Insertion of an α-Diketo Group into a Strained Molecule *via* an Acyltetracarbonylferracycle

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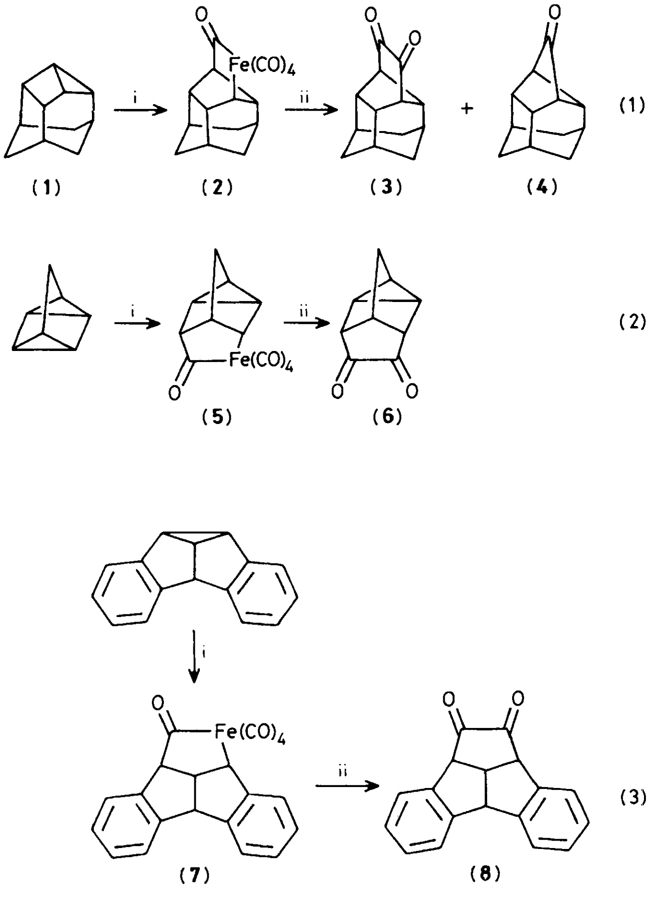
Acyltetracarbonylferracycles obtained from strained molecules and iron carbonyls on oxidative treatment with $CuCl_2$ afford α-diketones exclusively in good yields.

Insertion of a monoketo group into a strained molecule *via* its acylmetallacycle has been reported.[1] The reaction using a rhodium carbonyl species is representative: an oxidative insertion of $[Rh(CO)_2Cl_2]_2$ into a strained C–C σ-bond produces an acylrhodacycle, which, on subsequent treatment with triphenylphosphine, yields a monocarbonylated product.[2] In this communication, we report that the insertion of an α-diketo group into a strained molecule can be accomplished *via* the acyltetracarbonylferracycle to afford a two-carbon homologated α-diketone.

Irradiation of the 3,5-didehydronoriceane (**1**),[3] which contains a bicyclo[2.1.0]pentane system, in the presence of an



Reagents: i, $Fe(CO)_5$, $h\nu$ or $Fe_2(CO)_9$; ii, $CuCl_2$ or $FeCl_3$.

excess of $Fe(CO)_5$ in diethyl ether, afforded an acyltetracarbonylferracycle (**2**)† in 90% yield (equation 1).[4] The reaction of (**1**) with $Fe_2(CO)_9$ also gave (**2**) in 70% yield.

When (**2**) was oxidized with mild oxidizing agents such as $CuCl_2$ and $FeCl_3$, the α-diketone (**3**) was produced predominantly, along with a small amount of the monoketone (**4**) (equation 1). The results are summarized in Table 1. The best selectivity was obtained in the oxidation with $CuCl_2$ in aqueous MeCN, and (**3**) was produced almost exclusively in 94% yield. Thus, the net result is that an α-diketo group is inserted into a bicyclo[2.1.0]pentane system *via* an acyltetracarbonylferracycle in only two steps.

The above transformation can be applied to other strained systems as well. The acyltetracarbonylferracycle (**5**)[5] derived from quadricyclane was oxidized with $CuCl_2$ in aqueous MeCN to give the α-diketone (**6**)[6] exclusively in 81% yield (equation 2). Similarly, the oxidation of the acyltetracarbonylferracycle (**7**)[7] derived from dibenzosemibullvalene with $CuCl_2$ in aqueous MeCN afforded the α-diketone (**8**) exclusively in 78% yield (equation 3).‡

Table 1. Oxidation of (**2**).

Oxidizing agent	Aqueous solvent	Yield (**3**) + (**4**)/%[a]	Ratio (**3**)/(**4**)[b]
$CuCl_2$	Me_2CO	89	81/19
$CuCl_2$[c]	Me_2CO	91	84/16
$CuCl_2$	MeCN	94	97/3
$FeCl_3$	Me_2CO	92	69/31

[a] Isolated yield. [b] Determined by vapour pressure chromatography. [c] Under a CO atmosphere.

It is well-known that oxidation of a variety of acyclic and cyclic acylcarbonyliron complexes gives monocarbonylated products, *i.e.* carboxylic acids, esters, amides, ketones, β-lactams, and lactones, depending on the oxidation conditions.[1,9] However, to the best of our knowledge, there is no precedent for the formation of the dicarbonylated compounds reported here. Since it has been suggested that multiple CO insertions do not take place because of the inability of the acyl group to migrate,[9,10] the metallacyclic structure seems to be essential for reaction to occur. Although the precise mechanism remains to be clarified,§ the present sequence provides an effective method for insertion of an α-diketo group into a strained C–C σ-bond in only two steps *via* an acyltetracarbonylferracycle.

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† All new compounds gave spectral data (mass, i.r., ^1H and ^{13}C n.m.r.) consistent with the proposed structures.

‡ It has been reported (ref. 8) that oxidation of a tetracarbonylferracycle, but not (**7**), derived from dibenzosemibullvalene with Ce^{IV} induces a direct C–Fe bond cleavage to give a β-diketone without migratory insertion of a carbonyl group.

§ Oxidation with other oxidants gave different, rather complicated mixtures of products. It should be noted that Cu^{II} and Fe^{III} are typical one-electron oxidants (ref. 11).