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Manganese(III)-based oxidation of 1,2-disubstituted pyrazolidine-3,5-diones in the presence of alkenes

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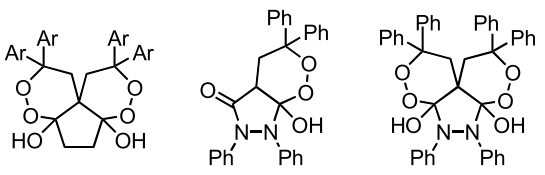
Abstract—The manganese(III)-catalyzed aerobic oxidation of 1,2-disubstituted pyrazolidine-3,5-diones **1** in the presence of alkenes **2** gave the corresponding pyrazolidinediones **3** which were doubly hydroperoxyalkylated at the 4-position in high yields. On the other hand, pyrazolidinediones **1** were oxidized with manganese(III) acetate in the presence of alkenes **2** at elevated temperature to produce the 4,4-bis(alkenyl)pyrazolidinediones **4** in good yields instead of the pyrazolidine-fused dihydrofuran analogue **IV**. A similar cerium(IV)-mediated oxidation of pyrazolidinedione **1a** with an alkene **2a** afforded the doubly 4-methoxyethylated derivative **5**. The stability of the free hydroperoxyl group and the reaction pathway for the aerobic and the metal-mediated oxidation reactions were also discussed.

1. Introduction

In recent years, attention has been placed on the synthetic opportunities offered by high-valent metal salt oxidations of carbonyl compounds in the presence of unsaturated substrates.[1a–d] Among the numerous metals, trivalent manganese occupies a very prominent position.[1e–g] A variety of carbonyl compounds can be oxidized by manganese(III) acetate to generate electrophilic α-carbonyl radicals, which can add to a number of electron-rich alkenes to form new carbon–carbon bonds.[2] Thus, it provides a versatile protocol for the formation of highly functionalized products from simple precursors. In connection with our current research interest to synthesize functionalized heterocyclic compounds with potent biological activities,[3] we carried out the manganese(III) acetate-catalyzed oxidation of pyrazolidine-3,5-diones **1** in the presence of electron-rich alkenes **2**.[4] With regard to the economic and ecological aspects, atmospheric oxygen (air) represents the oxidant of choice. Therefore, these reactions were investigated with particular attention being paid to the use of a combination of a catalytic amount of manganese(III) or manganese(II) acetate and air.[3f] It was reported that cyclic peroxides were formed by the manganese(III)-based oxidation of 1,3-dicarbonyl compounds in the presence of alkenes under mild reaction conditions in air.[5] In particular, the reaction with 1,3-cyclopentanedione resulted in a unique double 1,2-dioxane ring formation to produce octahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diols **I** in good yields.[6a] Therefore, we were intrigued with the possibility of achieving a similar single **II** and/or double cyclic peroxidation product **III** of the pyrazolidine-3,5-diones **1** with alkenes **2**. Contrary to our prediction, the oxidation led to free double hydroperoxides **3** instead of cyclic peroxides. It was the only known precedent that the aerobic oxidation of a mixture of alkenes and barbituric acid derivatives in the presence of manganese(II) acetate tetrahydrate furnished hydroperoxyalkylated barbituric acids in 62–99 % yields.[6b] In this study, we delineated a convenient one-pot synthesis of 4,4-bis(2-hydroperoxyalkyl)pyrazolidine-3,5-diones **3** by the manganese(III)-catalyzed autoxidation of readily available alkenes **2** with a number of pyrazolidine-3,5-diones **1** at ambient temperature in air. We also mentioned the double alkenylation of pyazolidinediones **1** using manganese(III) acetate at elevated temperature. In addition, we showed the result of a similar reaction mediated by ammonium cerium(IV) nitrate (CAN) in methanol in order to compare the reaction using manganese(III) acetate.



I II III

Keywords: hydroperoxydation; catalytic oxidation; aerobic oxidation; oxidative radical reaction; heterocyclic compounds; manganese(III) acetate; CAN.

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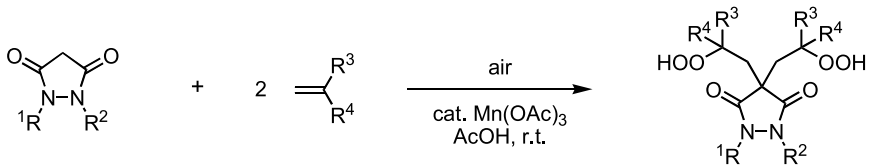


1a-f **2a-h** **3**

1a : $R^1 = R^2 = Ph$
1b : $R^1 = Bn$, $R^2 = Ph$
1c : $R^1 = Bn$, $R^2 = Me$
1d : $R^1 = Bn$, $R^2 = Bn$
1e : R^1, $R^2 = -(CH_2)_4-$
1f : $R^1 = R^2 = Et$

2a : $R^3 = R^4 = Ph$
2b : $R^3 = R^4 = 4\text{-Me-}C_6H_4$
2c : $R^3 = R^4 = 4\text{-F-}C_6H_4$
2d : $R^3 = R^4 = 4\text{-Cl-}C_6H_4$
2e : $R^3 = R^4 = Me$
2f : $R^3 = R^4 = Et$
2g : $R^3 = Me$, $R^4 = Ph$
2h : $R^3 = 4\text{-Me-}C_6H_4$, $R^4 = Ph$

Scheme 1.

2. Results and discussion

2.1. Preparation of pyrazolidine-3,5-dione derivatives

1,2-Diphenylpyrazolidine-3,5-dione (**1a**) and 1,2-diethylpyrazolidine-3,5-dione (**1f**) were prepared by the condensation of the corresponding hydrazines with diethyl malonate in the presence of sodium hydride.[7a] The rest of the pyrazolidine-3,5-diones **1b**–**e** were prepared according to the methods described in the literature.[7b] All of these pyrazolidine-3,5-diones **1a**–**f** exist in the keto form both in the solid state and in chloroform solution as evident from the IR and NMR spectroscopies, respectively (see Section 3, Scheme 1).

2.2. Manganese(III) acetate-catalyzed molecular oxygen-trapping reaction of pyrazolidine-3,5-diones 1 with alkenes 2 at 23°C

1,2-Diphenylpyrazolidine-3,5-dione (**1a**) was allowed to react with 1,1-diphenylethene (**2a**) in acetic acid in the presence of manganese(III) acetate in air, and the 4,4-bis(2-hydroperoxyalkyl) derivative **3aa** was formed (Table 1). When the reaction was carried out with a stoichiometric amount of manganese(III) acetate, the yield of **3aa** was found to be 67% (Table 1, entry 1). Probably, this could be attributed to the decomposition of the pyrazolidinedione ring by being exposed to the excess amount of the oxidant present in the reaction mixture for a longer period of time.[8]

Table 1. Reaction of pyrazolidine-3,5-diones **1a**–**f** with alkenes **2a**–**h** in the presence of manganese(III) or manganese(II) acetate

Entry	Pyrazolidinedione	Alkene	**1**:**2**:$Mn(OAc)_3$	Reaction time (h)	Bis(hydroperoxide) (yield, %)[a]
1	**1a**	**2a**	1:1:1	12[b]	**3aa** (67)
2	**1a**	**2a**	1:1:1	1	**3aa** (80)
3	**1a**	**2a**	1:2:0.2	3	**3aa** (85)
4	**1a**	**2a**	1:1:0.1	2	**3aa** (96)
5	**1a**	**2b**	1:1:0.1	5	**3ab** (80)
6	**1a**	**2c**	1:1:0.1	3	**3ac** (95)
7	**1a**	**2d**	1:1:0.1	2	**3ad** (98)
8	**1a**	**2e**	1:Excess:0.5[c]	2	**3ae** (91)[d]
9	**1a**	**2f**	1:1:0.1	5	**3af** (95)
10	**1a**	**2g**	1:1:0.1	3	**3ag** (95)
11	**1a**	**2h**	1:1:0.1	14	**3ah** (75)
12	**1b**	**2a**	1:2:0.2	3	**3ba** (85)
13	**1b**	**2c**	1:2:0.2	2	**3bc** (90)
14	**1b**	**2d**	1:2:0.2	4	**3bd** (87)
15	**1c**	**2a**	1:2:0.2	4	**3ca** (91)
16	**1c**	**2c**	1:2:0.2	6	**3cc** (74)
17	**1d**	**2a**	1:2:0.2	6	**3da** (87)
18	**1d**	**2a**	1:1:1[e]	15	**3da** (95)
19	**1d**	**2b**	1:1:1[e]	10	**3db** (93)
20	**1d**	**2c**	1:1:1[e]	1	**3dc** (78)
21	**1e**	**2a**	1:2:0.2	13	**3ea** (98)
22	**1f**	**2a**	1:2:0.2	6	Complex mixture[f]

The reaction was carried out at 23°C in glacial acetic acid (25 mL) in air.
[a] Isolated yield based on the alkene **2** used except for entry 8.
[b] Manganese(III) acetate was completely consumed.
[c] 2-Methypropene and dry air were bubbled through the reaction mixture.
[d] The yield based on the pyrazolidinedione **1a** used.
[e] Manganese(II) acetate was used instead of manganese(III) acetate.
[f] The reaction gave an intractable mixture.

By using a catalytic amount of manganese(III) acetate and carrying out the reaction for a shorter time period, the yield of the product **3aa** could be improved to 96% yield (entry 4). The reactions of other pyrazolidinediones **1b–e** were also applicable with different substituted ethenes **2b–h**, giving the corresponding 4,4-bis(2-hydroperoxyalkyl)-pyrazolidine-3,5-diones **3** in comparable yields (entries 5–17). The tetrahydro-1*H*-pyrazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (**1e**) also reacted with **2a** under similar manganese(III)-catalyzed oxidation conditions to give the corresponding bis(hydroperoxide) **3ea** in quantitative yield (entry 21). However, a similar reaction of 1,2-diethyl-pyrazolidine-3,5-dione (**1f**) with **2a** resulted in an intractable mixture (entry 22). Using manganese(II) acetate instead of manganese(III) acetate was also effective for the double hydroperoxyalkylation of **1d** (entries 18–20).

2.3. Structure determination of 4,4-bis(2-hydroperoxyalkyl)pyrazolidinediones 3

The structural assignment of the bis(hydroperoxide)s **3** was based on their ^{1}H NMR, ^{13}C NMR, and IR spectra, as well as their elemental analyses. For example, the bis(hydroperoxide) **3ac** showed an absorption band at 3230 cm^{-1} in the IR spectrum and a peak at 9.32 ppm in the ^{1}H NMR spectrum which were due to the corresponding hydroperoxy group. In the ^{13}C NMR spectrum of **3ac**, the amide carbonyl carbon appeared at δ 170.7 ppm, and the peak at δ 86.0 ppm was assigned to the C-2 carbon of the ethyl group attached to the hydroperoxy group. In addition, the elemental analysis and high resolution FAB mass spectral data supported the molecular formula of $C_{43}H_{32}F_4N_2O_6$. The structure of **3ac** was finally confirmed by X-ray crystallography. The ORTEP drawing of **3ac** is shown in Figure 1.

The most characteristic feature of **3ac** was that two hydroperoxy groups are individually hydrogen-bonded to the two amide carbonyl oxygens since the interatomic distance between the carbonyl O(1′) and the peroxy O(3) was found to be 2.688 Å. The hydrogen-bonding is stronger in the solid state than that in solution. This could be seen from the IR absorption bands of the hydroperoxy and carbonyl groups, i.e. 3230 (OOH), 1706, 1662 (>C=O) cm^{-1} in the KBr pellet and 3298 (OOH), 1720, and 1683 (>C=O) cm^{-1} in $CHCl_3$. Whereas, in the case of the parent 1,2-diphenylpyrazolidine-3,5-dione (**1a**), the carbonyl stretching vibration appears at 1754, 1723 cm^{-1} in the KBr pellet, and 1753 and 1724 cm^{-1} in $CHCl_3$. Nevertheless, in the $CDCl_3$ solution, the hydrogen-bonding exists to a considerable extent, which is evident from the ^{13}C NMR spectrum as the carbonyl carbon appeared at δ 170.7 ppm, quite downfield compared to that of the parent **1a** (δ 166.6 ppm). A similar conclusion could be drawn by comparing the IR carbonyl stretching vibrations of the bis(hydroperoxide) **3ac** and the parent pyrazolidinedione **1a** as mentioned above. As a result, it appears that the hydroperoxy group must be stabilized in the solid state as well as in solution. This type of stabilization could lead to the preferential formation of the open chain hydroperoxyalkyl derivatives, i.e. **3**, and vis-à-vis, discourages the formation of the rather strained bicyclic or tricyclic analogues, e.g. **II** and/or **III**. A similar stabilization of the hydroperoxy group was also observed in 5,5-bis(hydroperoxy-2,2-diphenylethyl)barbituric acid in which the corresponding interatomic distance was 2.73 and 2.81 Å, respectively.[6b] In addition, the hydroperoxy O–O bond length of O(2)–O(3) (1.465 Å) in **3ac** was analogous to those of the bis(hydroperoxyethyl)barbituric acid (1.450 and 1.464 Å).[6b] Moreover, unlike many alkylhydroperoxides, these bis(hydroperoxide)s **3** were found to be thermally stable at ambient temperature[9a] and to prolonged exposure to sunlight or visible light,[9b] which could also be attributed to the stabilization through strong hydrogen-bonding.

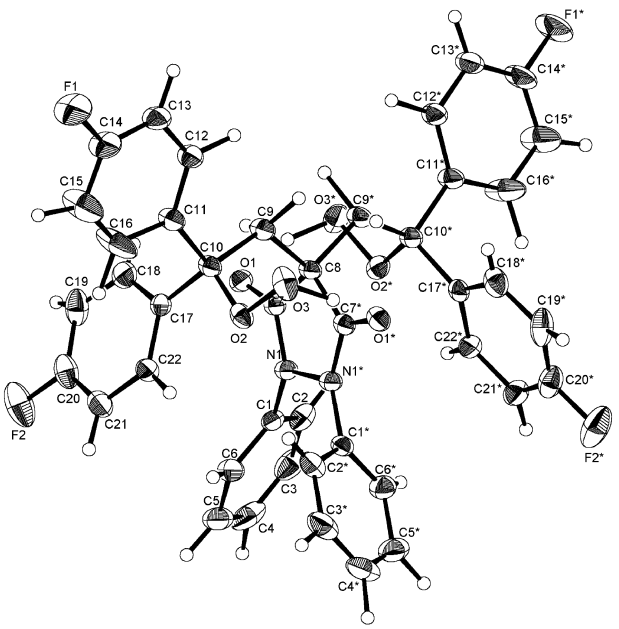
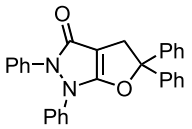


Figure 1. ORTEP Drawing of **3ac**.

2.4. Oxidation of a mixture of pyrazolidine-3,5-diones 1 and alkenes 2 with manganese(III) acetate at elevated temperature

The manganese(III) acetate-mediated reaction of alkenes with 1,3-dicarbonyl compounds at elevated temperature represents a general and versatile method for the synthesis of polysubstituted dihydrofurans.[1e–g,2b,c] With this anticipation, we carried out a similar type of oxidation of pyrazolidinedione **1a** and ethene **2a** with manganese(III) acetate at reflux temperature. However, the isolated product was found to be double alkenylated pyrazolidinedione **4aa** (yield 55%) (Table 2, entry 1) rather than the expected dihydrofuran derivative **IV**. The yield of **4aa** was improved (74%) when the oxidation was carried out at 80°C (entry 2), and further improvised (83%) by taking a two-fold excess of **1a** and carrying out the reaction at 100°C (entry 3). Altering the electron-donating capability of the aryl groups of the alkenes **2** and/or replacing phenyl substituents on the nitrogen atom of the pyrazolidinediones **1** with much more electron-donating benzyl or ethyl groups, however, resulted in no change in the ultimate product structure



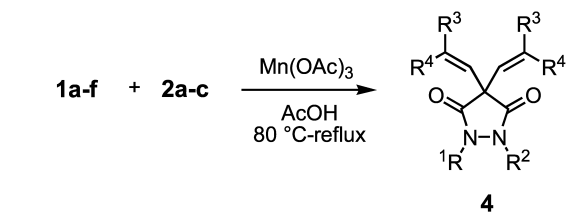
IV

Table 2. Oxidation of a mixture of pyrazolidine-3,5-diones **1** and alkenes **2** with manganese(III) acetate in acetic acid at elevated temperature

Entry	Pyrazolidinedione	Alkene	**1**:**2**:$Mn(OAc)_3$	Temperature (°C)	Reaction time	Product yield (%)[a]
1	**1a**	**2a**	1:3:8	Reflux	30 min	**4aa** (55)
2	**1a**	**2a**	1:2:4	80	6 h	**4aa** (74)
3	**1a**	**2a**	1:1:2	100	3 h	**4aa** (83)
4	**1a**	**2b**	1:1:2	Reflux	4 h	**4ab** (54)
5	**1a**	**2c**	1:1:2	100	6 h	**4ac** (70)
6	**1b**	**2a**	1:1:3	100	30 min	Complex mixture[b]
7	**1b**	**2b**	1:1:3	100	30 min	Complex mixture[b]
8	**1c**	**2b**	1:1:3	100	30 min	**4cb** (74)
9	**1d**	**2b**	1:2:2	100	20 min	**4db** (69)
10	**1e**	**2a**	1:1:3	100	20 min	**4ea** (65)
11	**1e**	**2b**	1:1:3	100	30 min	**4eb** (80)
12	**1f**	**2b**	1:1:2	100	25 min	**4fb** (65)

The reaction was carried out in acetic acid (25 mL) in air.
[a] Isolated yield based on the alkene **2** used.
[b] The reaction gave an intractable mixture.

(entries 8–12). In addition, the reaction of dibenzyl-substituted pyrazolidinedione **1b** gave an intractable mixture and no products were isolated (entries 6,7). Nevertheless, to the best of our knowledge, this type of double alkenylation of 1,3-dicarbonyl compounds in the manganese(III) acetate-mediated reaction with alkenes has never been reported before, and it could be considered as a convenient route to introduce alkenyl groups at the 4-position of pyrazolidine-3,5-diones **1**. The structural assignment of **4aa** was based on the ^1H NMR, ^{13}C NMR, and IR spectra, elemental analysis, and finally by X-ray crystallography. The ORTEP drawing of **4aa** is shown in Figure 2.



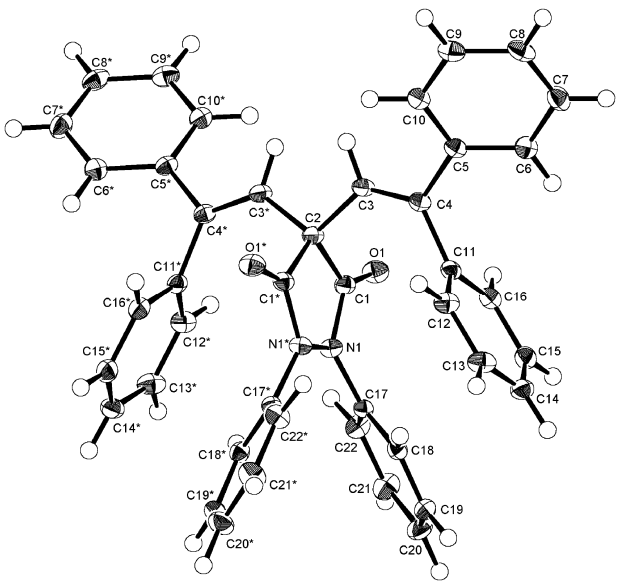
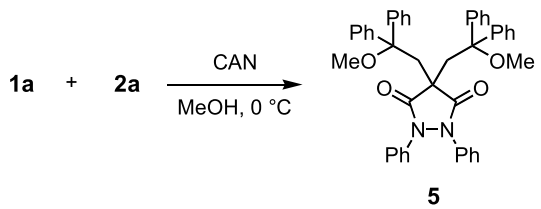


Figure 2. ORTEP Drawing of **4aa**.

2.5. Reaction of pyrazolidinedione 1a with ethene 2a in the presence of ammonium cerium(IV) nitrate

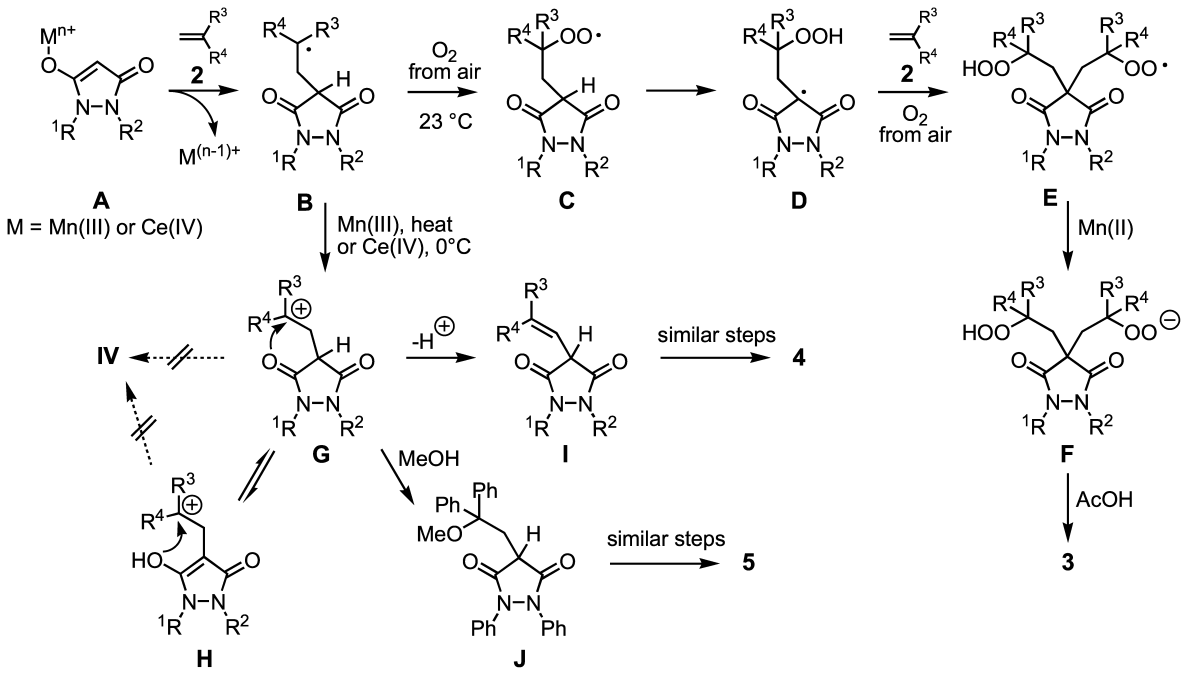
In order to synthesize the dihydrofuran analogue **IV**, we investigated the reaction of **1a** with **2a** in the presence of ammonium cerium(IV) nitrate (CAN). Unlike the typical oxidative cyclization of alkenes with 1,3-dicarbonyl compounds using CAN,[3e,10] the reaction of **1a** with **2a** in the presence of CAN gave 4,4-bis(2-methoxy-2,2-diphenylethyl)-1,2-diphenylpyrazolidine-3,5-dione (**5**). When the molar ratio of the reaction was **1a**:**2a**:CAN=1:2:2, the yield of **5** was 65%, while using a two-fold excess of the **1a** (the molar ratio, 1:1:2) afforded the improved yield up to 91%. In both cases, the yield was based on the amount of added **2a** (Scheme 2).



Scheme 2.

2.6. Mechanism

The formation of **3**, **4**, and **5** can be accounted for according to the mechanism outlined in Scheme 3. The manganese(III)- or cerium(IV)-pyrazolidinedione enolate complex **A** should be formed in the first step.[1e] Rapid electron transfer with the loss of manganese(II) or cerium(III) followed by subsequent addition to the alkene **2** gave the adduct radical **B**. The fate of this radical **B** would depend on the ambient temperature and the nature of the oxidant metal ion. At 23°C, the radical **B** could be trapped by dissolved molecular oxygen in the solvent to form the peroxy radical **C**.[5b–d,11] The peroxy radical **C** could be converted to radical **D** either by intramolecular hydrogen abstraction or by a series of reactions, that is, reduction of the peroxy radical with manganese(II), protonation,[12] and further oxidation at the C-4 position.[6] A similar process from **D** to the peroxy anion **F** would yield **3**. When the manganese(II) acetate was used as the catalyst, the manganese(II)–pyrazolidinedionate complex should be



Scheme 3.

formed and aerobically oxidized to produce active manganese(III) species in situ such as **A**.[6,12b] For the reactions at elevated temperature and with a stoichiometric amount of manganese(III) acetate, the alternative path, i.e. the oxidation of the tertiary alkyl radical **B** to the corresponding cation **G**, becomes more facile than the molecular oxygen trapping process,[3,5,12b,13] since the concentration of dissolved oxygen at the elevated temperature could be considered as negligible. In the case of the cerium(IV)-mediated oxidation reaction, which is a stronger oxidant than the manganese(III), the oxidation of the alkyl radical **B** to the corresponding cation **G** would be faster than being trapped by dissolved molecular oxygen. Now, the reaction path involving this carbocation **G** would be expected to undergo nucleophilic attack by the adjacent amide carbonyl oxygen of **G** or the hydroxyl oxygen of the enol **H** to give the five-membered dihydrofuran-type product **IV**. However, probably due to the strain that would be imposed as two five-membered rings fuse together, the open chain analogue preferentially formed. The structure of these open-chain products depends on the oxidizing system, e.g. (a) in the case of the manganese(III)-mediated reaction at elevated temperature, the carbocation **G** readily looses a proton to give the mono-alkenylated intermediate **I**, and (b) in the case of the cerium(IV)-mediated reaction, the cation **G** reacted with the solvent methanol to afford the methoxyalkylated intermediate **J**, neither of the mono-substituted intermediates **I** nor **J** could be isolated from the reaction mixture. The intermediates **I** and **J** undergo similar processes to give the double-alkenylated and double-methoxyalkylated products **4** and **5**, respectively. Since the 4-monoalkylated pyrazolidine-3,5-diones are known to have pK_a values in the range 4–5,[14] the intermediates **I** and **J** are supposed to possess similar pK_a values, and thus the formation of the manganese-enolate or cerium-enolate type complexes (e.g. **A**) would be better accomplished than in the case of the parent 4-nonsubstituted pyrazolidinediones **1**. Consequently, intermediates **I** and **J** should be very reactive towards the oxidative carbon–carbon bond formation leading to the double substitution at the 4-position.[15] Presumably, for this reason, we were not able to isolate the 4-mono-hydroperoxyalkylated, alkenylated, and methoxyalkylated derivatives from the reaction mixture.

2.7. Conclusion

In summary, we have demonstrated a facile one-pot synthetic route for double 2-hydroperoxyakylation, double 2-alkenylation, and double 2-methoxyalkylation of the pyrazolidine-3,5-diones **1** at the C-4 position. These reactions were applicable to a wide variety of both 1,2-disubstituted pyrazolidine-3,5-diones and alkenes. It is also noteworthy that the doubly substituted pyrazolidine-3,5-diones at the 4-position possess altered biological profiles compared to their non- or mono-substituted parent pyrazolidinedione derivatives.[16] The bis(hydroperoxyethyl)pyrazolidine-3,5-dione **3aa** (R^1=R^2=R^3=R^4=Ph) showed a weak antimalarial activity.[17,18]

3. Experimental

NMR spectra were recorded using a JNM EX300 FT NMR spectrometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported in δ values (ppm). The IR spectra are measured by a Shimadzu 8400 FT IR spectrophotometer, and expressed in cm^{-1}. The EI MS spectra were recorded by a Shimadzu QP-5050A gas chromatograph-mass spectrometer. The high resolution mass spectra were measured at the Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan. The elemental analyses were performed at the Analytical Center of Kumamoto University, Kumamoto, Japan. Manganese(II) acetate tetrahydrate was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate

dihydrate, $Mn(OAc)_3{\cdot}2H_2O$, was prepared according to the method described in the literature.[19] The alkenes **2** were synthesized according to the literature,[3,5,6] except for **2e** and **2f** which were purchased from Tokyo Kasei Co., Ltd.

3.1. Preparation of pyrazolidine-3,5-diones

The pyrazolidine-3,5-dione derivatives **1a–f** were prepared according to the literature methods,[7] and their physical data are given below.

3.1.1. 1,2-Diphenylpyrazolidine-3,5-dione (1a). Colorless plates (from CH_2Cl_2–MeOH); mp 177–180°C (lit.,[7a] mp 177–179°C); IR (KBr) ν 1754, 1723 (C=O); ($CHCl_3$) 1753, 1724; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.15 (10H, m, arom H), 3.52 (2H, s, $-CH_2-$, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6 (C=O), 135.5 (arom C), 128.9, 126.9, 122.7 (arom CH), 36.9 (C-4).

3.1.2. 1-Benzyl-2-phenylpyrazolidine-3,5-dione (1b). Pale yellow microcrystals (from CH_2Cl_2–diethy ether); mp 108°C (lit.,[7b] mp 109.5°C); IR (KBr) ν 1739, 1708 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–6.92 (10H, m, arom H), 4.71 (2H, s, $-CH_2Ph$), 3.33 (2H, s, $-CH_2-$, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 166.2 (C=O), 134.2, 134.1 (arom C), 129.3, 128.7, 128.6, 128.4, 128.0, 124.7 (arom CH), 47.9 ($-CH_2-$Ph), 36.8 ($-CH_2-$, C-4).

3.1.3. 1-Benzyl-2-methylpyrazolidine-3,5-dione (1c). Colorless needles (from CH_2Cl_2–hexane); mp 103–104°C (lit.,[7b] mp 104°C); IR (KBr) ν 1730, 1691 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.26 (10H, m, arom H), 4.83 (2H, s, $-CH_2Ph$), 3.22 (2H, s, $-CH_2-$, H-4), 3.05 (3H, s, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 166.5 (C=O), 134.5 (arom C), 128.6, 127.9, 127.1 (arom CH), 46.3 ($-CH_2-$Ph), 35.9 ($-CH_2-$, C-4), 30.0 (Me).

3.1.4. 1,2-Dibenzylpyrazolidine-3,5-dione (1d). Pale yellow microcrystals (from CH_2Cl_2–hexane); mp 127°C (lit.,[7b] mp 128.5°C); IR (KBr) ν 1739, 1730, 1693 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.13 (10H, m, arom H), 4.69 (4H, s, 2×$-CH_2Ph$), 3.33 (2H, s, $-CH_2-$, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9 (C=O), 134.6 (arom C), 128.9, 128.3, 127.3 (arom CH), 46.7 ($-CH_2-$Ph), 36.4 (C-4).

3.1.5. Tetrahydro-1*H*-pyrazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (1e). Colorless cubes (from ethyl acetate–hexane); mp 118°C (lit.,[7b] mp 119.5°C); IR (KBr) ν 1735, 1679 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59–3.55 (4H, m, $-CH_2-$), 3.16 (4H, s, $-CH_2-$), 1.77–1.74 (4H, m, $-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8 (C=O), 42.8 ($-CH_2-$, C-4), 36.7 ($-CH_2-$), 22.1 ($-CH_2-$).

3.1.6. 1,2-Diethylpyrazolidine-3,5-dione (1f). Colorless blocks (from ethyl acetate–hexane); mp 123°C; IR (KBr) ν 1735, 1689 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (4H, q, J=7.2 Hz, 2×CH_2-CH_3), 3.08 (2H, s, $-CH_2-$, H-4), 1.11 (6H, t, J=7.2 Hz, 2×CH_2-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9 (C=O), 37.8 ($-CH_2-CH_3$), 36.7 (C-4), 11.8 ($-CH_2-CH_3$). Anal. calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.51; H, 7.61; N, 17.76.

3.2. Manganese(III) acetate-catalyzed molecular oxygen-trapping reaction of pyrazolidine-3,5-diones 1 with alkenes 2 at 23°C

To a solution of pyrazolidine-3,5-dione **1** (1 mmol) and alkene **2** (1 mmol) in glacial acetic acid (25 mL), manganese(III) acetate dihydrate (0.1 mmol) was added. The mixture was stirred at 23°C in air until the alkene **2** was completely consumed, and then the reaction was quenched by adding water (25 mL) to the mixture. The aqueous reaction mixture was extracted three times with CH_2Cl_2 (30 mL) and the combined extract was washed with water, then a saturated aqueous solution of sodium hydrogencarbonate, dried over anhydrous sodium sulfate, and concentrated to dryness. The residue was separated by a silica gel column. The products **3** were further purified by recrystallization from appropriate solvents.

3.2.1. 4,4-Bis(2-hydroperoxy-2,2-diphenylethyl)-1,2-diphenylpyrazolidine-3,5-dione (3aa). Colorless blocks (from CH_2Cl_2–MeOH); mp 190–192°C (decompd); IR (KBr) ν 3222, (OOH), 1712, 1670 (C=O); ($CHCl_3$) 3294, 1726, 1683; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.27 (2H, s, OOH), 7.43–6.60 (30H, m, arom H), 3.59 (4H, s, 2×$-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8 (C=O), 142.8, 133.1 (arom C), 128.3, 128.1, 127.2, 126.9, 125.7, 123.4 (arom CH), 86.5 (>C–O), 48.6 (C-4), 44.0 ($-CH_2-$). Anal. calcd for $C_{43}H_{36}N_2O_6$: C, 76.31; H, 5.36; N, 4.14. Found: C, 76.54; H, 5.19; N, 4.15.

3.2.2. 4,4-Bis[2-hydroperoxy-2,2-bis(4-methylphenyl)-ethyl]-1,2-diphenylpyrazolidine-3,5-dione (3ab). Colorless microcrystals (from diethyl ether–hexane); mp 176–183°C (decompd); IR (KBr) ν 3269 (OOH), 1733, 1695, 1662 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (2H, s, OOH), 7.30–6.55 (26H, m, arom H), 3.54 (4H, s, 2×$-CH_2-$), 2.26 (12H, s, 4×Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7 (C=O), 140.1, 136.9, 133.0 (arom C), 128.8, 128.2, 126.8, 125.6, 123.5 (arom CH), 86.3 (>C–O), 48.6 (C-4), 43.9 ($-CH_2-$), 20.96 (Me). Anal. calcd for $C_{47}H_{44}N_2O_6$: C, 77.03; H, 6.05; N, 3.82. Found: C, 77.25; H, 6.08; N, 3.92.

3.2.3. 4,4-Bis[2,2-bis(4-fluorophenyl)-2-hydroperoxy-ethyl]-1,2-diphenylpyrazolidine-3,5-dione (3ac). Colorless blocks (from diethyl ether–hexane); mp 170°C (decompd); IR (KBr) ν 3230 (OOH), 1706, 1662 (C=O); ($CHCl_3$) 3298, 1720, 1683; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (2H, s, OOH), 7.36–6.62 (26H, m, arom H), 3.52 (4H, s, 2×$-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7 (C=O), 163.4, 160.1, 138.3, 133.0 (arom C), 128.5, 127.5, 127.4, 127,1, 122.9, 115.3, 115.0, (arom CH), 86.0 (>C–O), 48.6 (C-4), 44.0 ($-CH_2-$). Anal. calcd for $C_{43}H_{32}N_2O_6F_4$: C, 68.98; H, 4.31; N, 3.74. Found: C, 69.06; H, 4.37; N, 3.80. FAB HRMS (Acetone–NBA). Found: m/z 748.2173. Calcd for $C_{43}H_{32}N_2O_6F_4$: M, 748.2197.

X-Ray crystallographic data of **3ac**. Empirical formula $C_{43}H_{32}F_4N_2O_6$; formula weight 748.73; colorless cube; crystal dimensions 0.40×0.43×0.36 mm; monoclinic; space group $P2/c$(#13); a=12.062(1), b=9.637(1), c=16.136(2) Å, β=107.484(2)°, V=1789.1(3) Å^3, Z=2; D_{calcd}=1.390 g/cm^3; F_{000}=776.00; μ (Mo K$_\alpha$)=1.07 cm^{-1}; $2\theta_{max}$=55.0°; no. of reflections measured 16676; no. of

observations ($I>0.00\sigma(I)$, $2\theta<54.97°$) 3895; no. of variables 249; reflection/parameter ratio 15.64; R=0.128; Rw=0.164; GOF 1.74. The crystallographic data deposition number: CCDC 216765.

3.2.4. 4,4-Bis[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl]-1,2-diphenylpyrazolidine-3,5-dione (3ad). Pale yellow needles (from diethyl ether–hexane); mp 175°C (decompd); IR (KBr) ν 3350, 3244 (OOH), 1735, 1697 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (2H, s, OOH), 7.32–7.19, 6.58–6.55 (26H, m, arom H), 3.49 (4H, s, 2×–CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4 (C=O), 140.6, 133.6, 132.7 (arom C), 128.5, 128.5, 127.2, 127.1, 123.0 (arom CH), 85.9 (>C–O), 48.4 (C-4), 43.4 (–CH_2–). Anal. calcd for $C_{45}H_{32}N_2O_6Cl_4$: C, 63.41; H, 3.96; N, 3.44. Found: C, 63.50; H, 4.00; N, 3.52.

3.2.5. 4,4-Bis(2-hydroperoxy-2-methylpropyl)-1,2-diphenylpyrazolidine-3,5-dione (3ae). Colorless blocks (from diethyl ether–hexane); mp 186–191°C; IR (KBr) ν 3419, 3319 (OOH), 1724, 1679 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (2H, s, OOH), 7.34–7.21 (10H, m, arom H), 2.36 (4H, s, 2×–CH_2–), 1.27 (12H, s, 4×Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5 (C=O), 133.8 (arom C), 129.1, 127.8, 124.2, (arom CH), 81.4 (>C–O), 48.6 (C-4), 46.1 (–CH_2–), 25.4 (Me). Anal. calcd for $C_{23}H_{28}N_2O_6$: C, 64.47; H, 6.59; N, 6.54. Found: 64.47; H, 6.61; N, 6.43.

3.2.6. 4,4-Bis(2-ethyl-2-hydroperoxybutyl)-1,2-diphenylpyrazolidine-3,5-dione (3af). Colorless microcrystals (from diethyl ether–hexane); mp 148°C; IR (KBr) ν 3313, 3282 (OOH), 1718, 1679 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (2H, s, OOH), 7.33–7.20 (10H, m, arom H), 2.33 (4H, s, 2×–CH_2–), 1.69–1.56 (4H, m, 2×–CH_2–CH_3), 1.42–1.30 (4H, m, 2×–CH_2–CH_3), 0.84–0.79 (12H, m, 4×–CH_2–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7 (C=O), 134.0 (arom C), 129.1, 127.7, 124.04 (arom CH), 86.6 (>C–O), 48.1 (C-4), 43.5 (–CH_2–), 25.2 (4×–CH_2–CH_3), 7.32 (4×–CH_2–CH_3). Anal. calcd for $C_{27}H_{36}N_2O_6$: C, 66.92; H, 7.49; N, 5.78. Found: C, 66.85; H, 7.50; N, 5.70.

3.2.7. 4,4-Bis(2-hydroperoxy-2-phenypropyl)-1,2-diphenylpyrazolidine-3,5-dione (3ag). Colorless microcrystals (from diethyl ether–hexane); mp 191–198°C (decompd); IR (KBr) ν 3334, 3262 (OOH), 1722, 1687 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.09 (2H, s, OOH), 7.46–6.79 (20H, m, arom H), 2.91 (4H, s, –CH_2–), 1.42 (6H, s, 2×Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0 (C=O), 142.8, 133.5 (arom C), 128.6, 128.1, 127.4, 127.2 125.3, 123.7 (arom CH), 84.6 (>C–O), 48.8 (C-4), 45.1 (–CH_2–), 28.5 (Me). Anal. calcd for $C_{33}H_{32}N_2O_6$: C, 71.72; H, 5.84; N, 5.07. Found: C, 71.70; H, 5.82; N, 5.01.

3.2.8. 4,4-Bis[2-hydroperoxy-2-(4-methylphenyl)-2-phenylethyl]-1,2-diphenylpyrazolidine-3,5-dione (3ah). Colorless microcrystals (from MeOH–hexane); mp 171–172°C (decompd); IR (KBr) ν 3230 (OOH), 1710, 1666 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (2H, s, OOH), 7.40–6.57 (28H, m, arom H), 3.56 (4H, s, –CH_2–), 2.25 (6H, s, 2×Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.7, 170.6 (C=O), 143.1, 139.8, 136.9, 133.0 (arom C), 128.8, 128.2, 128.1, 127.1, 126.8, 125.6, 123.4 (arom CH), 86.4 (>C–O), 48.6 (C-4), 43.9 (–CH_2–), 20.9 (Me). Anal. calcd for $C_{45}H_{40}N_2O_6$: C, 76.68; H, 5.72; N, 3.97. Found: C, 76.87; H, 5.70; N, 3.99.

3.2.9. 4,4-Bis(2-hydroperoxy-2,2-diphenylethyl)-1-benzyl-2-phenylpyrazolidine-3,5-dione (3ba). Colorless blocks (ethyl acetate–hexane); mp 187°C (decompd); IR (KBr) ν 3226 (OOH), 1718, 1674 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (2H, s, OOH), 7.45–6.61 (30H, m, arom H), 3.98 (2H, s, –CH_2Ph), 3.53 (4H, s, 2×–CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.8 (C=O), 143.0, 142.8, 134.3, 131.6 (arom C), 128.8, 128.7, 128.3, 128.1, 127.9, 127.2, 127.0, 126.7, 125.5 (arom CH), 86.5 (>C–O), 48.5 (–CH_2Ph), 48.2 (C-4), 43.4 (–CH_2–). Anal. calcd for $C_{44}H_{38}N_2O_6$: C, 76.50; H, 5.54; N, 4.06. Found: C, 76.33; H, 5.54; N, 3.84.

3.2.10. 4,4-Bis[2,2-bis(4-fluorophenyl)-2-hydroperoxyethyl]-1-benzyl-2-phenylpyrazolidine-3,5-dione (3bc). Colorless microcrystals (from ethyl acetate–hexane); mp 179°C; IR (KBr) ν 3240 (OOH), 1708, 1660 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (2H, s, OOH), 7.38–6.58 (26H, m, arom H), 4.11 (2H, s, –CH_2Ph), 3.46 (4H, s, 2×–CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 169.7 (C=O), 163.4, 163.3, 160.1, 160.0, 138.6, 138.2, 133.8 (arom C), 131.5, 129.0, 128.9, 128.4, 128.3, 127.4, 127.3, 126.1, 115.3, 115.1, 115.0 (arom CH), 86.0 (>C–O), 48.8 (–CH_2Ph), 48.1 (C-4), 43.3 (–CH_2–). Anal. calcd for $C_{44}H_{34}N_2O_6F_4$: C, 69.29; H, 4.49; N, 3.67. Found: C, 69.11; H, 4.47; N, 3.70.

3.2.11. 4,4-Bis[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl]-1-benzyl-2-phenylpyrazolidine-3,5-dione (3bd). Colorless microcrystals (from ethyl acetate–hexane); mp 182–184°C; IR (KBr) ν 3246 (OOH), 1708, 1658 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (2H, s, OOH), 7.34–6.50 (26H, m, arom H), 4.14 (2H, s, –CH_2Ph), 3.43 (4H, s, 2×–CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 169.3 (C=O), 141.1, 140.5, 133.7, 133.5, 131.2 (arom C), 129.1, 129.0, 128.9, 128.5, 128.4, 128.3, 126.9, 126.1 (arom CH), 85.9 (>C–O), 48.7 (–CH_2Ph), 48.0 (C-4), 42.8 (–CH_2–). Anal. calcd for $C_{44}H_{34}N_2O_6Cl_4$: C, 63.78; H, 4.14; N, 3.38. Found: C, 63.76; H, 4.14; N, 3.39.

3.2.12. 4,4-Bis(2-hydroperoxy-2,2-diphenylethyl)-1-benzyl-2-methylpyrazolidine-3,5-dione (3ca). Colorless microcrystals (from diethyl ether–hexane); mp 115°C (decompd); IR (KBr) ν 3249 (OOH), 1712, 1658 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (2H, s, OOH), 7.46–7.03 (25H, m, arom H), 4.26 (2H, s, –CH_2Ph), 3.41 (2H, d, J=14.3 Hz, –HCH–), 3.33 (2H, d, J=14.3 Hz, –HCH–), 2.30 (3H, s, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 168.3 (C=O), 143.6, 141.9, 134.7 (arom C), 128.9, 128.8, 128.6, 128.3, 128.2, 128.1, 127.6, 127.3, 127.0 125.7, 125.6 (arom CH), 86.1 (>C–O), 47.3 (C-4), 46.3 (–CH_2Ph), 42.9 (–CH_2–), 28.6 (Me). Anal. calcd for $C_{39}H_{36}N_2O_6$: C, 74.50; H, 5.77; N, 4.46. Found: C, 74.69; H, 5.85; N, 4.08.

3.2.13. 4,4-Bis[2,2-bis(4-fluorophenyl)-2-hydroperoxyethyl]-1-benzyl-2-methylpyrazolidine-3,5-dione (3cc). Colorless microcrystals (from diethyl ether–hexane); mp 191°C (decompd); IR (KBr) ν 3236 (OOH), 1712, 1660

(C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (2H, s, OOH), 7.49–6.71 (21H, m, arom H), 4.38 (2H, s, $-CH_2Ph$), 3.35 (2H, d, J=14.3 Hz, $-HCH-$), 3.25 (2H, d, J=14.3 Hz, $-HCH-$), 2.40 (3H, s, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 168.0 (C═O), 163.4, 1.63.2, 160.2, 159.5, 139.2, 137.3, 134.3 (arom C), 129.1, 129.0, 127.6, 127.5, 127.4, 115.3, 115.0, 114.8, 114.5 (arom CH), 85.5 (>C–O), 47.2 (C-4), 46.5 ($-CH_2Ph$), 42.8 ($-CH_2-$), 28.6 (Me). Anal. calcd for $C_{39}H_{32}F_4N_2O_6{\cdot}2.5H_2O$: C, 62.81; H, 4.33; N, 3.76. Found: C, 62.83; H, 4.33; N, 3.78.

3.2.14. 4,4-Bis(2-hydroperoxy-2,2-diphenylethyl)-1,2-dibenzylpyrazolidine-3,5-dione (3da). Colorless blocks (from ethyl acetate–hexane); mp 205°C; IR (KBr) ν 3390 (OOH), 1733, 1676 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (2H, s, OOH), 7.43–7.10 (30H, m, arom H), 3.61 (4H, s, 2×$-CH_2-$), 3.48 (4H, s, 2×$-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8 (C═O), 142.7, 135.5 (arom C), 128.7, 128.2, 128.0, 127.9, 127.1, 125.7 (arom CH), 86.2 (>C–O), 47.86 (C-4), 47.2 ($-CH_2-$), 43.2 ($-CH_2-$). Anal. calcd for $C_{45}H_{40}N_2O_6{\cdot}1/2H_2O$: C, 75.71; H, 5.80; N, 3.92. Found: C, 75.72; H, 5.66; N, 3.86. FAB HRMS (acetone–NBA). Found: m/z 704.2982. Calcd for $C_{45}H_{40}N_2O_6$: M, 704.2886.

3.2.15. 4,4-Bis[2-hydroperoxy-2,2-bis(4-methylphenyl)-ethyl]-1,2-dibenzylpyrazolidine-3,5-dione (3db). Colorless blocks (from $CHCl_3$–hexane); mp 220–224°C; IR (KBr) ν 3323 (OOH), 1718, 1676 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (2H, s, OOH), 7.44–6.96 (26H, m, arom H), 3.63 (4H, s, 2×$-CH_2-$), 3.43(4H, s, 2×$-CH_2-$), 2.20 (12H, s, 4×4-$Me-C_6H_4$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2 (C═O), 140.1, 136.7, 135.6 (arom C), 128.7, 128.2, 127.8, 125.5 (arom CH), 86.1 (>C–O), 47.8 (C-4), 47.3 ($-CH_2-$), 43.3 ($-CH_2-$), 20.9 (Me). Anal. calcd for $C_{49}H_{48}N_2O_6{\cdot}1/2H_2O$: C, 76.43; H, 6.42; N, 3.63. Found: C, 76.47; H, 6.32; N, 3.58. FAB HRMS (acetone–NBA). Found: m/z 760.3512. Calcd for $C_{49}H_{48}N_2O_6$: M, 760.3539.

3.2.16. 4,4-Bis[2,2-bis(4-fluorophenyl)-2-hydroperoxy-ethyl]-1,2-dibenzylpyrazolidine-3,5-dione (3dc). Colorless blocks (from ethyl acetate–hexane); mp 210–212°C; IR (KBr) ν 3294 (OOH), 1732, 1676 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.85 (2H, s, OOH), 7.47–6.82 (26H, m, arom H), 3.76 (4H, s, 2×$-CH_2-$), 3.40 (4H, s, 2×$-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2 (C═O), 163.3, 160.0, 138.2, 135.0 (arom C), 128.9, 128.6, 128.1, 127.5, 127.4, 115.2, 114.9 (arom CH), 85.6 (>C–O), 47.3 (C-4), 47.1 ($-CH_2-$), 43.1 ($-CH_2-$). Anal. calcd for $C_{45}H_{36}N_2O_6F_4$: C, 69.58; H, 4.67; N, 3.61. Found: C, 69.51; H, 4.70; N, 3.70. FAB HRMS (acetone–NBA). Found: m/z 776.2512. Calcd for $C_{45}H_{36}N_2O_6F_4$: M, 776.2509.

3.2.17. Tetrahydro-4,4-bis(2-hydroperoxy-2,2-diphenylethyl)-1*H*-pyrazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (3ea). Colorless needles (from MeOH–hexane); mp 202–207°C (decompd); IR (KBr) ν 3415, 3307 (OOH), 1718, 1662 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.77 (2H, s, OOH), 7.32–7.11 (20H, m, arom H), 3.33 (4H, s, $-CH_2-$), 2.99 (4H, m, $-CH_2-$), 1.53 (4H, m, $-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5 (C═O), 142.8 (arom C), 127.8, 127.2 125.8 (arom CH), 86.1 (>C–O), 47.9 (C-4), 42.6 ($-CH_2-$), 41.7 ($-CH_2-$), 20.8 ($-CH_2-$). Anal. calcd for $C_{35}H_{34}N_2O_6$: C, 72.65; H, 5.92; N, 4.84. Found: C, 72.37; H, 5.89; N, 4.79.

3.3. Oxidation of a mixture of pyrazolidine-3,5-diones 1 and alkenes 2 with manganese(III) acetate at elevated temperature

A mixture of pyrazolidine-3,5-dione **1** (1 mmol) and alkene **2** (1 mmol) was stirred in glacial acetic acid (25 mL) in the presence of manganese(III) acetate dihydrate (2 mmol) at 80°C to reflux temperature shown in Table 2 using an oil-bath until the brown color of Mn(III) disappeared. The reaction mixture was then cooled, and the reaction was quenched by adding water (25 mL). The aqueous reaction mixture was extracted three times with CH_2Cl_2 (30 mL), and the combined extracts were 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. The obtained 4,4-bis(alkenyl)pyrazolidine-3,5-diones **4** were further purified by recrystallization from appropriate solvents as already mentioned.

3.3.1. 4,4-Bis(2,2-diphenylethenyl)-1,2-diphenylpyrazolidined-3,5-ione (4aa). Yellow cubes (from CH_2Cl_2–MeOH); mp 189–190°C; IR (KBr) ν 1753, 1714 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–6.85 (30H, m, arom H), 6.07 (2H, s, 2×CH═C<); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8 (C═O), 146.6 (–CH═C<), 142.3, 138.2, 134.9 (arom C), 130.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 126.2, 122.3 (arom CH), 123.5 (–CH═C<), 57.3 (C-4). Anal. calcd for $C_{43}H_{32}N_2O_2$: C, 84.84; H, 5.30; N, 4.60. Found: C, 84.84; H, 5.22; N, 4.68.

X-Ray crystallographic data of **4aa**. Empirical formula $C_{43}H_{32}N_2O_2$; formula weight 608.74; yellow needles; crystal dimensions 0.60×0.10×0.10 mm; monoclinic; space group $C2/c$(# 15); a=18.2013(4), b=9.5447(2), c=17.9951(5) Å, β=100.815(1)°, V=3070.7(1) Å^3, Z=4; D_{calcd}=1.317 g/cm^3; F_{000}=1280.00; μ (Mo K$_\alpha$)=0.81 cm^{-1}; $2\theta_{max}$=55.0°; no. of reflections measured 14066; no. of observations (I>3.00σ(I)) 3003; no. of variables 229; reflection/parameter ratio 13.11; R=0.043; R_w=0.054; GOF 2.54. The crystallographic data deposition number: CCDC 216766.

3.3.2. 4,4-Bis[2,2-bis(4-methylphenyl)ethenyl]-1,2-diphenylpyrazolidine-3,5-dione (4ab). Pale yellow needles (from CH_2Cl_2–hexane); mp 220°C; IR (KBr) ν 1753, 1710 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–6.74 (26H, m, arom H), 5.98 (2H, s, 2×CH═C<), 2.36 (6H, s, 2×CH_3), 2.26 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2 (C═O), 146.4 (–CH═C<), 139.8, 137.6, 137.5, 135.5, 135.0 (arom C), 130.4, 128.9, 128.5, 128.3, 127.5, 126.1, 122.5 (arom CH), 122.3 (–CH═C–), 57.4 (C-4), 21.3, 21.0 (CH_3). Anal. calcd for $C_{47}H_{40}N_2O_2{\cdot}1/2H_2O$: C, 83.77; H, 5.99; N, 4.15. Found: C, 83.90; H, 5.90; N, 4.05.

3.3.3. 4,4-Bis[2,2-bis(4-fluorophenyl)ethenyl]-1,2-diphenylpyrazolidine-3,5-dione (4ac). Yellow liquid; IR ($CHCl_3$) ν 1753, 1710 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–6.82 (26H, m, arom H), 5.97 (2H, s,

2×C*H*=C<); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9 (C=O), 164.4, 161.1, 161.0 (arom C), 145.0 (–CH=*C*<), 138.1, 138.0, 134.9, 133.8, 132.3, 132.2, 129.2, 129.1, 128.7, 126.6, 123.3 (arom CH), 122.0 (2×–*C*H=C–) 115.5, 115.3, 115.1, 114.8 (arom CH), 57.4 (C-4). FAB HRMS (acetone–NBA). Found: *m/z* 680.2119. Calcd for $C_{43}H_{28}N_2O_2F_4$: M, 680.2087.

3.3.4. 4,4-Bis[2,2-bis(4-methylphenyl)ethenyl]-1-benzyl-2-methylpyrazolidine-3,5-dione (4cb). Colorless microcrystals (from CH_2Cl_2–MeOH); mp 171°C; IR (KBr) ν 1735, 1681 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–6.76 (21H, m, arom H), 5.91 (2H, s, 2×C*H*=C<), 4.28 (2H, s, –CH_2Ph), 2.48 (3H, s, Me), 2.33 (6H, s, 2×CH_3, 4-*Me*C_6H_4); 2.28 (6H, s, 2×CH_3, 4-*Me*C_6H_4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 169.2 (C=O), 145.9, 139.7, 137.4, 137.3, 135.6, 135.4 (arom C), 130.3, 128.8, 128.5, 128.2, 128.0, 127.3, (arom CH), 123.2 (–*C*H=C<), 55.8 (C-4), 46.7 (–*C*H_2Ph), 29.3 (Me), 21.2 and 21.0 (4-*Me*C_6H_4). Anal. calcd for $C_{49}H_{44}N_2O_2$: C, 84.94; H, 6.40; N, 4.04. Found: C, 85.17; H, 6.38; N, 4.08.

3.3.5. 4,4-Bis[2,2-bis(4-methylphenyl)ethenyl]-1,2-dibenzylpyrazolidine-3,5-dione (4db). Colorless cubes (from CH_2Cl_2–diethyl ether–hexane); mp 183°C; IR (KBr) ν 1737, 1685 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–6.71 (26H, m, arom H), 5.85 (2H, s, 2×C*H*=C<), 4.13 (4H, s, 2×–CH_2Ph), 2.32 (6H, s, 2×CH_3), 2.28 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 (C=O), 145.8 (–CH=*C*<), 140.0, 137.4, 137.3, 135.7, 135.4 (arom C), 130.3, 128.6, 128.4, 127.8, 127.4 (arom CH), 122.6 (–*C*H=C<), 56.0 (C-4), 48.4 (–*C*H_2Ph), 21.2, 21.0 (CH_3). Anal. calcd for $C_{49}H_{44}N_2O_2$: C, 84.94; H, 6.40; N, 4.04. Found: C, 85.17; H, 6.38; N, 4.08.

3.3.6. Tetrahydro-2,2-bis(2,2-diphenylethenyl)-1*H*-pyrazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (4ea). Colorless cubes (from CH_2Cl_2–MeOH); mp 260°C; IR (KBr) ν 1737, 1687, 1679 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–6.98 (20H, m, arom H), 6.16 (2H, s, 2×C*H*=C<), 2.89 (4H, m, –CH_2–), 1.26 (4H, m, –CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 (C=O), 146.0 (–CH=*C*<), 141.8, 138.0 (arom C), 130.2, 127.9, 127.8, 127.5, 127.0 (arom CH), 125.5 (–*C*H=C<), 55.9 (C-4), 41.2 (–CH_2–), 21.1 (–CH_2–). Anal. calcd for $C_{35}H_{30}N_2O_2{\cdot}2/3H_2O$: C, 80.36; H, 5.74; N, 5.35. Found: C, 80.58; H, 5.86; N, 5.27.

3.3.7. Tetrahydro-2,2-bis[2,2-bis(4-methylphenyl)-ethenyl]-1*H*-pyrazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (4eb). Colorless microcrystals (from diethyl ether–hexane); mp 242°C; IR (KBr) ν 1720, 1670 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–6.85 (16H, m, arom H), 6.05 (2H, s, 2×–C*H*=C<), 2.95 (4H, m, –CH_2–), 2.34 (6H, s, 2×CH_3), 2.27 (6H, s, 2×CH_3), 1.30 (4H, m, –CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2 (C=O), 145.9 (–CH=*C*<), 139.4, 137.3, 137.0, 135.4 (arom C), 130.3, 128.5, 127.1, (arom CH), 124.5 (–*C*H=C<), 56.1 (C-4), 41.4 (–CH_2–), 21.2 (–CH_2–), 21.1 and 20.9 (Me). Anal. calcd for $C_{39}H_{38}N_2O_2{\cdot}1/2H_2O$: C, 81.28; H, 6.67; N, 4.86. Found: C, 81.03; H, 6.80; N, 4.89.

3.3.8. 1,2-Diethyl-4,4-bis[2,2-bis(4-methylphenyl)-ethenyl]pyrazolidine-3,5-dione (4fb). Colorless needles (from CH_2Cl_2–hexane); mp 148–150°C; IR (KBr) ν 1735, 1693, 1679 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23–6.72 (16H, m, arom H), 5.83 (2H, s, 2×–C*H*=C<), 3.20 (4H, q, *J*=6.9 Hz, 2×–CH_2–CH_3), 2.34 (6H, s, 2×4-*Me*–C_6H_4), 2.26 (6H, s, 2×4-*Me*–C_6H_4), 1.01 (6H, t, *J*=6.9 Hz, 2×–CH_2–CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0 (C=O), 145.6 (–CH=*C*<), 140.0, 137.3, 137.2, 135.5, (arom C), 130.3, 128.4, 127.3, (arom CH), 123.1 (–*C*H=C<), 56.1 (C-4), 38.3 (–*C*H_2–CH_3), 21.2 (Me), 20.9 (Me). Anal. calcd for $C_{39}H_{40}N_2O_2$: C, 82.36; H, 7.09; N, 4.93. Found: C, 82.52; H, 7.08; N, 4.86.

3.4. Reaction of pyrazolidinedione 1a with ethene 2a in the presence of ammonium cerium(IV) nitrate

To an ice-cooled solution of 1,2-diphenylpyrazolidine-3,5-dione (**1a**) (1 mmol) and 1,1-diphenylethene (**2a**) (1 mmol) in MeOH (15 mL), a solution of ammonium cerium(IV) nitrate (CAN) (2 mmol in 10 ml of methanol) was dropwise added in air. After the addition was completed, the reaction mixture was further stirred in air until the orange color of Ce(IV) disappeared (normally for 30 min). The reaction was quenched by adding water (25 mL). The aqueous reaction mixture was extracted three times with CH_2Cl_2 (30 mL), and the combined extract was washed with water, saturated brine, dried over anhydrous sodium sulfate, and then concentrated to dryness. The residue was separated by a silica gel column, eluted with ethyl acetate–hexane (7:3 v/v). The obtained product **5** was further purified by recrystallization from CH_2Cl_2–MeOH.

3.4.1. 4,4-Bis(2-methoxy-2,2-diphenylethyl)-1,2-diphenylpyrazolidine-3,5-dione (5). Colorless needles (from CH_2Cl_2–MeOH); mp 203–205°C; IR (KBr) ν 1762, 1732 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.07 (30H, m, arom H), 3.17 (4H, s, 2×CH_2–), 2.24 (6H, s, 2×OMe); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4 (C=O), 144.1, 136.9 (arom C), 128.1, 127.6, 127.5, 127.0, 124.8, 121.4 (arom CH), 81.6 (>C–O), 52.6 (2×OMe), 47.7 (C-4), 46.2 (2×–CH_2–). Anal. calcd for $C_{45}H_{40}N_2O_4{\cdot}1/3H_2O$: C, 76.62; H, 5.95; N, 4.13. Found: C, 76.86; H, 5.80; N, 4.01.

3.5. X-Ray crystallographic study

All measurements were made using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo K_α radiation (λ=0.71069 Å). The data reductions were carried out by the PROCESS-AUTO program package, and Lorentz and polarization corrections were performed. Corrections for the secondary extinctions were applied. The structures were solved by the direct method and were refined on SIR-92.[20] The refinements were done by the least-squares full matrix method, with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were included but not refined. All calculations were performed using the teXsan[21] crystallographic software package of Molecular Structure Corporation. The crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 216765 and 216766. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2

1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

4. Supplementary material

X-Ray structural informations for **3ac** and **4aa** are collected in Tables 3–5. Copies of FAB MS, IR, ^{1}H NMR, ^{13}C NMR, and DEPT spectra for **3ac**, and copies of IR, ^{1}H NMR, ^{13}C NMR, and DEPT spectra for **4aa**.

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