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Selective Synthesis and Stabilization of Peroxides via Phosphine Oxides

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X-Ray Crystallography

1. A solution of **1** in dichloromethane was layered with pentane, and then concentrated by slow evaporation. A colorless block with very well-defined faces from a representative sample of crystals of the same habit was collected and data obtained as outlined in Table **S1**. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Mo-Iμs X-ray tube (K_α = 0.71073 Å). 45 data frames were taken at widths of 1.0°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the $h\ k\ l$ overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (4 sets) was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program *APEX3*.[S1] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program *SADABS* [S2] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data were used to determine the space group. A solution was obtained readily using *XT/XS* in *APEX3*.[S1,S3] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Absence of additional symmetry and voids were confirmed using *PLATON (ADDSYM)*.[S4] The structure was refined (weighted least squares refinement on F^2) to convergence.[S3,S5] *Olex2* and *Mercury* were employed for the final data presentation and structure plots.[S5,S6]

2. A solution of **2** in toluene was concentrated by slow evaporation. A colorless block with very well-defined faces from a representative sample of crystals of the same habit was collected and data were obtained, and the structure was solved as in **1**. The X-ray radiation employed was generated from a Cu-Iμs X-ray tube (K_α = 1.5418 Å with a potential of 50 kV and a current of 1.0 mA). After careful examination of the unit cell, an extended data collection procedure (30 sets) was initiated using omega and phi scans. Residual electron density peak near (~1.5 Å) C17 indicated a possibility of disorder of the ethyl (C15-C16) and the methyl (C17) groups which were modeled successfully between two positions with an occupancy ratio of 0.85:0.15. Appropriate restraints and constraints were added to keep the bond distances, angles, and thermal ellipsoids of the disordered atoms meaningful.

3. A solution of **3** in acetylacetone was concentrated by slow evaporation. A colorless block with very well-defined faces from a representative sample of crystals of the same habit was collected and data were obtained, and the structure was solved as in **1**. The X-ray radiation employed was generated from a Cu sealed X-ray tube (K_α = 1.5418 Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes). 180 data frames were taken at widths of 0.5°. These reflections were used to determine the unit cell using Cell_Now.[S7] After careful examination of the unit cell, an extended data collection procedure (26 sets) was initiated using omega and phi scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with *APEX2*.[S8]

4. A solution of **4** in acetylacetone was layered with benzene. A colorless block with very well-defined faces from a representative sample of crystals of the same habit was collected and data were obtained, and the structure was solved as in **1**. The absorption correction program *TWINABS* was employed to correct the data for absorption effects, as well as to separate files: twin4.hkl, containing reflections from only the major component, and twin5.hkl, containing reflections from both the twin components.[S9] While the former was used for structure solution, the latter was used for final least squares refinement.

Table S1. Crystallographic data for **1** and **2**.

	1	**2**
empirical formula	$C_{26}H_{50}O_4P_2$	$C_{34}H_{42}O_8P_2$
formula weight	488.60	640.61
temperature [K]	110.0	100.01
diffractometer	Bruker Quest	Bruker Venture
wavelength [Å]	0.71073	1.54178
crystal system	monoclinic	triclinic
space group	*C*2/*c*	*P*-1
unit cell dimensions:		
a [Å]	24.4329(13)	8.6352(2)
b [Å]	11.0268(6)	9.0229(2)
c [Å]	10.9841(6)	11.5477(3)
α [°]	90	85.762(2)
β [°]	114.110(2)	81.565(2)
γ [°]	90	67.8510(10)
V [Å^3]	2701.1(3)	824.16(3)
Z	4	1
ρ_{calc} [Mg/m^3]	1.201	1.291
μ [mm^{-1}]	0.190	1.611
F(000)	1072	340
crystal size [mm^3]	0.519 × 0.122 × 0.106	0.249 × 0.1 × 0.045
Θ limit [°]	2.619 to 27.543	3.870 to 70.148
index range (h, k, l)	–31, 31; –14, 14; –13, 14	–9, 10; –11, 11; –14, 14
reflections collected	27843	19043
independent reflections	3109	3099
R(int)	0.0532	0.0686
completeness to Θ	99.9 %	99.4 %
max. and min. transmission	0.7431 and 0.6901	0.7533 and 0.6466
data/restraints/parameters	3109 / 0 / 145	3099 / 124 / 231
goodness-of-fit on F^2	1.049	1.101
R indices (final) [$I > 2\sigma(I)$]		
R_1	0.0435	0.0534
wR_2	0.0945	0.0990
R indices (all data)		
R_1	0.0597	0.0718
wR_2	0.1016	0.1072
largest diff. peak and hole [eÅ^{-3}]	0.427 and -0.362	0.391 and -0.287

Table S2. Crystallographic data for **3** and **4**.

	3	**4**
empirical formula	$C_5H_{10}O_4$	$C_5H_{10}O_6$
formula weight	134.13	166.13
temperature [K]	110.15	100.03
diffractometer	Bruker GADDS	Bruker Quest
wavelength [Å]	1.54178	0.71073
crystal system	tetragonal	monoclinic
space group	$P4_32_12$	$P2_1/n$
unit cell dimensions:		
a [Å]	8.9845(4)	5.5661(6)
b [Å]	8.9845(4)	15.4167(15)
c [Å]	8.5007(5)	8.8545(9)
α [°]	90	90
β [°]	90	92.306(3)
γ [°]	90	90
V [Å^3]	686.19(7)	759.20(13)
Z	4	4
ρ_{calc} [Mg/m^3]	1.298	1.453
μ [mm^{-1}]	0.975	0.136
F(000)	288	352
crystal size [mm^3]	0.18 × 0.13 × 0.1	0.225 × 0.214 × 0.104
Θ limit [°]	6.970 to 60.489	2.642 to 25.000
index range (h, k, l)	–10, 10; –10, 10; –9, 9	–6, 6; 0, 18; 0, 10
reflections collected	15337	2327
independent reflections	518	2327
R(int)	0.0584	0.0545
completeness to Θ	83.8 %	97.5 %
max. and min. transmission	0.7388 and 0.6510	0.745 and 0.555
data/restraints/parameters	518 / 0 / 45	2327 / 0 / 103
goodness-of-fit on F^2	1.195	1.036
R indices (final) [$I > 2\sigma(I)$]		
R_1	0.0246	0.0507
wR_2	0.0555	0.1094
R indices (all data)		
R_1	0.0261	0.0676
wR_2	0.0557	0.1186
largest diff. peak and hole [eÅ^{-3}]	0.116 and -0.092	0.183 and -0.266

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