# Supporting Information 

# Manganese(III)-Catalyzed Facile Direct Hydroperoxidation of Some Heterocyclic 1,3-Dicarbonyl Compounds 

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1. A typical procedure is as follows. A mixture of 4-alkyl-1,2-diphenylpyrazolidine-3,5dione $1(1 \mathrm{mmol})$ and manganese(III) acetate dihydrate ( 0.1 mmol ) in glacial acetic acid ( 30 mL ) was stirred at $23^{\circ} \mathrm{C}$ for 2 h in air, and then the reaction was quenched by adding water ( 25 mL ) to the mixture. The aqueous reaction mixture was extracted three times with dichloromethane ( 30 mL ) and the combined extract was washed with water, a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was separated by silica gel column chromatography by eluting with diethyl ether/hexane ( $7: 3 \mathrm{v} / \mathrm{v}$ ). The obtained hydroperoxide $\mathbf{2}$ was further purified by recrystallization from diethyl ether-hexane or dichloromethane-benzene.
2. 4-Benzyl-4-hydroperoxy-1,2-diphenylpyrazolidine-3,5-dione (2: $\mathrm{R}=\mathrm{Bn}$ ): Colorless blocks (from dichloromethane-benzene); mp 103-107 ${ }^{\circ} \mathrm{C}$ (Decompd); IR (KBr) $v 3300(\mathrm{OOH}), 1753,1705(\mathrm{C}=\mathrm{O})$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.21(1 \mathrm{H}, \mathrm{s}$, $\mathrm{OOH}), 7.24-6.80\left(15 \mathrm{H}, \mathrm{m}\right.$, arom H), $3.31\left(2 \mathrm{H}, \mathrm{s},-\mathrm{CH}_{2}-\right.$ of Bn$) ;{ }^{13} \mathrm{C} \mathrm{NMR} \mathrm{(75MHz} \mathrm{}$, $\mathrm{CDCl}_{3}$ ) $\delta 167.6(\mathrm{C}=\mathrm{O}$ ), 134.0, 130.3 (arom C), 130.6, 128.8, 127.9, 127.6, 123.9 (arom CH), $86.6(\mathrm{C}-\mathrm{O}), 38.0\left(-\mathrm{CH}_{2}-\right.$ of Bn$)$. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{4} \bullet 2 / 3 \mathrm{H}_{2} \mathrm{O}: \mathrm{C}$, 68.38; H, 4.69; N, 7.24. Found C, 68.13; H, 4.55; N, 7.11. FAB HRMS (acetoneNBA) Found: $m / z$ 375.1344. Calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{4}: \mathrm{M}+1,375.1267$.
3. X-ray crystallographic data of $2(\mathrm{R}=\mathrm{Bn})$ : empirical formula $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{4}$; formula weight 374.3894 ; colorless plates; crystal dimensions $0.25 \times 0.50 \times 0.10 \mathrm{~mm}$; triclinic; space group $P-1 ; a=10.3233(5), b=10.4273(4), c=12.9985(6) \AA, \alpha=95.792(1)^{\circ}, \beta$ $=104.504(3)^{\circ}, \gamma=105.643(2)^{\circ}, V=1283.0(1) \AA^{3}, \mathrm{Z}=2 ; D_{\text {calcd }}=1.272 \mathrm{~g} / \mathrm{cm}^{3} ; F_{000}=$ 518.00; $\mu(\mathrm{MoK} \alpha)=0.85 \mathrm{~cm}^{-1} ; 2 \theta_{\max }=55.0^{\circ}$; no. of reflections measured 11910; no. of observations ( $\mathrm{I}>3.00 \sigma(\mathrm{I}), 2 \theta<54.96^{\circ}$ ) 4605 ; no. of variables 442 ; reflection/parameter ratio $10.42 ; R=0.038 ; R_{w}=0.058$; GOF 1.14.


Figure 1. ORTEP Drawing of $2(\mathrm{R}=\mathrm{Bn})$

