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 mmol) and manganese(III) acetate dihydrate (0.1 mmol) in glacial acetic acid (30 mL) was stirred at 23 °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 v/v). The obtained hydroperoxide 2 was further purified by recrystallization from diethyl ether-hexane or dichloromethane-benzene.
- 4-Benzyl-4-hydroperoxy-1,2-diphenylpyrazolidine-3,5-dione (2: R = Bn): Colorless blocks (from dichloromethane-benzene); mp 103-107 °C (Decompd); IR (KBr) v 3300 (OOH), 1753, 1705 (C=O) ; ¹H NMR (300 MHz, CDCl₃) δ 11.21 (1H, s, OOH), 7.24-6.80 (15H, m, arom H), 3.31 (2H, s, -CH₂- of Bn); ¹³C NMR (75 MHz, CDCl₃) δ 167.6 (C=O), 134.0, 130.3 (arom C), 130.6, 128.8, 127.9, 127.6, 123.9 (arom CH), 86.6 (C-O), 38.0 (-<u>C</u>H₂- of Bn). Anal. Calcd for C₂₂H₁₈N₂O₄•2/3 H₂O: C, 68.38; H, 4.69; N, 7.24. Found C, 68.13; H, 4.55; N, 7.11. FAB HRMS (acetone-NBA) Found: *m/z* 375.1344. Calcd for C₂₂H₁₈N₂O₄: M+1, 375.1267.
- 3. X-ray crystallographic data of **2** (R = Bn): empirical formula $C_{22}H_{18}N_2O_4$; formula weight 374.3894; colorless plates; crystal dimensions $0.25 \times 0.50 \times 0.10$ mm; triclinic; space group *P*-1; *a* = 10.3233(5), *b* = 10.4273(4), *c* = 12.9985(6) Å, α = 95.792(1)°, β = 104.504(3)°, γ = 105.643(2)°, *V* = 1283.0(1) Å³, Z = 2; D_{calcd} = 1.272 g/cm³; F_{000} = 518.00; μ (MoK α) = 0.85 cm⁻¹; $2\theta_{max}$ = 55.0°; no. of reflections measured 11910; no. of observations (I>3.00 σ (I), 2θ <54.96°) 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** (R = Bn)