



Manganese(III) Acetate Initiated Oxidative Free Radical Reaction between 1,4-Naphthoquinone and α -Benzylmalonates

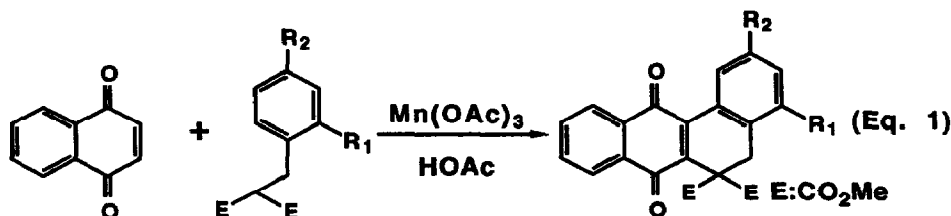
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Abstract: The manganese(III) initiated oxidative free radical reaction between 1,4-naphthoquinone and α -benzyl malonates giving benzo[a]anthraquinones is described.

Recently, there has been a growing interest in the application of free radical cyclization reactions to the formation of ring systems.¹ Benzo[a]anthraquinone systems have been found in various types of cytotoxic natural compounds,² and numerous synthetic approaches to such systems have been reported.³ The manganese(III) - based oxidative free radical reaction have been studied by several groups.^{4,5} These reactions can be performed intermolecularly and intramolecularly. The free radical addition of a carbon center radical to quinones has been reported.^{3a,6} This report described our preliminary results on the synthesis of benzo[a]anthraquinones from 1,4-naphthoquinone and α -benzylmalonates via manganese(III) initiated oxidative free radical reaction.

We began our studies with the reaction shown in equation 1. Thus, treatment of 1,4-naphthoquinone (0.78 mmol) and **1a** (1.63 mmol) with manganese(III) acetate (3.93 mmol) in acetic acid (10 ml) at 80°C for 8 h. The reaction mixture was diluted with ethyl acetate, washed successively with sat. aqueous sodium bicarbonate and water, then dried (Na_2SO_4). The crude product was purified by column chromatography and recrystallization to afford **2a** in 59% yield. The generality of this reaction is illustrated in Table I (Method A).



It is known that 1,4-dihydroquinones can be oxidized to 1,4-quinones by a variety of oxidants. We also studied the reaction shown in equation 1 by using 1,4-dihydroxynaphthalene as a starting material. When 1,4-dihydroxynaphthalene and **1a** (2 eq) was treated with manganese(III) acetate (6 eq), **2a** was obtained in 51% yield. The results also shown in Table I (Method B) are similar to those starting from 1,4-naphthoquinone.

Table I: The Free Radical Reaction Between 1,4-Naphthoquinone And Dimethyl α -Benzylmalonates

Entry	Substrate 1		Method	Yield
	R ₁	R ₂		
a	H	H	A	59%
			B	51%
b	H	CH ₃	A	51%
			B	58%
c	H	OCH ₃	A	58%
			B	54%
d	H	Br	A	51%
			B	40%
e	CH ₃	CH ₃	A	35%
			B	32%
f	CH ₃	H	A	32%

In conclusion, this oxidative free radical reaction provides a novel method for the synthesis of benzo[a]anthraquinones from readily available 1,4-naphthoquinone (or 1,4-dihydroxynaphthalene) and dimethyl α -benzylmalonates.

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