

Synthesis and X-Ray Crystal Structure of the First Pure and Air-Stable Salt of Peroxymonosulphuric Acid: $(\text{Ph})_4\text{PHSO}_5$

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Abstract: In this paper we describe the synthesis of tetraphenylphosphonium peroxy-monosulphate, its crystal structure and packing mode. The asymmetric unit accomodates two independent molecules of the monopersulphate anion, which are held together by hydrogen bonds. In the packing mode, rows of such dimers are surrounded by four rows of tetraphenyl cations. The consequence is that the highly water sensitive HSO_5^- anions are segregated inside hydrophobic channels composed by the lipophilic cations. This circumstance presumably accounts for the exceptional stability of the title compound.

Keywords: Monopersulphate, X-Ray Crystallography, Oxidation.

Introduction

Peroxymonosulphuric acid (**1**) (Caro's acid) [1] is a powerful oxidant ($E^\circ +1.82$ V) [2] and it has been used in the preparation of a large variety of compounds. As an example, the syntheses of esters from ketones, glycols from olefins, iodoxybenzene from iodobenzene, and nitrosylcyclohexane from cyclohexylamine have been accomplished [3].



1



2



3



4

Utilization of Caro's acid is hampered by its great instability. In fact, pure Caro's acid is a highly hygroscopic and explosive solid [4]. Owing to these features, X-ray data for the pure Caro's acid have been obtained only quite recently at -130°C [5]. Furthermore, even pure and air stable salts of Caro's acid have never been reported up to now. While the mechanism of Caro's acid decomposition in aqueous solutions has been established [6], no data are available on the decomposition mechanism in the solid state. On the other hand, it may be envisaged that crystals hydration plays a role, thus triggering the decomposition within a highly concentrated solution of (1). The first stable derivative of Caro's acid prepared was the water soluble mixed salt (2), which is commercially available under the names of Oxone[®], Carcoat[®] or Curox[®]. The X-ray structure of KHSO_5 in (2) [7] and then in $(\text{KHSO}_5)(\text{H}_2\text{O})$ [8] confirmed the existence of a short and non symmetrical O-O bond (1.460 \AA compared to 1.453 in H_2O_2 and 1.497 in $\text{S}_2\text{O}_8^{2-}$) with a hydrogen atom on one side and SO_3^- group on the other side. The triple salt (2), likewise (1), is a powerful oxidant with a wide range of applications. As an example, triple salt (2) is used for both the oxidation of water-soluble substrates [9] and for oxidations catalyzed by metal porphyrins in two-phase systems [10]. Moreover, olefin epoxidations and alkane hydroxylations by (2) via the formation of a intermediate dioxirane have been accomplished [11]. In order to extend the use of monopersulphate to organic solvents, the lipophilic salt (3) has been prepared by extracting aqueous solutions of (2) with organic solutions of tetrabutylammonium inorganic salts [12]. However, compound (3) is never obtained with purity higher than 70-80% and its gum-like consistence prevents its further purification from sulphate and bisulphate salts, which always accompany organic extracts of (2). The presence of these contaminants greatly affects the monopersulphate anion reactivity. In fact, the high acidity of $(\text{Bu})_4\text{NHSO}_4$ inhibits the olefins epoxidation by (3) catalysed by metalloporphyrins [13]. In this paper we present the synthesis and the X-Ray structure of a stable lipophilic salt of Caro's acid, *i.e.* tetraphenylphosphonium monopersulphate (4), which can be obtained in pure form. Compound (4) is insoluble in water whereas it is fairly soluble in chlorinated organic solvents. Moreover, it is absolutely air stable. Owing to its stability and fair solubility in organic solvents, (4) is particularly suitable as oxygen donor for the mechanistic study of oxidative processes, for instance those involving metal complexes as catalysts. As an additional advantage, (4) can be obtained in crystalline form, allowing its purification simply by crystallization from a suitable solvent. The structure of compound (4) and its packing arrangement provide useful hints to rationalise its exceptional stability in the solid state.

Results and Discussion

Crystal Data and Structure

Single crystals of (4) were grown from 1,2-dichloroethane by diethyl ether vapor diffusion, at room temperature. The crystals are stable without mother liquor, even when exposed to the air for several weeks. Crystals are triclinic, space group P-1, with $a = 13.976(2)$, $b = 14.672(3)$, $c = 11.388(2) \text{ \AA}$, $\alpha = 91.1(1)$, $\beta = 109.6(1)$, $\gamma = 81.5(1)^{\circ}$; $V = 2174.5(7) \text{ \AA}^3$, $M = 452.4 (\text{HSO}_5 \times \text{PC}_{24}\text{H}_{20})$; $Z = 4$; $D_{\text{calc}} =$

1.382 Mg/m³. A total of 6451 independent reflections were collected on a Philips PW 1100 diffractometer, using graphite-monochromated CuK α radiation ($\lambda = 1.54184 \text{ \AA}$) in the θ -2 θ scan mode up to $\theta=60^\circ$ with variable scan speed ranging from 1.5 to 0.375 deg/min. Index ranges: $-15 \leq h \leq 14$, from $-16 \leq k \leq 16$, $0 \leq l \leq 12$. An absorption correction based on psi-scan was applied to the data (max. and min. transmission factors 1.000 and 0.626, respectively, for a crystal of approximate dimension 0.20 x 0.20 x 0.10 mm and $\mu = 2.307 \text{ mm}^{-1}$).

The structure was solved by direct methods of SHELXS 86 program [14] and refined by full-matrix least-squares on F^2 , using all data, with the SHELXL 93 program [15]. The non-H atoms were anisotropically refined. A planarity restraint was applied to all phenyl rings. H-atoms were calculated at idealized position, and during the refinement they were allowed to ride on their carrying atom. The analysis of possible intermolecular H-bonds in the structure indicated that, in principle, the H-atom of each monopersulphate molecule could be covalently bonded either to one of the terminal oxygen atoms or to the peroxy moiety. The latter assignment was assumed to be the correct one, on the basis of the relative acidities of the SOH and SOOH groups ($\text{pK}_a \text{ SOH} < 0$; $\text{pK}_a \text{ SOOH} = 9.4$) [16]. The refinement converged to $R_1 = 0.0677$ [on $F \geq 4(\sigma)F$] and $wR_2 = 0.2045$ (on F^2 , all data). The data / restraints / parameters ratio was 6451 / 24 / 559. Fractional atomic coordinates of the non-H atoms, along with their equivalent isotropic displacement parameters, are listed in Table 1. Bond distances and bond angles of (4) are reported in Tables 2 and 3, respectively.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (4). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
S1	5778(2)	5092(2)	2327(2)	97(1)	S2	-193(2)	259(1)	7759(2)	81(1)
O1	6179(4)	4688(4)	1408(5)	107(2)	O6	-827(3)	531(3)	8504(5)	95(2)
O2	6181(5)	5936(4)	2808(6)	147(3)	O7	-612(6)	-351(4)	6803(6)	155(3)
O3	5728(6)	4478(5)	3219(7)	185(3)	O8	183(4)	1026(4)	7369(6)	131(2)
O4	4626(4)	5543(4)	1607(6)	123(2)	O9	858(4)	-262(4)	8683(5)	113(2)
O5	4046(4)	4902(4)	943(6)	131(2)	O10	637(5)	-1073(4)	9178(6)	134(2)
P1	5463(1)	891(1)	7658(2)	55(1)	P2	487(1)	5857(1)	7797(2)	56(1)
C1	5761(5)	1437(4)	9144(6)	53(2)	C25	869(5)	6441(4)	9240(6)	55(2)
C2	6675(5)	1160(4)	10077(6)	69(2)	C26	1884(5)	6555(4)	9732(6)	63(2)
C3	6933(6)	1644(5)	11167(7)	80(2)	C27	2251(6)	6982(4)	10853(7)	75(2)
C4	6277(6)	2397(5)	11309(7)	79(2)	C28	1582(7)	7305(5)	11458(7)	83(2)
C5	5356(6)	2674(5)	10391(7)	81(2)	C29	564(6)	7212(4)	10987(7)	80(2)
C6	5078(5)	2189(4)	9288(7)	72(2)	C30	183(5)	6757(4)	9851(7)	72(2)
C7	6143(4)	-258(4)	7813(5)	55(2)	C31	854(4)	6462(4)	6704(6)	59(2)
C8	7212(5)	-407(5)	8097(6)	71(2)	C32	567(5)	7413(5)	6582(6)	68(2)

Continuation of the Table 1.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
C9	7738(5)	-1280(5)	8194(6)	79(2)	C33	782(5)	7901(5)	5703(7)	78(2)
C10	7213(6)	-2030(5)	7989(7)	85(2)	C34	1279(6)	7457(6)	4961(7)	85(2)
C11	6159(5)	-1888(4)	7699(7)	83(2)	C35	1599(6)	6515(6)	5106(7)	88(2)
C12	5628(5)	-1016(4)	7617(6)	69(2)	C36	1395(5)	6014(5)	5991(7)	68(2)
C13	4107(5)	877(4)	7025(6)	53(2)	C37	-866(5)	5835(4)	7203(6)	59(2)
C14	3594(5)	593(4)	7780(6)	68(2)	C38	-1489(5)	6287(4)	6088(6)	69(2)
C15	2558(5)	530(4)	7307(8)	73(2)	C39	-2528(6)	6212(5)	5638(7)	86(2)
C16	2038(5)	744(4)	6075(8)	76(2)	C40	-2958(6)	5714(5)	6287(8)	88(2)
C17	2516(5)	1030(4)	5307(7)	77(2)	C41	-2344(6)	5264(5)	7399(8)	83(2)
C18	3561(5)	1099(4)	5778(6)	64(2)	C42	-1309(5)	5327(4)	7831(6)	73(2)
C19	5800(4)	1552(4)	6602(6)	56(2)	C43	1095(4)	4682(4)	8005(6)	58(2)
C20	6276(5)	1153(5)	5805(7)	74(2)	C44	1885(5)	4368(4)	9078(6)	71(2)
C21	6461(6)	1661(6)	4926(7)	89(2)	C45	2342(5)	3452(5)	9226(7)	86(2)
C22	6167(6)	2610(6)	4844(7)	83(2)	C46	1974(6)	2844(5)	8296(9)	97(3)
C23	5705(5)	3024(5)	5644(7)	76(2)	C47	1187(6)	3156(5)	7241(8)	96(3)
C24	5516(5)	2509(4)	6524(6)	64(2)	C48	745(5)	4050(4)	7092(7)	79(2)

Table 2. Bond lengths [\AA] for (4).

S1-O3	1.396(6)	C13-C14	1.394(8)	C26-C27	1.381(8)
S1-O1	1.426(5)	C13-C18	1.387(8)	C27-C28	1.365(9)
S1-O2	1.458(6)	C14-C15	1.382(8)	C28-C29	1.368(9)
S1-O4	1.588(6)	C15-C16	1.364(9)	C29-C30	1.419(9)
O4-O5	1.378(7)	C16-C17	1.369(9)	C31-C36	1.380(8)
P1-C7	1.790(6)	C17-C18	1.396(8)	C31-C32	1.390(8)
P1-C19	1.779(6)	C19-C20	1.371(8)	C32-C33	1.378(8)
P1-C1	1.803(6)	C19-C24	1.397(8)	C33-C34	1.363(9)
P1-C13	1.790(6)	C20-C21	1.372(9)	C34-C35	1.384(10)
C1-C2	1.370(8)	C21-C22	1.388(9)	C47-C48	1.353(9)
C1-C6	1.395(8)	C22-C23	1.369(9)	C35-C36	1.386(9)
C2-C3	1.383(8)	C23-C24	1.383(8)	C37-C38	1.390(8)
C3-C4	1.372(9)	S2-O7	1.421(6)	C37-C42	1.380(8)
C4-C5	1.369(9)	S2-O6	1.432(5)	C38-C39	1.389(9)
C5-C6	1.397(8)	S2-O8	1.445(5)	C39-C40	1.374(9)
C7-C8	1.402(8)	S2-O9	1.584(6)	C40-C41	1.383(9)
C7-C12	1.387(7)	O9-O10	1.442(7)	C41-C42	1.381(9)
C8-C9	1.367(8)	P2-C25	1.792(6)	C43-C44	1.375(8)
C9-C10	1.385(8)	P2-C31	1.791(6)	C43-C48	1.392(8)
C10-C11	1.381(9)	P2-C43	1.788(6)	C44-C45	1.388(8)
C11-C12	1.369(8)	C25-C26	1.374(8)	C45-C46	1.384(9)
		C25-C30	1.387(8)	C46-C47	1.359(10)

Table 3. Bond angles [deg] for (4).

O3-S1-O1	115.6(4)	C14-C13-P1	119.7(5)	C30-C25-P2	122.1(5)
O3-S1-O2	115.6(5)	C18-C13-P1	121.3(5)	C25-C26-C27	121.0(7)
O1-S1-O2	113.0(4)	C13-C14-C15	121.2(7)	C28-C27-C26	118.7(7)
O3-S1-O4	105.9(4)	C16-C15-C14	118.8(7)	C27-C28-C29	121.8(7)
O1-S1-O4	106.7(3)	C15-C16-C17	121.6(7)	C30-C29-C28	120.0(7)
O2-S1-O4	97.8(4)	C18-C17-C16	120.0(7)	C29-C30-C25	117.6(7)
O5-O4-S1	111.7(5)	C17-C18-C13	119.4(6)	C36-C31-C32	120.2(6)
C7-P1-C19	109.6(3)	C20-C19-C24	118.3(6)	C36-C31-P2	122.2(5)
C7-P1-C1	111.0(3)	C20-C19-P1	122.4(5)	C32-C31-P2	117.5(5)
C19-P1-C1	109.3(3)	C24-C19-P1	119.1(5)	C33-C32-C31	119.5(7)
C7-P1-C13	110.2(3)	C19-C20-C21	122.1(7)	C32-C33-C34	120.4(7)
C19-P1-C13	107.5(3)	C20-C21-C22	119.3(7)	C35-C34-C33	120.4(8)
C1-P1-C13	109.2(3)	C23-C22-C21	119.6(7)	C34-C35-C36	119.9(7)
C2-C1-C6	120.8(6)	C24-C23-C22	120.9(7)	C35-C36-C31	119.4(7)
C2-C1-P1	120.6(5)	C23-C24-C19	119.8(6)	C38-C37-C42	118.3(6)
C6-C1-P1	118.5(5)	O7-S2-O6	113.5(4)	C38-C37-P2	121.8(5)
C3-C2-C1	119.7(6)	O7-S2-O8	115.3(4)	C42-C37-P2	119.8(5)
C2-C3-C4	120.0(7)	O6-S2-O8	112.9(3)	C37-C38-C39	119.5(7)
C3-C4-C5	120.8(7)	O7-S2-O9	108.2(4)	C40-C39-C38	121.3(7)
C4-C5-C6	119.9(7)	O6-S2-O9	106.0(3)	C41-C40-C39	119.6(7)
C5-C6-C1	118.7(7)	O8-S2-O9	99.2(3)	C40-C41-C42	118.8(7)
C8-C7-C12	118.6(6)	O10-O9-S2	107.6(4)	C41-C42-C37	122.4(7)
C8-C7-P1	120.2(5)	C25-P2-C31	107.1(3)	C44-C43-C48	118.1(6)
C12-C7-P1	121.2(5)	C25-P2-C43	110.5(3)	C44-C43-P2	121.6(5)
C9-C8-C7	120.8(6)	C31-P2-C43	110.8(3)	C48-C43-P2	120.2(5)
C8-C9-C10	119.9(7)	C25-P2-C37	112.3(3)	C43-C44-C45	120.8(6)
C11-C10-C9	119.6(7)	C31-P2-C37	109.5(3)	C46-C45-C44	119.4(7)
C10-C11-C12	120.8(6)	C43-P2-C37	106.6(3)	C45-C46-C47	119.7(7)
C11-C12-C7	120.3(6)	C26-C25-C30	120.9(6)	C46-C47-C48	121.1(7)
C14-C13-C18	118.9(6)	C26-C25-P2	117.0(5)	C43-C48-C47	121.0(7)

The asymmetric unit is composed of two independent molecules of monopersulphate (A and B) and two of the tetraphenylphosphonium cation (see Fig. 1).

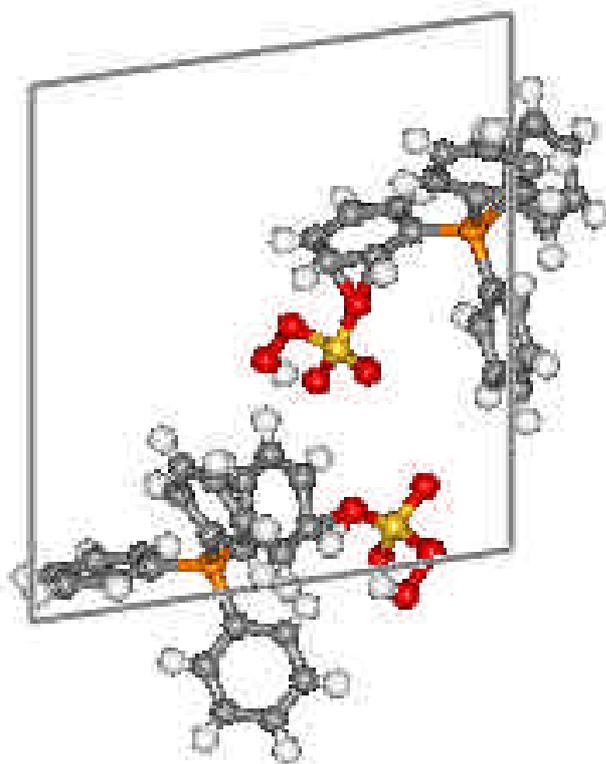


Figure 1. A view of the two independent molecules of (4) in the asymmetric unit.

The three terminal S-O bond distances range from 1.396(6) to 1.458(6) Å at S1 (monopersulphate A), while from 1.421(5) to 1.445(5) Å at S2 (monopersulphate B). The S-O (peroxo) distance is 1.588(6) Å at S1 and 1.584(6) Å at S2. These values are in general agreement with those reported by Flanagan et al. [7] for HSO_5^- in (2). The O-O distances are 1.378(7) and 1.442(7) Å, in the two independent molecules A and B, respectively. In the crystal, each monopersulphate is intermolecularly H-bonded to a centrosymmetric counterpart. More specifically, the O5-H group of monopersulphate molecule A is H-bonded to O1 atom of its (1-x, 1-y, -z) symmetry equivalent, while in the monopersulphate molecule B the O10-H group is H-bonded to the O6 atom of its (-x, -y, 2-z) symmetry equivalent. The geometry of these rather strong H-bonds is defined by the following parameters: distance $\text{O5}\cdots\text{O1}$ 2.659(9) Å, distance $\text{HO5}\cdots\text{O1}$ 2.15 Å, angle $\text{O5-HO5}\cdots\text{O1}$ 120°; distance $\text{O10}\cdots\text{O6}$ 2.679(9) Å, distance $\text{HO10}\cdots\text{O6}$ 2.18 Å, angle $\text{O10-HO10}\cdots\text{O6}$ 119°. Because of the symmetry, such H-bonds give rise to dimers of each monopersulphate. In the packing mode, rows of monopersulphate dimers are formed along the z direction, each row being surrounded by four rows of tetraphenylphosphonium cations (see Fig. 2).

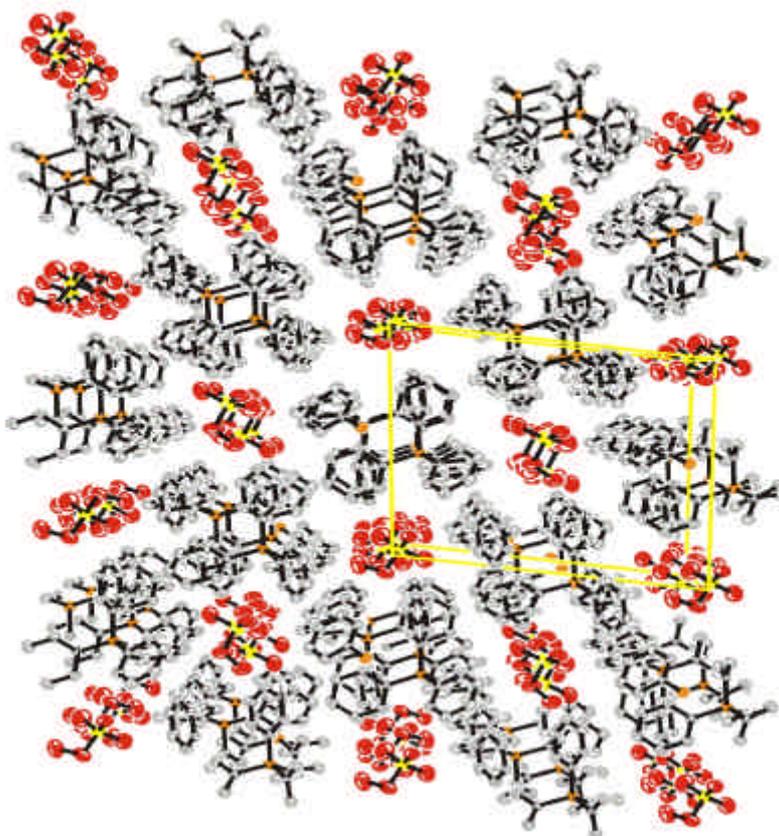


Figure 2. Packing mode in the X-ray structure of (4) as viewed down the *c* axis.

Additional stabilization of the structure may be attributed to some (phenyl)C-H \cdots O(monopersulphate) interactions. By taking the H \cdots O distance ≤ 2.8 Å as the cutoff criterion [17], seven C-H \cdots O contacts have been detected for monopersulphate A and eight for monopersulphate B, with C \cdots O distances ranging from 3.140(9) to 3.656(10) Å, and C-H \cdots O angle $\geq 120^\circ$.

Infrared Absorption

Spectra were recorded averaging 50 scans at 2 cm^{-1} nominal resolution on a Perkin-Elmer 1720X FTIR spectrometer, nitrogen flushed. For the solution spectra, CaF₂ cells with pathlength of 0.1 and 1.0 mm were used. In the solid state (KBr pellet), the O-H stretching falls at 3272 cm^{-1} , consistently with the H-bonding observed in the crystal structure. In 1,2-dichloroethane solution at 50 mM concentration, the O-H group give rise to two bands, at 3457 cm^{-1} (free O-H) and at 3224 cm^{-1} (H-bonded O-H). The intensity of the latter band sharply decreases upon dilution to 10 mM concentration, to eventually vanish at 1.0 mM concentration.

Conclusions

The segregation of the highly water sensitive monopersulphate anions inside the hydrophobic channels generated by tetraphenylphosphonium cation rows nicely accounts for the remarkable stability of (4). However, when (4) is dissolved in 1,2-dichloroethane, free monopersulphate anions are released in solution. In fact, infrared spectra of diluted solution of (4) (up to 1.0 mM) show only the absorption at 3457 cm^{-1} corresponding to free OH. Conversely, infrared spectra in the solid state show the OH stretching at 3272 cm^{-1} consistently with the H-bonding observed in the crystal structure. In conclusion, compound (4) represent a perfectly stable font of pure monopersulphate anions, which may be used for both synthetic and mechanistic purposes.

Experimental

Synthesis and purification of Ph_4PHSO_5

To a solution of Oxone[®] (4.0 gr, 6.5 mmol), in deionized water (40 mL) a solution of tetraphenylphosphonium chloride (2.0 gr, 5.3 mmol), in distilled dichloromethane (40 mL) was added under vigorous stirring for 3 min. The organic phase was then separated and the crude product recovered after evaporation of the solvent. The crude material was washed with cold water (15 mL), dried under vacuum (0.05 mm Hg), and then dissolved in distilled dichloromethane (40 mL). The resulting turbid solution was filtered on paper and the solvent removed by rotavapor. The product was dissolved again in distilled dichloromethane (20 mL) and *n*-pentane was added dropwise until the solution becomes opaque. The solution was then frozen overnight in order to complete precipitation of the product. Crystals were filtered on a n. 3 Gooch filter and dried under vacuum (0.05 mm Hg). Ph_4PHSO_5 (1.3 gr, 54% yield) was thus obtained with a purity better than 97% (determined by iodometric titration). Ph_4PHSO_5 crystals are stable upon warming until 175°C when they become opaque with crackling. With continuous warming, a melting point at $272\text{-}273^\circ\text{C}$ is observed. **CAUTION:** this peroxide should be considered as potentially explosive and despite a number of safe syntheses we never surpassed this preparation scale.

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