	0.5932 (3)
O(6)	0.3676 (4)	-0.1025 (10)	0.6180 (2)
H(11)	0.3746	0.2463	0.2278
H(12)	0.3735	-0.0847	0.2446
H(13)	0.2463	0.0561	0.1726
H(31)	0.1279	-0.1646	0.2401
H(41)	0.0276	-0.0751	0.3239
H(61)	0.2667	0.5660	0.4070
H(71)	0.3691	0.4651	0.3249
H(81)	0.0984	0.1808	0.5418
H(82)	0.1341	-0.0367	0.4927

Table II. Bond Lengths (Å) and Interbond Angles (deg) with Standard Deviations in Units of the Last Digit in Parentheses

A. Bond Lengths	
C(1)-C(2)	1.503 (10)
C(2)-C(3)	1.386 (8)
C(3)-C(4)	1.383 (8)
C(4)-C(5)	1.384 (6)
C(5)-C(6)	1.382 (7)
C(6)-C(7)	1.390 (9)
C(7)-C(2)	1.377 (7)
C(5)-S(1)	1.757 (6)
S(1)-O(1)	1.432 (3)
S(1)-O(2)	1.435 (4)
S(1)-C(8)	1.805 (4)
C(8)-O(3)	1.423 (5)
O(3)-Cl(1)	1.641 (4)
Cl(1)-O(4)	1.397 (5)
Cl(1)-O(5)	1.379 (5)
Cl(1)-O(6)	1.407 (6)
B. Interbond Angles	
C(1)-C(2)-C(3)	120.3 (5)
C(2)-C(3)-C(4)	121.5 (5)
C(3)-C(4)-C(5)	119.0 (5)
C(4)-C(5)-C(6)	121.0 (5)
C(5)-C(6)-C(7)	118.4 (5)
C(6)-C(7)-C(2)	122.0 (5)
C(1)-C(2)-C(7)	121.6 (5)
C(4)-C(5)-S(1)	119.3 (4)
C(6)-C(5)-S(1)	119.6 (4)
C(5)-S(1)-O(1)	109.8 (2)
C(5)-S(1)-O(2)	109.0 (3)
C(5)-S(1)-C(8)	106.2 (2)
O(1)-S(1)-O(2)	119.1 (2)
C(8)-S(1)-O(1)	104.6 (2)
C(8)-S(1)-O(2)	107.2 (2)
S(1)-C(8)-O(3)	108.4 (3)
C(8)-O(3)-Cl(1)	114.1 (3)
O(3)-Cl(1)-O(4)	104.9 (2)
O(3)-Cl(1)-O(5)	101.0 (3)
O(3)-Cl(1)-O(6)	105.4 (3)
O(4)-Cl(1)-O(5)	114.9 (3)
O(4)-Cl(1)-O(6)	114.6 (3)
O(5)-Cl(1)-O(6)	114.0 (3)
C(3)-C(2)-C(7)	118.1 (6)

= 0.71069 Å (Zr-filtered Mo radiation), μ(Mo) = 5.57 cm<sup>-1</sup>. The cell dimensions were obtained from the θ values measured on a zero layer line Weissenberg photograph around the *b* axis (calibrated with NaCl reflections, Ni-filtered Cu radiation) and from the θ values of 15 reflections measured on a Nonius CAD 3 diffractometer (Zr-filtered Mo radiation). Positive intensities were measured at room temperature with Zr-filtered Mo radiation for 2165 independent reflections on the automatic diffractometer. The dimensions of the crystal used were 0.3 × 0.3 × 0.5 mm. Corrections for Lorentz and polarization effects and for absorption were applied. The structure was found by direct methods. In the refinement 1723 reflections with |*F*<sub>o</sub>| > 3σ<sub>c</sub>(*F*<sub>o</sub>) were used, where σ<sub>c</sub>(*F*<sub>o</sub>) is the standard deviation in |*F*<sub>o</sub>| due to counting statistics. The minimized function is represented by Σ<sub>*h*</sub> *W*(*H*)[*F*<sub>o</sub>(*H*) - *kF*<sub>c</sub>(*H*)]<sup>2</sup> with *W*(*H*) = [σ<sup>2</sup>(*F*<sub>o</sub>) + 0.0006|*F*<sub>o</sub>|<sup>2</sup>]<sup>-1</sup>. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Mann,<sup>11</sup> and those for hydrogen from

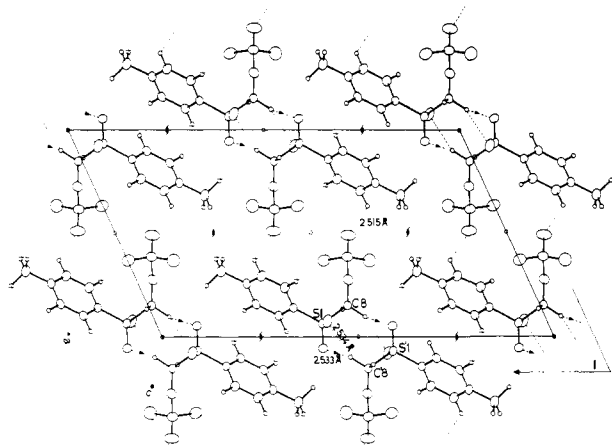


Figure 3. Projection of the structure of **2a** along the *b* axis.

Stewart et al.<sup>12</sup> Anisotropic temperature factors were employed for the nonhydrogen atoms and isotropic ones for the hydrogens. The hydrogen atoms were positioned at geometrically reasonable positions with C–H = 1.08 Å. The value of *R* decreased to 7.2%. The final coordinates are given in Table I.

### Results and Discussion

The actual molecular structure of **2a** is depicted in Figure 1. The bond distances and bond angles are listed in Table II. The bond lengths and angles in the *p*-tolylsulfonyl part are as observed in other *p*-tosyl compounds.<sup>13</sup> We note that the bond lengths and angles around C(8) clearly imply covalent bonding between C(8) and O(3). The lengths of the bonds C(8)–S(1) = 1.805 (4) Å and C(8)–O(3) = 1.423 (5) Å do not show significant deviations from the lengths of the corresponding covalent bonds in, for instance, dimethyl disulfide (C–S = 1.806 (2) Å)<sup>14</sup> and 1,4-dioxane (C–O = 1.423 (3) Å).<sup>15</sup> The angle S(1)–C(8)–O(3) = 108.4 (3)° lies close to the tetrahedral value, whereas Cl(1)–O(3)–C(8) = 114.1 (3)° is somewhat larger as has also been observed for the angle at oxygen in 1,4-dioxane (C–O–C = 112.5 (5)°).<sup>15</sup> In the perchlorate moiety Cl(1)–O(3) = 1.641 (4) Å, which is almost identical with the sum of the tetrahedral covalent single bond radii (1.658 Å)<sup>16</sup> and closely similar to the Cl–O–(H) bond length (1.630 Å) in HClO<sub>4</sub> as deduced from gas-phase electron diffraction studies.<sup>17</sup> The other three Cl(1)–O bonds of **2a** are much shorter (1.397 (5), 1.379 (5), and 1.407 (6) Å, respectively) which can be ascribed to their relatively strong  $\pi$  character. Previously, strongly varying  $\pi$  character for Cl–O bonds has been invoked to explain the large difference in Cl–O bond length between ClO<sub>4</sub><sup>–</sup> (1.42–1.46 Å)<sup>18</sup> and Cl<sub>2</sub>O (1.70 Å)<sup>19</sup> or Cl<sub>2</sub>O<sub>7</sub> (1.71 Å, central bond).<sup>20</sup> Figure 2 displays a Newman projection along the C(8)–S(1) bond of **2a** and indicates the antiperiplanar position of the perchlorate function with respect to one oxygen atom of the sulfonyl group. This preference for the gauche–syn conformation rather than the more symmetrical trans–anti form has often been found for related systems in solution<sup>21</sup> and has recently been interpreted in terms of core symmetry by means of a Jahn–Teller second-order effect.<sup>22</sup>

The packing of the molecules is shown in Figures 3 and 4. It will be noted that molecules related by the inversion centers along the *a* direction or by translation along the *b* direction are connected by C–H...O interactions. In this way layers parallel to (001) are formed. From the short distance H(82)...O(2) = 2.184 (3) Å, which is 0.32 Å smaller than the sum of the van der Waals radii,<sup>23</sup> we infer that a surprisingly strong hydrogen bond is present between the methylene protons of **2a** and the sulfonyl oxygen acceptor group of an adjacent molecule in the

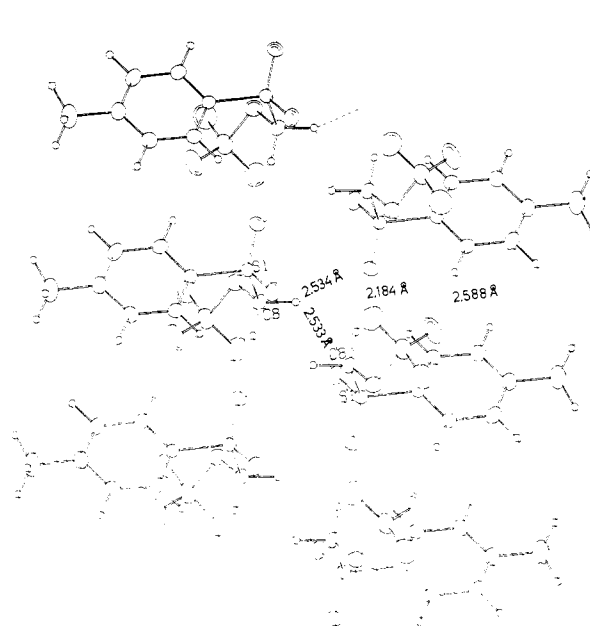


Figure 4. Arrangement of the molecules around the line  $[0\frac{1}{2}]$ .  $\odot$  = oxygens of SO<sub>2</sub> group,  $\ominus$  = oxygen of perchlorate group.

crystal. This extreme degree of C–H hydrogen bonding<sup>24</sup> to acceptor sites as weakly basic as the sulfonyl moiety is consistent with the easy deprotonation of **2a** in solution<sup>9</sup> and is indicative for the strong electron-withdrawing character of a perchlorate group covalently bound to sp<sup>3</sup> carbon.<sup>25</sup>

**Supplementary Material Available:** Listings of observed and calculated structure factors and lists of thermal parameters (18 pages). Ordering information is given on any current masthead page.

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## Reactions of Metal-to-Metal Multiple Bonds. 1. $\mu$ -Allene-bis(cyclopentadienyl)tetracarbonyldimolybdenum and -ditungsten Compounds. Preparation, Properties, and Structural Characterization

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**Abstract:** The reaction of  $\text{Cp}_2\text{M}_2(\text{CO})_4$  compounds ( $\text{M} = \text{Mo}$  and  $\text{W}$ ), which contain  $\text{M}-\text{M}$  triple bonds, with allenes leads to the 1:1 adducts  $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{C}_3\text{H}_4)$ , where  $\text{M} = \text{Mo}$  and  $\text{W}$ , and  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{allene}')$  where  $\text{allene}' = \text{MeCH}=\text{C}=\text{CH}_2$  and  $\text{MeCH}=\text{C}=\text{CHMe}$ . These new compounds have been characterized by infrared spectroscopy, mass spectroscopy, NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{13}\text{C}[\text{H}]$ ), and in the case of  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_3\text{H}_4)$  by single-crystal x-ray crystallography. The compound crystallizes in the nonstandard space group  $Pn$  with  $a = 10.932$  (2) Å,  $b = 7.776$  (2) Å,  $c = 10.015$  (1) Å,  $\beta = 107.82$  (2)°, and  $V = 810.5$  (5) Å<sup>3</sup>. Full-matrix least-squares refinement gave final discrepancy factors  $R_1 = 0.030$  and  $R_2 = 0.046$ . For  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_3\text{H}_4)$  the  $\text{Mo}-\text{Mo}$  distance is 3.117 (1) Å and the molecule has virtual  $C_s$  symmetry with the rotational axis passing through the central allenic carbon atom and the center of the  $\text{Mo}-\text{Mo}$  bond. The allene is V-shaped ( $\text{C}-\text{C}-\text{C} = 146^\circ$ ) and may be considered to form one olefin-metal bond to each molybdenum atom. NMR data indicate that in solution the compounds  $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{allene})$  adopt a structure akin to that found in the solid state for  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_3\text{H}_4)$ ; enantiomerization and CO site exchange are slow on the NMR time scale up to 100 °C.

### Introduction

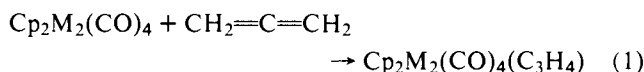
There is currently a certain optimism that transition metal cluster chemistry could lead to a new era in homogeneous hydrocarbon catalysis.<sup>2</sup> The reactivity of metal-to-metal bonds and the synthesis of new cluster compounds are clearly two topics requiring study if such aspirations are to be realized. Bimetallic compounds containing metal-to-metal multiple bonds<sup>3</sup> will surely occupy a unique position in this field of chemistry. They are the smallest examples of unsaturated metal cluster compounds and provide building blocks for the systematic synthesis of polynuclear compounds. Furthermore, the organometallic reaction schemes<sup>4</sup> of mononuclear complexes may be extended to dinuclear systems.

We have previously shown that an extensive coordination chemistry surrounds metal-to-metal triple bonds in the chemistry of molybdenum<sup>5-10</sup> and tungsten.<sup>11-20</sup> Others have shown<sup>21</sup> that acetylenes, but *not* olefins,<sup>22</sup> add across metal-to-metal triple bonds, although the same products can be obtained directly by reaction of the acetylenes with  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  without isolating the presumed  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  intermediate.<sup>23</sup> In this paper we describe the addition of allenes to the  $\text{M}-\text{M}$  triple bonds in  $\text{Cp}_2\text{M}_2(\text{CO})_4$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) and the properties of the products, including a full structural characterization of the prototypal compound,  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_3\text{H}_4)$ . A preliminary report of some of this work has appeared.<sup>24</sup>

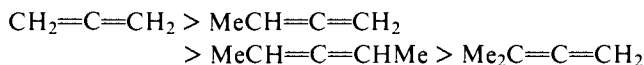
### Results and Discussion

**Syntheses.** Addition of allene (1 equiv) to hydrocarbon solutions of  $\text{Cp}_2\text{M}_2(\text{CO})_4$ , where  $\text{M} = \text{Mo}$  or  $\text{W}$ , leads to deep

red solutions and to the formation of microcrystalline, orange- or tan-colored precipitates, the latter being formed in ca. 10% yield based on molybdenum or tungsten. Deep red crystals of the compound  $\text{Cp}_2\text{M}_2(\text{CO})_4(\text{C}_3\text{H}_4)$  were the only products isolated from solution. NMR tube experiments showed that reaction 1 is both rapid and irreversible.



The preparation of two substituted allenic derivatives  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{allene}')$ , where  $\text{allene}' = 1$ -methylallene (1,2-butadiene) or 1,3-dimethylallene (2,3-pentadiene), has also been achieved but more forcing conditions were required, namely, sealed tube techniques and elevated temperatures, 60–80 °C. No reaction between 1,1-dimethylallene and  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  has been observed under analogous conditions. Thus, for the addition of allenes to the metal-to-metal triple bond in  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  we observe the reactivity order



This suggests that steric factors are important, although whether this is primarily a kinetic or thermodynamic effect is uncertain.

We have found that when allene is added to a hydrocarbon solution containing both  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  and  $\text{Cp}_2\text{W}_2(\text{CO})_4$  the red, crystalline product showed only homodinuclear ions in the mass spectrometer. The absence of heterodinuclear ions ( $\text{Mo}-\text{W}$  containing) leads us to believe that the formation of