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THE SELECTIVE FUNCTIONALIZATION OF SATURATED HYDROCARBONS. PART 28[1]. THE ACTIVATION OF BENZYLIC METHYLENE GROUPS UNDER GOAGG^{IV} AND GOAGG^{V} CONDITIONS

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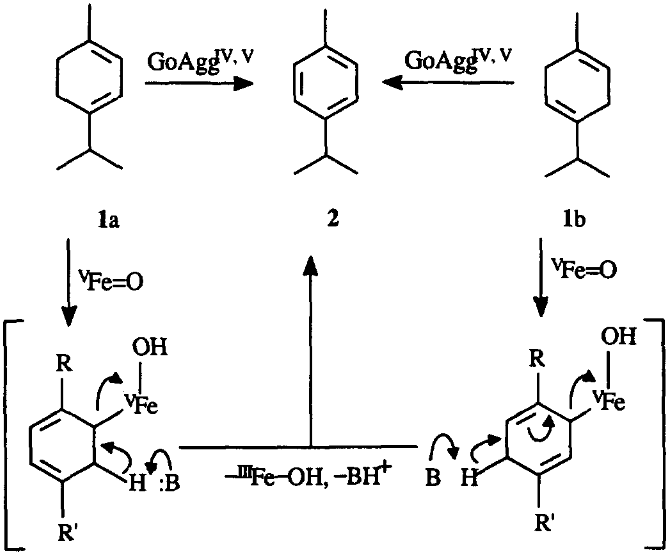
Abstract: Under GoAgg^{IV} and GoAgg^{V} conditions, cyclohexadienes were oxidized to give aromatic products instead of ketones and alcohols. At the same time, anthracene was oxidized to give anthraquinone. Under GoAgg^{IV} and GoAgg^{V} conditions, xanthene, fluorene and diphenylmethane were oxidized to give the corresponding xanthone, fluorenone and benzophenone following two possible pathways: a) alkane to alkyl t-butylperoxide to ketone, and b) alkane to ketone, in which alkyl hydroperoxide, derived from oxygen, may be the reaction intermediate. Xanthyl azide was formed when sodium azide was added to the reaction mixture of xanthene under GoAgg^{IV} and GoAgg^{V} conditions. The reaction of triphenylmethane under GoAggV conditions gave triphenylmethyl t-butyl peroxide as the major product and hydroperoxide as the minor product. When TEMPO was added, triphenylmethyl hydroperoxide was the only product.

Enzyme-catalyzed reactions involving dioxygen are found extensively in Nature, but their molecular mechanism are not so clear as in other biological reactions.[2] Using model compounds to emulate the enzymatic activity is an important approach to gain a deeper understanding of these biological processes.[3] We have developed a family of chemical systems named as Gif systems.[4] All of them involve a pyridine/acetic acid solution of the hydrocarbon being oxidized, an Fe-catalyst and an oxidant. Non-activated methylene groups were ketonized with near quantitative yield at conversions from 15% to 30%. Usually H_2O_2 was used as the oxidizing reagent. Recently t-butyl hydroperoxide (TBHP) has been recognized as a convenient source of activation.[5] Fe^{III}-catalyzed ketonization of saturated hydrocarbons by TBHP followed the pathway alkane to alkyl hydroperoxide to ketone or alcohol and dioxygen (O_2) was the precursor of oxygen atoms in hydroperoxide, alcohol and ketone. The dioxygen was mainly from the air. When oxygen was removed from the reaction mixture, the mixed alkyl t-butylperoxide and the corresponding olefin were the major products[6] Life chemistry, with certain rare and detectable exceptions, does not involve carbon radicals. We consider[4] that Fe^V oxenoid species are involved. These selectively react with saturated hydrocarbons at secondary position to furnish Fe^V-C bonded species (intermediate A). By trapping, many different functionalities can be introduced into saturated hydrocarbons from intermediate A.[7] Without traps intermediate A evolves into intermediate B, which has been thoroughly characterized as the corresponding hydroperoxide. Under normal conditions, intermediate B affords ketones (major product) and alcohols (minor product). Although Fe^V reagents have not yet been isolated, there is extensive circumstantial evidence for their existence.[4c] In the sequel we present a study of the ketonization of benzylic type methylene groups, and related reactions, using GoAgg^{IV} (Fe^{III}-TBHP) and GoAgg^{V} [Fe^{III}-TBHP + picolinic acid (PA)] conditions.

Results and Discussion



a, R=CH_3, R'=$CH(CH_3)_2$; b, R=CH_3, R'=$CH(CH_3)_2$

Table 1 Aromatization of Terpinenes under GoAgg^{IV} and GoAgg^{V} Conditions

Entry	Terpinene	PA mmol	NaSCN mmol	TBHP mmol	Time h	1 mmol	2 mmol	M.B. %
1	1a			10	0.5	9.77	0.04	98.1
2	1a			10	20	5.97	3.68	96.5
3	1b			10	0.5	8.76	0.82	95.8
4	1b			10	20	1.87	8.05	99.2
5	1a	3		10	0.5	1.49	7.81	97.3
6	1b	3		10	0.5	1.33	8.21	95.4
7a)	1b	3		10	1	0	8.57	99.5
8	1b	1.5		5	0.5	5.46	4.36	98.2
9b)	1b	3		10	0.5	5.75	4.00	97.5
10c)	1b	3		10	0.5	7.00	2.61	96.1
11d)	1b	3		5	0.5	8.53	1.35	98.8
12d)	1b	3		9	0.5	7.10	2.58	96.8
13c)	1bd)	3		5	2	8.54	1.63	101.7
14	1a		10	10	0.5	2.25	7.30	95.5
15	1b		10	10	0.5	3.74	5.93	96.7

Conditions: $Fe(NO_3)_3 \cdot 9H_2O$1 mmol,' Pyridine '30 mL, HOAc 3 mL, Terpinene 10 mmol, 20 °C under argon. G.C. Analysis. a) 1.28 mmol of 4-isopropylbenzoic acid were detected; b) -20 °C; c) -40 °C; d) 10 mmol of $P(OMe)_3$ were added. M.B.=Mass Balance

Under GoAgg^{IV} conditions, α- 1a and γ-terpinene 1b underwent aromatization to give p-cymene 2 as the only product;[7d] neither ketone nor alcohol were found. When NaSCN was added to the reaction system, no thiocyanate was detected, but it accelerated the aromatization (Table 1, Entry 14, 15). Under GoAgg^{V} conditions, the reaction was much faster (Entry 5-8). Blank experiments showed that there were no reactions taking place in the absence of the Fe^{III}-catalyst. One example (Entry 8) showed that the aromatic product was proportional to the amount of TBHP. We consider that 2 may be formed from the elimination of the reaction intermediate bearing an ^{V}Fe-C bond. The large driving force for aromatization resulted in a fast elimination. The life time of the reaction intermediate was very short and no other reactions were competitive. Under GoAgg^{V}conditions, the aromatization of γ-terpinene 1b took place even at -20° and -40° (Entry 9, 10). Therefore there must be ^{V}Fe=O and ^{V}Fe-C species formed at that low

Table 2 Competitions between **1a** and **1b**

Entry	PA mmol	NaSCN mmol	Time h	**1a**$^{a)}$ mmol	**1b**$^{a)}$ mmol	**2** mmol	M.B. %	(10-**1a**)/(10-**1b**)
1			20	8.64	7.24	4.21	100.5	1.60
2	1.5		0.5	8.73	5.88	4.8	97.5	3.24
3		5	0.5	8.66	7.86	4.12	103.2	2.04

Conditions: Terpinene 10 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Pyridine 30 mL, Acetic acid 3 mL, TBHP 5 mmol, 20 °C a) The amount left.

Table 3 The Reactions of **3** under GoAgg^{IV} Conditions

Entry	**3** mmol	Fe$^{III\ a)}$ mmol	NaSCN mmol	TBHP mmol	Time h	**3**$^{b)}$ mmol	**4** mmol	M.B. %
1	10	1		10	1	8.73	0.82	95.5
2	10	1		10	20	9.02	1.40	104.0
3	5	1	5	5	1	2.60	2.15	95.0
4	5	0.5	5	5	1	2.70	2.30	100.0
5	10	1	10	10	1	5.15	4.97	101.1
6	10	1	10	10	1	2.85	7.00$^{c)}$	98.5

Conditions: Pyridine 30 mL, Acetic acid 3 mL. 20 °C. Under argon. a) Fe^{III}= $Fe(NO_3)_3 \cdot 9H_2O$; b) The amount left; c) 10 mmol of cyclooctane was added and 0.44 mmol of cyclooctyl thiocyanate was detected after the reaction.

temperature. Under GoAgg^{V} conditions, the competition experiments between γ-terpinene **1b** and trimethylphosphite showed that the aromatization of γ-terpinene **1b** was competitive to the oxidation of trimethylphosphite (Entry 11-13). The alternative to formation of a discrete ^{V}Fe-C bond would be electron transfer. The first would require that **1a** would react faster than **1b**, which is not true. The second could also explain the observed results. The competition between α-terpinene **1a** and γ-terpinene **1b** under GoAgg^{IV}, GoAgg^{V} + NaSCN and GoAgg^{V} conditions showed that the skipped diene **1b** was more reactive than the conjugated diene **1a** (Table 2). It is of interest that a recent thorough study of the reaction of 1,4-dihydrobenzene (the analogue of **1a**) with hydroxyl radical in the presence of oxygen shows the formation of benzene as well as a plethora of oxidation products.[7e]

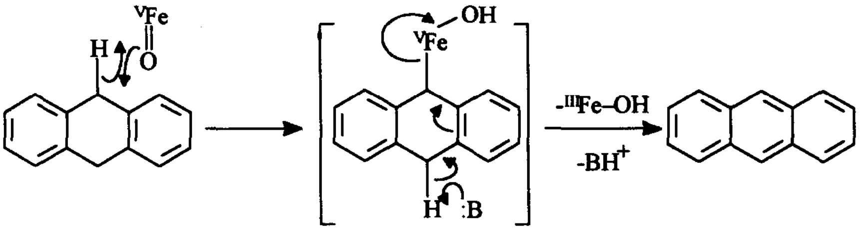
Under GoAgg^{IV} conditions (Table 3), 9,10-dihydroanthracene **3** underwent aromatization to give anthracene **4** instead of ketone and alcohol. Under GoAgg^{IV}

Table 4 Aromatizations of 9,10-Dihydroanthracene **3** under GoAgg^V Conditions

Enty	Temp °C	Conditions	TBHP mmol	**3** mmol	**4** mmol	**5** mmol	M. B. %
1	20	Ar	5	1.19	3.43	0.17	95.9
2	20	Air	5	0.92	2.02	1.32a)	97.6
3	20	100 psi O_2	5	0.74	0.07	2.88a)	98.2
4	20	65mmHg	5	1.04	3.60	0.20	96.8
5	0	15mmHg	5	3.70	1.07	0.03	96.0
6	20	15mmHg	5	2.02	2.60	0.13	95.0
7	20	Ar	10	0.08	4.12	0.80	100.0
8	20	Air	10	trace	2.28	2.52	96.0
9	20	15mmHg	10	1.28	3.23	0.39	98.0

Conditions: **3** 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine 30 mL, HOAc 3 mL; 1 h. All the results were based on ^1H NMR spectra. a).0.31 mmol of **6** was detected.

conditions, thiocyanation of 9,10-dihydroanthracene **3** failed, the only product wasanthracene **4** (Table 3, Entry 3-5). Under the same conditions, cyclooctane can be thiocyanated to give cyclooctyl thiocyanate.[7] But in the competition experiment between 9,10-dihydroanthracene **3** and cyclooctane, anthracene (70%) and cyclooctyl thiocyanate 4.4%) were detected (entry 6). The aromatization of **3** is 64 times faster than the thiocyanation of cyclooctane for each C-H bond.



3 **4**

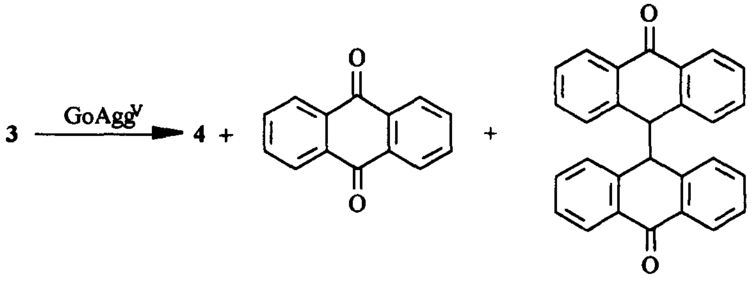
When the reaction of **3** under GoAgg^V conditions was run under argon, in addition to anthracene **4**, 9,10-anthraquinone **5** and bianthrone **6** were detected (Table 4, Entry 1, 7). When the reaction was run in the air, the amount of **5** was increased (Entry 2,

Table 5 Oxidation of Anthracene **4** under GoAgg^V Conditions

Entry	Time h	TBHP mmol	Temp °C	Conditions	**4** mmol	**5** mmol	**8** mmol	M.B. %
1	1	5	20	Ar	4.03	0.61	0.31	99.0
2	4	5	20	Ar	3.73	1.10	trace	96.4
3	20	5	20	Ar	3.75	1.17	trace	98.4
4	1	5	20	Air	3.61	0.87	0.38	97.2
5	20	5	20	Air	2.65	2.17	trace	96.2
6	1	10	20	Ar	3.01	1.30	0.56	97.4
7	1	5	20	15 mmHg	4.42	0.35	0.21	99.6
8	1	5	0	15 mmHg	4.61	0.13	trace	94.8

Reaction Conditions: **4** 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine 30 mL, HOAc 3 mL; All the results were based on ^1H NMR spectra

8). When 2 equiv of TBHP was used, the amounts of **4** and **5** were increased (Entry 7, 8). To prove the relation between the formation of anthraquinone **5** and oxygen in the air, the same reaction was run under vacuum and the amount of **5** was largely reduced (Entry 4-6, 9). Therefore the formation of **5** must be related to the dioxygen in the air. When the reaction was run under 100 psi oxygen pressure with 5 mmol of TBHP, 0.31 mmol of bianthrone **6** was detected (Entry 3).



5 **6**

A blank experiment showed that Fe^{III} can not catalyze the oxidation of anthracene **4** under air. Under GoAgg^V conditions, the reaction of **4** under air gave more product than under argon (Table 5, Entry 1-5). When the reaction was run under vacuum, the amount of **5** was reduced (Entry 7, 8). When the reaction of **3** was run under 100 psi oxygen pressure, the amount of **5** increased largely and that of **4** decreased proportionally

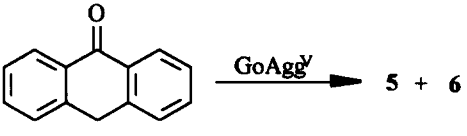
Table 6 Kinetics of the Oxidation of **4** under GoAgg^V Conditions

Entry	Time min	**4** mmol	**5** mmol	**8** mmol	M.B. %
1	3	4.71	0.18	0	97.8
2	5	4.23	0.23	0.26	94.4
3	15	4.44	0.19	0.22	97.0
4	30	4.11	0.59	0.30	99.8
5	60	3.76	0.87	0.38	100.2
6	20x60	2.83	2.17	trace	98.0

Reaction Conditions: **4** 5 mmol, $Fe(NO_3)_3{\cdot}9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine 30 mL, HOAc 3 mL, under air; All the samples were quenched by oxalic acid and all the results were based on ^1H NMR spectra

(Table 4, Entry 3). Therefore dioxygen is very important for the oxidation of **4** to **5**, even though it can not oxidize **4** to **5** directly. A kinetic study of oxidation of anthracene **4** under GoAgg^{V}conditions (Table 6) showed that the formation of anthraquinone **5** was comparable with that of anthracenediol **8**[8]. The latter resulted from the insertion of dioxygen into the ^{V}Fe-C bond as depicted later.

Anthrone exists in the ketonic form **9** as shown by its ^1H (CH_2, 3.95 ppm, s) and ^{13}C (C=O, 184.16, CH_2, 32.24 ppm) NMR spectra. With air anthrone **9** was slowly oxidized (Table 7, Entry 1) to anthraquinone **5** and bianthrone **6**. The addition of Fe^{III} catalyzed this process (Entry 2). However, under GoAgg^V conditions the reaction was much faster (Entry 3-6) and no anthrone **9** remained. The formation of dimer **6** was not affected by oxygen (Entry 4-6). These, and the proceeding results, suggested that anthrone **9** was isomerized to anthrol which was oxidized by ^{V}Fe=O to the corresponding stabilized phenoxy radical. Dimerization and prototropy then gave the dimer **6**. The latter is stable to GoAgg^V conditions. Anthrone **9** could be oxidized to **6** even with nitrobenzene.[9]



9

A kinetic study of the reaction 9,10 dihydroanthracene **3** showed that the formation of anthracene **4** was faster than that of **5** (Table 8 and Table 9). When the

Table 7 Reactionsof Anthrone **9** under GoAgg^{V} Conditions

Entry	Catalyst	Conditions	Temp. °C	TBHP mmol	**9**$^{a)}$ mmol	**5** mmol	**6** mmol	M.B. %
1	No	Air	20	0	4.50	0.26	0.05	97.2
2	Yes	Air	20	0	3.46	0.88	0.26	96.0
3	Yes	Ar	20	10	0	1.35	1.76	97.4
4	Yes	Air	20	5	0	0.97	1.93	96.5
5	Yes	Ar	20	5	0	0.88	1.99	97.2
6	Yes	15mmHg	0	5	0	0.80	2.16	102.0
7$^{b)}$	Yes	Air	20	2.5	0	0.59	2.18	99.0

Conditions: **9** 5 mmol, Catalyst=$Fe(NO_3)_3 \cdot 9H_2O$ (0.5 mmol) + Picolinic acid (1.5 mmol), Pyridine 30 mL, HOAc 3 mL, TBHP 5 mmol, 1 h; All the results were based on ^{1}H NMR spectr. a) the amount left; b) 5 mmol of anthracene was added and 4.9 mmol was recovered after the reaction.

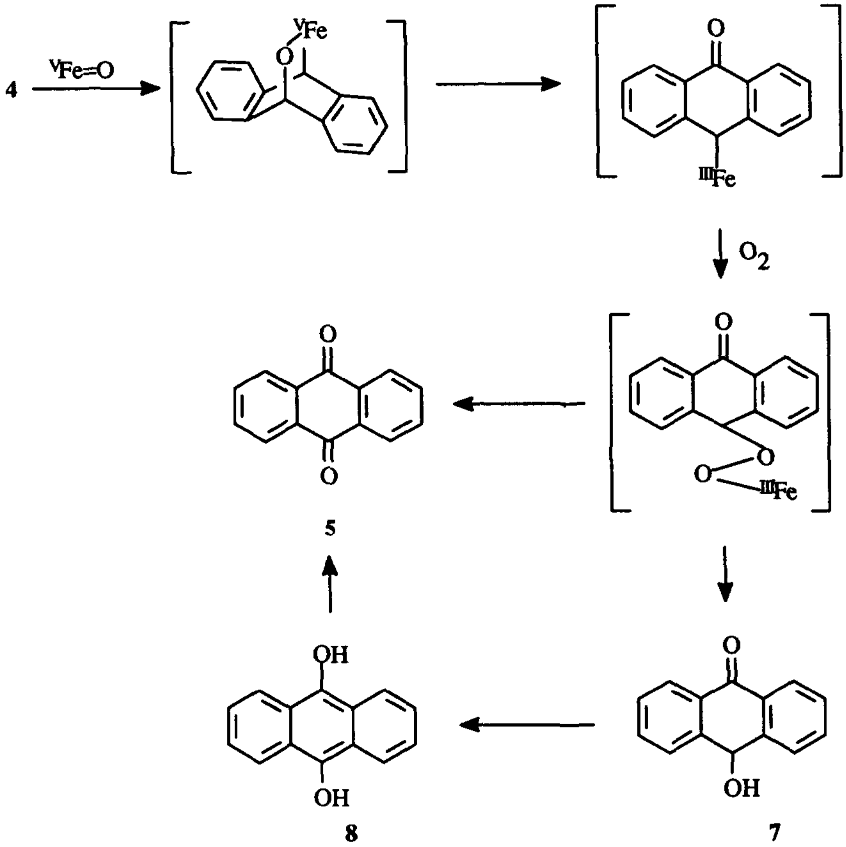
Table 8 Reactions of **3** with TBHP (5 mmol) under GoAgg^{V} Conditions

Entry	Time minute	**3** mmol	**4** mmol	**5** mmol	**6** mmol	**8** mmol	M.B. %
1	1	4.80	0.13	0	0	0.19	102.4
2	3	4.65	0.17	0.03	0	0.16	100.2
3	5	4.51	0.31	0.07	0	trace	97.8
4	10	4.02	0.48	0.30	trace	0	96.2
5	30	1.30	1.64	1.46	0.25	0	98.0
6	60	1.01	2.02	1.27	0.30	0	98.0

Reaction Conditions: **3** 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid, 1.5 mmol, Pyridine 30 mL, HOAc 3 mL, TBHP 5 mmol, under air; All the results were based on ^{1}H NMR spectra

reaction was run under air with 5 mmol of TBHP, 0.3 mmol of bianthrone **6** was detected (Table 8, Entry 6). Prosumably it resulted from the oxidative-coupling of anthrone **9**. **9** should be formed from the insertion of dioxygen into the ^{V}Fe-C bond. When 10 mmol of TBHP were used, no bianthrone **6** was detected (Table 9). The competition between anthracene **4** and anthrone **9** under GoAgg^{V} conditions under argon showed that all of the anthrone **9** was transformed to **6** and **5** (Table 7, Entry 7), while anthracene **4** remained unchanged. Anthrone **9** was much more easily oxidized than anthracene **4**.

Therefore anthrone **9** must not be the precursor of anthraquinone **5**, otherwise much **6** would have been detected. Therefore the probable precursor of anthraquinone **5** is anthracene **4**. A possible mechanism is proposed as follows:



To avoid the problem of aromatization, xanthene **10** was chosen as a substrate with a similar structure. Under $GoAgg^{V}$ conditions, the reaction of xanthene **10** gave xanthone **11** in 50% yield when the reaction was run under argon for 1 h (Table 10, Entry 1). When the reaction of **10** under $GoAgg^{V}$ conditions was run under vacuum 15 mmHg), xanthone **10** was obtained in 46% yield (Entry 2). Therefore the formation of **11** had nothing to do with the oxygen and it must have be formed in another way.

Table 9 Reactions of **3** with TBHP (10 mmol) under GoAggV Conditions

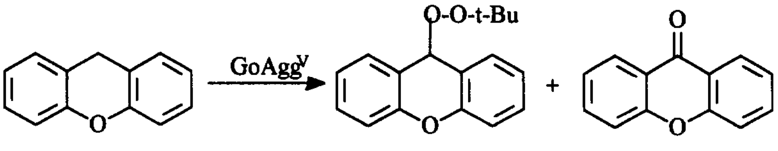
Entry	Time minute	**3** mmol	**4** mmol	**5** mmol	M.B. %
1	1	4.77	0.16	0	98.6
2	3	4.56	0.28	0.07	98.2
3	5	3.72	0.83	0.26	96.2
4	10	1.90	2.01	0.91	96.4
5	30	0.11	2.21	2.40	95.6
6	60	0	2.21	2.62	95.6
7	180	0	2.12	2.66	95.6

Reaction Conditions: **3** 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine 30 mL, HOAc 3 mL, TBHP 10 mmol, under air.; All the results were based on ^1H NMR spectra

Table 10 Oxidations of Xanthene**10** under GoAggV Conditions

Entry	Time min	TBHP mmol	**10** mmol	**12** mmol	**11** mmol	M.B. %
1	60	5	2.31	0	2.50	96.2
2	60	5	2.57	0	2.30	97.4
3	1	10	3.48	1.53	trace	100.2
4	2	10	2.50	2.38	o.11	99.8
5	3	10	1.32	3.24	0.17	94.6
6	5	10	0.71	3.78	0.42	98.2
7	15	10	0.38	3.04	1.38	96.0
8	30	10	0.50	2.33	2.01	96.8
9	60	10	0.59	1.31	3.01	98.2
10	20X60	10	0.73	trace	4.11	96.8

Conditions: **10** 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine 30 mL, HOAc 3 mL, 20 °C under argon. All the results were based on ^1H NMR spectra.



10 **12** **11**

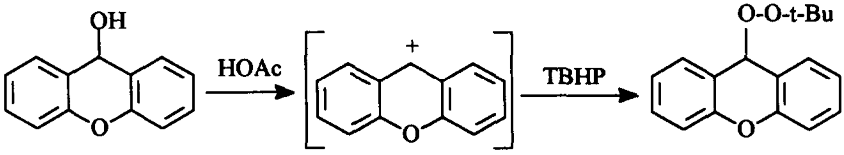
Table 11 Azidation under GoAgg^{IV} Conditions

Entry	Time h	**10** mmol	**12** mmol	**14** mmol	**11** mmol	M.B. %
1	1	4.25	0.29	0.29	0.17	96.0
2	2	4.41	0.13	0.17	0.15	97.2
3	3	3.85	0.26	0.58	0.13	96.4
4	20	2.25	0.46	1.74	0.30	95.o

Conditions: Xanthene 5 mmol, $Fe(NO_{33} \cdot 9H_2O$ 0.5 mmol, NaN_3 10 mmol, Pyridine 30 mL, HOAc 3 mL, TBHP 5 mmol, 20 °C under argon. All the results were based on ^1H NMR spectra.

The kinetics were studied by analysis of the products with the elapse of time. All of the samples were quenched by oxalic acid before work-up and analyzed by ^1H NMR spectra to avoid possible decomposition of some compounds during gas chromatography. The results (Table 10, Entry 3-10) showed that xanthyl t-butylperoxide **12** was the precursor of xanthone **11**. It formed from the ligand coupling of the ^VFe-C species with TBHP.

The mixed peroxide **12** can be prepared by the reaction of TBHP with 9-hydroxyxanthene **13** in acetic acid and the intermediate is a cation.[10]



13 **12**

The transformation of the peroxide **12** under various conditions was studied. In pyridine/acetic acid (9:1), only 15% was transformed to give xanthone **11** in 1 h. Experimental result showed that $Fe(NO_3)_3$ did not catalyze the transformation. When the peroxide was submitted to GoAgg^V conditions, 66% of the peroxide **12** transformed to xanthone **11** in 1h. Therefore the transformation of peroxide must have been catalyzed by the $^VFe{=}O$ species.

Blank experiments showed that xanthene **10** did not react with sodium azide to afford azide **14** in the presence of TBHP and absence of Fe^{III} catalyst. Under GoAgg^{IV} (Table 11) and GoAgg^V conditions (Table 12 and 13), the reaction of xanthene **10** in the presence of NaN_3 gave xanthyl azide **14**. Under GoAgg^V conditions, the formation of

Table 12 Azidation under GoAgg^{V} Conditions

Entry	Time min	**10** mmol	**12** mmol	**14** mmol	M.B. %
1	1	4.70	0.27	trace	99.4
2	3	4.26	0.38	o.17	96.2
3	5	4.20	0.32	0.18	94.0
4	10	3.90	0.59	0.37	97.2
5	30	2.85	0.62	1.32	95.8
6	60	2.2	0.52	2.27	96.2

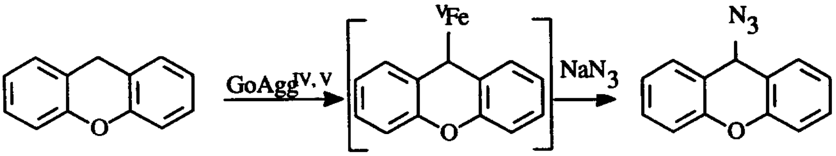
Conditions: **10** 5 mmol, $Fe(NO_3)_3{\cdot}9H_2O$ 0.5 mmol Picolinic acid 1.5 mmol, NaN_3 10 mmol, Pyridine 30 mL, HOAc 3 mL, TBHP 5 mmol, 20° C under argon. All the results were based on ^1H NMR spectra. Experimental result showed that there was no reaction between **12** and NaN_3 in pyridine/HOAc (10/1).

Table 13 Azidation under GoAgg^{V} Conditions

Entry	Time min	**10** mmol	**12** mmol	**14** mmol	M.B. %
1	1	4.68	0.12	0	96.0
2	3	4.61	0.19	0.11	98.2
3	5	4.41	0.25	0.09	95.0
4	10	4.66	0.31	0.14	102.2
5	30	4.02	0.45	0.56	100.6
6	60	3.02	0.49	1.29	96.0

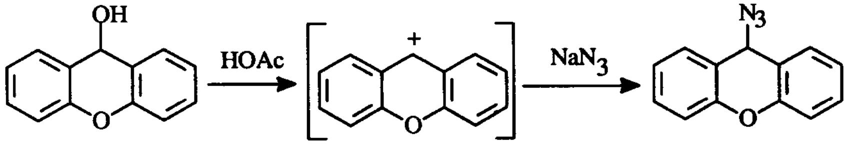
Conditions: **10** 5 mmol, $Fe(NO_3)_3{\cdot}9H_2O$ 0.5 mmol Picolinic acid 1.5 mmol, NaN_3 10 mmol, Pyridine 30 mL, HOAc 3 mL. The above mixture was stirred for 3 h at 20°C before the addition of TBHP. TBHP 5 mmol 20 °C under argon. The results were based on ^1H NMR spectra.

azide **14** was much faster than under GoAgg^{IV} conditions. When the mixture of Fe^{III}, picolinic acid, xanthene **10** and sodium azide in pyridine/HOAc was stirred for 3 h and then TBHP was added to start the reaction, the formation of azide **14** (Table 13) was slower than under GoAgg^{V} conditions (Table 12) but faster than under GoAgg^{IV} conditions (Table 11). Thus a possible ligand exchange from picolinic acid to azide resulted in the formation of a new complex containing picolinic acid and azide.



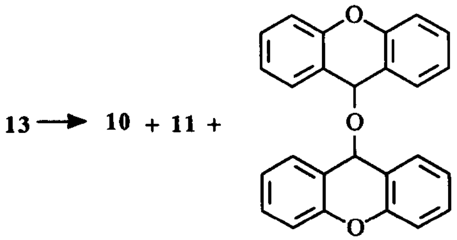
10 **14**

Xanthyl azide **14** was prepared by the reaction of NaN$_3$ with 9-hydroxyxanthene **13** in acetic acid *via* a cationic intermediate.



13 **14**

When the reaction of xanthene **10** under GoAgg^{V} conditions was run in the air, the same amount of xanthone **11** was obtained. The kinetic study (Table 18 in Experimental Section) showed that peroxide **12** was formed and transformed to xanthone **11**. At the same time, 9-hydroxyxanthene **13** was observed and dismutated to give xanthene **10**, xanthone **11** and dixanthyl ether **15**[11]. To prove the formation of 9-hydroxyxanthene **13** and dixanthyl ether **15**, the solution of 9-hydroxyxanthene **13** in pyridine/AcOH(10:1) was left to stand for 1 h at 20 °C. 80% of it dismutated to give xanthene **10** (22%), xanthone **11** (22%) and dixanthyl ether **15** (18%). The dismutation of **13** was reported already in the literature.[12]



15

Under GoAgg^{V} conditions, the reaction of xanthene **10** was run at -40 °C for 2 h and 8% of mixed peroxide **12** was detected. This meant that ^{V}Fe=O and ^{V}Fe-C species were formed even at -40 °C.

Under GoAgg^{IV} conditions, thiocyanation and azidation of fluorene **16** were not seen and, only a little fluorenone **18** was detected. When the reaction of fluorene **16**

Table 14 Oxidations of Fluorene **16** under GoAgg^V Conditions under Argon

Entry	Time min	**16** mmol	**17** mmol	**18** mmol	M.B. %
1	5	4.16	0.44	0.39	99.8
2	10	3.80	0.41	0.58	95.8
3	30	3.53	0.55	0.76	96.8
4	60	3.43	0.34	1.23	100.0
5	20x60	2.38	0	2.32	94.0
6	60	2.05	0.09	2.61$^{a)}$	95.0

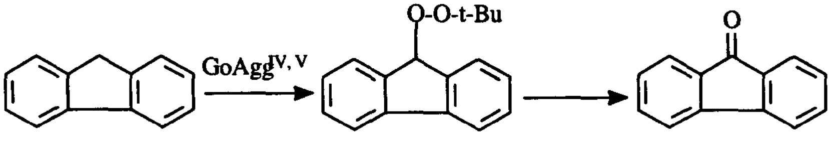
Conditions: Fluorene 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5mmol, Picolinic acid 1.5 mmol, Pyridine, 30 mL, HoAc 3 mL, Under argon. All the results were based on the ^1H NMR spectra. a) Tempo (1 mmol) was added.

Table 15 Oxidation of fluorene **16** under GoAggV Conditions under Air

Entry	Time min	**16** mmol	**17** mmol	**18** mmol	M.B. %
1	5	4.66	0	0.44	102.0
2	10	4.19	0.19	0.51	97.8
3	30	3.64	0.31	0.91	96.4
4	60	3.00	trace	1.87	97.4
5	20x60	1.48		3.37	97.0

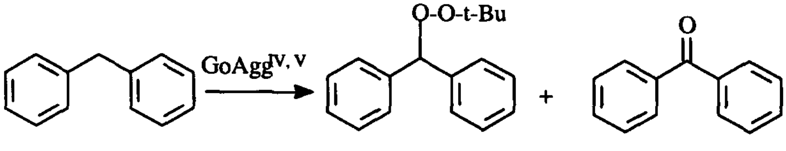
Conditions: Fluorene 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine, 30 mL, HoAc 3 mL, Under air. All the results were based on the ^1H NMR spectra.

under GoAgg^V conditions was run under argon, fluorenone **18** was formed. A kinetic study (Table 14) showed that fluorenyl t-butylperoxide **17**[13] was the precursor of fluorenone **18**. When the reaction was run under air (Table 15), fluorenone **18** appeared earlier than peroxide **17**, therefore the reaction intermediate could react with oxygen in the air to give the ketone **18** and with TBHP to give the mixed peroxide **17**. When 1 mmol of TEMPO was added to the reaction mixture of **16** under GoAgg^V conditions, more fluorenone **18** was obtained, but no coupling product was detected (Table 14, Entry 6). This suggested that the reaction intermediate was not a radical.



16 **17** **18**

The reaction of diphenylmethane **19** gave similar results to those obtained with fluorene **16**. When NaSCN or NaN_3 was added to the GoAgg^{IV} system, only a little benzophenone **21** was detected. Its reaction under GoAgg^{V} conditions gave a mixture of ketone **21** and diphenylmethyl t-butylperoxide **20**[14]. Ketone **21** must have been formed from the reaction of an intermediate with dioxygen, which resulted from the Fe^{III}-catalyzed decomposition of TBHP. A kinetic study showed that **20** was stable during the reaction (Table 19 in Experimental Section). When the reaction was run under air, peroxide **20** was not detected (Table 20 in Experimental Section). Therefore the ketone must be formed from the reaction of an intermediate with dioxygen.



19 **20** **21**

The reaction of triphenylmethane **22** was very slow. Under GoAgg^{IV} conditions, thiocyanate anion gave no products. Attempted azidation under GoAgg^{IV} conditions gave triphenylmethyl t-butylperoxide **23** and triphenylmethyl hydroperoxide **24** instead of azide (Table 16, Entry 6, 7). Under GoAgg^{V} conditions, triphenylmethane **22** was converted to mixed peroxide **23**[14] and to hydroperoxide **24**[14, 15] under argon. When the reaction was run in the air, more **24** was detected (Entry 4, 5).

$$\underset{\textbf{22}}{Ph_3C\text{–}H} \xrightarrow{\text{GoAgg}^{V}} \underset{\textbf{23}}{Ph_3C\text{-}O\text{-}O\text{-}t\text{-}Bu} + \underset{\textbf{24}}{Ph_3C\text{-}O\text{-}OH}$$

It was reported[16] that di-t-butyl nitroxide did not react with triphenylmethyl radical, but it reacted with triphenylmethyl cation or anion to form triphenylmethyl radical. TEMPO should show the same behavior. When the reaction of triphenylmethane under GoAgg^{V} conditions was run under argon (Entry 1-3), mixed peroxide **23** was the major product. Under vacuum, no hydroperoxide **24** was obtained (Entry 8, 9). When TEMPO

Table 16 The Reactions of Triphenylmethane **22** under GoAgg^V Conditions

Entry	Time h	NaN_3/TEMPO mmol	Ar/Air mmol	**22** mmol	**23** mmol	**24** mmol	**M.B.** %
1	10		Ar	4.62	0.20	trace	96.3
2	30		Ar	3.96	0.33	0.05	05.7
3	60		Ar	4.13	0.56	0.19	97.6
4	60		Air	3.92	0.62	0.23	95.4
5	20x60		Air	3.45	0.94	0.71	102.0
6	60	10a)	Ar	4.43	0.39	0.05	97.4
7	20x60	10a)	Ar	4.46	0.44	0.14	100.8
8	60		15 mmHg	4.43	0.49	0	98.4
9	20x60		15 mmHg	3.91	0.94	0	97.0
10	60	2b)	Ar	3.87	0	1.00	97.4
11	60	1b)	Ar	4.19	0	0.74	98.6
12	60	1b)	Air	4.27	0	0.49	95.2
13	20x60	1b)	Air	3.21	0	1.56	95.4

Conditions: Triphenylmethane 5 mmol, $Fe(NO_3)_3\cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol Pyridine 30 mL, HOAc 3 mL; The results were based on the ^1H NMR spectra. a) NaN_3; b) TEMPO.

Table 17 Relative Reaction Rates under GoAgg^V Conditions under Argon

Entry	Substrate	Relative rate	C-H bond strength (kcal/mol)
1	γ-terpinene	45.8	73±5[17]
2	α-terpinene	22.4	73±5[17]
3	xanthene	6.8	75[18]
4	9,10-dihydroanthracene	4.4	75.3±1.5[17]
5	fluorene	1.5	80[18]
6	diphenylmethane	1	81.4[17]
7	triphenylmethane	0.84	81[18], 75[19]
8	ehtylbenzene	0.4	84.4±1.4[17]
9	cyclooctane	0.2	94.5±1[17]

was added to the reaction mixture, the formation of peroxide **23** was diverted to the formation of hydroperoxide **24** (Entry 10-13). Since TEMPO does not react with triphenylmethyl radical, the addition of TEMPO would not expect to affect the reaction.[16]

Therefore the reaction in the presence or absence of TEMPO must be different. In the absence of TEMPO, the reaction intermediate was the ^{V}Fe-C species, which reacted with TBHP and dioxygen generated from the Fe^{III}-catalyzed dismutation of TBHP to form **23** and **24** respectively. This interesting TEMPO effect deserves more detailed investigation.

Relative reaction rates were determined by competition experiments and were normalized per C-H bond. All the results are shown in Table 17. These results showed that the reaction rates were not dependent on the strength of the C-H bond in every case.

Conclusions

We conclude from the above experiments that the ketonization of methylene groups conjugated with aromatic functionality under Fe^{III}-TBHP oxidation conditions follows the general pattern of Gif type oxidation and involves the chemistry of the ^{V}Fe-C bond. Bonding of TBHP to the ^{V}Fe-C species followed by ligand coupling affords the mixed t-butyl peroxide and Fe^{III}. Fragmentation of the mixed peroxide affords ketone and t-butanol. The second mechanism involves the insertion of oxygen into the Fe-C bond and gives, by fragmentation, the ketone or, by hydrolysis, the corresponding hydroperoxide. Triphenylmethane reacts only slowly showing that the C-H bond strength is not a controlling kinetic factor. It affords t-butyl mixed peroxide and the corresponding hydroperoxide.

Experimental Section

Melting points were determined with a Kofler hot stage apparatus and are not corrected. Proton and carbon spectra were run at 200 MHz or 50 MHz, respectively, on Varian XL-200 spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin Elmer Model 881 instrument. Gas chromatography was performed on a Hewlet Packard 5890 series instrument equipped with flame ionization detectors, with N_2 as a carrier gas. The columns used for chromatography were DB-WAX (30 m) or DB-5 (30 m) capillary columns from J&W Scientific (0.32 mm i.d.; 25 nm film thickness). Gas chromatography/mass spectrometry analysis was conducted on Hewlett-Packard gas chromatography Model 5890A coupled to a Hewlett-Packard 5971 mass selective detector (40eV, electron impact). Microanalyses were performed by Atlanta Microlab. Inc..

All the chemicals were purchased from commercial sources and, after verification, used without further purification. Authentic specimens of xanthyl t-butylperoxide[10], xanthyl hydroperoxide[10], dixanthyl ether[11], fluorenyl t-butylperoxide[13], diphenyl t-peroxide[14], triphenylmethyl t-butylperoxide[10] and triphenylmethyl hydroperoxide[14, 15] were prepared by following the literature procedure.

General Procedure for GoAgg^{IV} Reactions The substrate and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in pyridine/HOAc (10:1) in a 125 mL Erlenmeyer flask. TBHP was added dropwise with stirring to the mixture and the mixture was stirred for some time and worked up.

General Procedure for GoAgg^{V} Reactions The substrate and $Fe(NO_3)_3 \cdot 9H_2O$ and picolinic acid were dissolved in pyridine/HOAc (10:1) in a 125 mL Erlenmeyer flask. TBHP was added dropwise to the mixture with stirring and the mixture was stirred for some time and worked up. For kinetic studies, all the samples were quenched by oxalic acid before work-up.

Vacuum Experiments under GoAgg^{V} Conditions The same procedure as GoAggV reactions was followed but under vacuum. Volatiles were refluxed by a dry ice condenser. A second dry ice trap, in which nothing was found, verified that nothing volatile had escaped.

General Acidic Work-up: 1 mL aliquot of the reaction mixture was taken and poured into cold 25% sulfuric acid. The mixture was extracted with diethyl ether three times. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. The filtrate was analyzed by gas chromatography or gas chromatography/mass spectrometry after the introduction of an internal standard. For identification purpose, authentic samples of the appropriate compounds were coinjected with the reaction mixture samples. For quantification purpose, blank experiments concerning the work-up and gas chromatography response factors were carried out for each component to be detected. For NMR purposes, the above ethereal phases were evaporated to dryness in vacuum and the residue was dissolved in 0.8 mL of $CDCl_3$ (0.05% TMS). For quantification, an internal standard ($ClCH_2CH_2Cl$) was added.

. **Transformation of Xanthyl t-Butylperoxide 12** A solution of mixed peroxide **12** (1 mmol) in pyridine/acetic acid(10:1, 10 mL) was stirred for 1 h at 20 oC. After acidic work-up as above, ^1H NMR analysis showed that 0.85 mmol (85%) of peroxide **12** was recoverd and 0.15 mmol (15%) of xanthone **11** were found. When 1 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 3

Dismutation of 9-Hydroxyxanthene 13 A solution of hydroxyxanthene (1 mmol) in pyridine/acmmol of picolinic acid were added to the above mixture, after 1 h, 0.34 mmol (34%) Of **12** and 0.66 mmol (66%) of **11** were found.etic acid (10:1, 10 mL) was stirred for 1 h at 20 °C. After acidic work-up as above, ^1H NMR analysis showed

Table 18 Kinetic Study of the Formation of Xanthone **11** under Air

Entry	Time min	**10** mmol	**12** mmol	**13** mmol	**15** mmol	**11** mmol	M.B. %
1	1	3.19	0.90	0.46	0.15	0.22	101.0
2	3	1.90	0.56	1.25	0.50	0.40	102.2
3	5	0.92	0.31	2.72	0.30	0.36	98.2
4	30	1.61	0	0.54	0.42	1.65	92.4
5	60	1.99		0.56	0.33	1.89	102.0

Conditions: **10** 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol Picolinic acid 1.5 mmol, Pyridine 30 mL, HOAc 3 mL, TBHP 5 mmol, 20 °C under air. The results were based on ^1H NMR spectra.

Table 19 Kinetics of **19** under GoAgg^V Condition under Argon

Entry	Time min	**19** mmol	**20** mmol	**21** mmol	M.B. %
1	3	4.74	0	0.20	98.8
2	5	4.52	0	0.24	95.2
3	10	4.25	0	0.63	97.6
4	30	4.30	trace	0.61	98.2
5	60	3.45	0.43	0.94	96.4
6	5x60	2.45	0.74	1.55	94.8
7	20x60	2.46	0.81	1.60	97.4

a) 1 mmol of TEMPO was added. Conditions: **19** 5 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine, 30 mL, HoAc 3 mL, Under argon. All the results were based on the ^1H NMR spectra.

that 0.20 mmol (20%) of **13**, 0.22 mmol (22%) of xanthene **10**, 0.22 mmol (22%) of xanthone **11** and 0.18 mmol (18%) of xanthyl ether **15** were found.

Xanthyl Azide 14 A mixture of 9-hydroxyxanthene (12 , 1.98 g, 10 mmol) and NaN_3 (3.25 g, 50 mmol) in acetic acid (50 mL) was stirred for 3 h at 20 °C. Water (200 mL) was added and the mixture was extracted by CH_2Cl_2 (3X50 mL). The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent gave an oil which was purified by distillation under vacuum to give the title compound (**14**, 2.13 g, 95%). Bp, 110-20 °C/0.5 mmHg. IR (neat) 2088 ($N \equiv N$),

Table 20 Kinetic Study of **19** under GoAgg^V Condition under Air

Entry	Time min	**19** mmol	**21** mmol	M.B. %
1	5	4.63	0.25	97.6
2	10	4.19	0.53	94.4
3	20	4.05	0.71	95.2
4	60	3.38	1.45	96.6
5	20x60	2.48	2.32	96.0

Conditions: **19** 10 mmol, $Fe(NO_3)_3 \cdot 9H_2O$ 0.5 mmol, Picolinic acid 1.5 mmol, Pyridine, 30 mL, HoAc 3 mL, Under air. All the results were based on the ^1H NMR spectra.

1603, 1575, 1468, 1256, 1211, 751 cm^{-1}; ^1H NMR δ 7.26-7.41 (m, 3H), 7.06-7.16 (m, 2H), 5.44 ppm (s, 1H, CHN_3); ^{13}C NMR δ 151.287, 129.913, 129.421, 123.525, 117.792, 116.834, 56.833 ppm (CHN_3); Mass spectrum (M/Z) 196 (M-28), 195(100%, M-27), 168, 139; Anal. Calcd. for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82. Found C, 69.95; H. 3.99; N, 18.62.

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References

1, Part 26, Barton, D. H. R.; Chavasiri, W. *Tetrahedron*, submitted for publication, Part 27, Barton, D. H. R.; Chavasiri, W.; Hill, D. R.; Hu, B. *J. Am Chem. Soc.*, submitted for publication.

2, (a) Channa Reddy, C.; Hamilton, G. A.; Madyastha, K. M. In Biological Oxidation System; Academic Press: **1990**; San Diego, Vol, I, p xix-xx. (b) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, 17, 9. (c) Coon, M. J.; White, R. E. in *Metal Ion Activation of Dioxygen*, T. G. Spiro, Ed.; John Wiley and Sons, Inc. New York, **1980**. (d) Sligar, S. G.; Murray, R. J. *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Ortiz de Montellano P. R. Ed.; Plenum Press; New York, **1986**.p 429. (e) Groves, J. T. *J. Chem. Edu.* **1985**, 62, 928. (f) Poulous, T. L.; Finzel. B. C. Gunzalus, J. C.; Wagner, G. C.; Kraut, J. *J. Biol. Chem.* **1985**, 260, 16112. (g) Poulous, T. L.; Finzel. B. C.; Howard, A. J. *J. Biochemistry* **1986**, 25, 5314. (h) Mansuy, D. *Pure & Appl.*

Chem. **1987**, 59, 759. (i) Murch, B. P.; Bradley, F. C.; Que, L. Jr. *J. Am Chem. Soc.* **1986**, 108, 5027-5028. (j) Vincent, J. B.; Huffman, J. C.; Christou, G.; Li. Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *Ibid.* **1988**, 110, 6898. (k) Kitajima,N.; Fukui, H.; Mero-Oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 485. (l) Fox, B. G.; Froland, W. A.; Dege, J. E.; Lipscomb, J. D. *J. Biol. Chem.* **1989**, 264, 10023. (m) Green, J.; Dalton, H. *Ibid.* **1988**, 263, 17561. (n) Erickson, A.; Hedman, B.; Hodgson, K. O.; Green, J.; Dalton, H.; Bestsen, J. G.; Ber, R. H.; Lippard, S. *J. Am. Chem. Soc.* **1988**, 110, 2300. (o)Fox, B. G.; Surturs, K. K.; Munck, E.; Lipscomb, J. D. *J. Biol. Chem.* **1988**, 263, 10553. (p) Green, J. Dalton, H. J. *Ibid.* **1989**, 264, 17698.

3 (a) Clark, T.; Mckervey, M. A.; in *Comprehensive Organic Chemistry*, Barton, D. H. R.; Ollis, W. D.; Stoddart, J. F. Ed.; Pergamon Press; Oxford, **1979**; Vol. I, p 109. (b) Kurusu, Y.; Neckers, D. C. *J. Org. Chem.* **1991**, 56, 1982-1983. (c) Kitajima, N.; Ito, M.; Fukui, H.; Moro-oka, Y. *J. Chem Soc., Chem. Commun.* **1991**, 102-104. (d) Briffaud, T.; Larpent, C.; Patin, H. *Ibid.* **1990**, 1193-1194. (e) Norman, R. E.; Yan, S.; Que, Jr., L.; Bakes, G.; Ling, J.; Sandos-Lohr, J.; Zhang, J. H.; O'Connor, C. J. *J. Am. Chem. Soc.* **1990**, 112, 1554-1562. (f) Traylor, T. G.; Xu, F. *Ibid.* **1990**, 112, 178-186. (g) Sheu, C.; Sawyer, D. T. *Ibid.* **1990**, 112, 8212-8213. (h) Borovik, A. S; Hendrich, M. P.; Holman, T. R.; Munck, E.; Papaefthymiou, V.; Que, Jr. L. *Ibid.* **1990**, 112, 6031-6038. (i) Kitajima, N.; Fukui, H.; Moro-oka. Y. *J. Chem. Soc., Chem. Commun.* **1988**, 485-486. (j) Gorum. S. M.; Papaefthymiou. G. C.; Frankel. R. B.; Lippard, S. J. *J. Am. Chem,. Soc.* **1987**, 109, 3337-3348. (k) Murch, B. P.; Bradley, F. C.; Que, Jr., L. *Ibid.* **1986**, 108, 5027-5028. (l) Traylor, T. G.; Lee. W. A.; Lippard. S. J. *Ibid.* **1983**, 105, 4837-4838. (m) Leddy, B. P.; Merkervery, M. A.; McSweeny, P. *Tetrahedron Lett.* **1980**, 21, 2261. (n) Ingold, K. U. *Aldrichimica Acta*, **1989**, 22, 69. (o) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, **1981**, Chapter 11. (p) Meunier, B. *Chem. Rev.* **1992**, 92, 1411. (q) Khenkin, A. M.; Shilov, A. E. *New J. Chem.* **1989**, 17, 9. (r) Akhtar, M.; Wright, J. N. *Nat. Prod. Report* **1991**, 527. (s) McMurry, T. J.; Groves, J. T. *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Ortiz de Montellano P. R. Ed.; Plenum Press; New York, **1986**.

4, (a) Barton, D. H.R.; Gastiger, M. J.; Motherwell, W. B. *J. Chem. Soc. Chem Commun.*, 1983, 41-43; (c) Barton. D. H. R.; Halley, F.; Ozbalik, N.; Schmitt, M.; Young, E.; Balavoine, G. *J. Am. Chem. Soc.* **1989**, 111, 7114-7149. (c) Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, 25, 504-512.

5, (a) Faraj, M.; Hill, C. J. *J. Ckem. Soc., Chem. Commun.* **1987**, 1487-1489. (b) Fish, R. H.; Fong, R. H.; Vincent, J. B.; Christou, G. *Ibid.* 1988, 1504-1506. (c) Leising. R. A.; Norman. R. E.; Que, Jr. L. *Inorg. Chem.* **1990**, 29, 2555-2557. (d) Sarneski, J. E.;

Michos, D.; Thorp, H. H.; Diduik, M.; Poon, T.; Blewitt, J.; Bruwig, G. W.; Crabtree, R. *Tetrahedron Lett.* **1991**, 32, 1153-1156.

6, Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Doller, D.; Hu, B. *Tetrahedron Lett.* **1992**, 33, 5473-76.

7, (a) Barton, D. H. R.; Csuhai; E.; Doller, D.; Hu, B. *Tetrahedron Lett,* **1992**, 33, 3313-3316. (b) Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Doller, D.; Hu, B. *Ibid.* **1992**, 34, 9195-9206. (c)Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Doller, D.; Hu, B. *Ibid.* **1993**, 34, 1871-1874; (d) An example of the aromatization of γ-terpinene under GoAgg^{IV} conditions gave similar results: Chavasiri, W. Ph. D. Dissertation; Texas A&M University, **1990**; p158. (e) Pan, X. M.; Schuchmann, M. N.; Sonntag, C. von *J. Chem. Soc. Perkin. Trans. 2* **1993**, 1021-1028.

8, Meyer, K. H. *Annalen.* **1911**, 37-73.

9, Ingram. V. M. *J. Chem. Soc.* **1950**, 2246-2247.

10, Davis, A. G.; Foster, R. V.; White, A. M. *J. Chem. Soc.* **1954**, 2200.

11, Cupoano,, L.; Zander, R.; Bolour, A. *Chem. Ber.* **1971**, 104, 3750-3756.

12, Balfe, M. P.; Kenyon, J.; Thain, E. M. *J. Chem. Soc.* **1952**, 790-5.

13, a) Muzart, J. *Tetrahedron Lett.* **1986**, 27, 3138; b) Idem, *Syn. Commun.* **1989**, 2061.

14, Davis, A. G.; Feid, J. *J. Chem. Soc.* **1956**, 4669.

15, Wieland, H.; Maier, J. *Ber.* **1931**, 64b, 1205-1210.

16, Singh, H.; Tedder, J. M. *J. Chem. Soc. Chem. Commun.* **1981**, 70-71.

17, Lide, D. R. Ed.; *CRC Handbook of Chemistry and Physics*, 71st Ed.; CRC Press; Boca Raton, Fl, **1990-1991**, p 9-95-6.

18, Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1992**, 114, 9787-9792.

19, Szwarc, M. *Proc. Roy. Soc. London; Sect A* **1951**, A207, 5-13.

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