

FUNCTIONALISATION OF SATURATED HYDROCARBONS. PART XVII.<sup>1</sup> REACTIVITY OF  
CARBON-CARBON DOUBLE BONDS.

Derek H. R. Barton\*, Kyu Wan Lee<sup>2</sup>, Wolf Mehl, Nubar Ozbalik and Li Zhang

Department of Chemistry, Texas A&M University, College Station, TX 77843 and

Korea Research Institute of Chemical Technology, P. O. Box 9,

Daedeog-Danji, Taejeon

Chungnam, Korea 305-606

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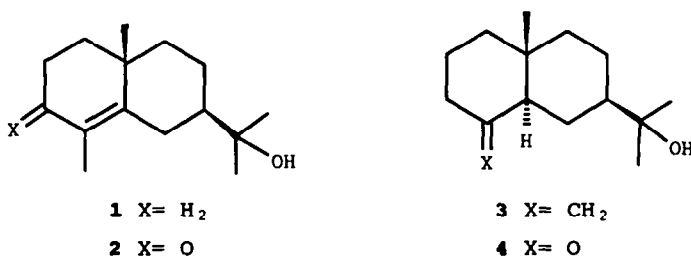
**Abstract:** The Gif oxidation systems cleave methylenediolefins into the ketone or aldehyde and formaldehyde. This is considered to be a further manifestation of an <sup>V</sup>Fe oxenoid species. Similarly, more substituted olefins are oxidized to the corresponding unsaturated ketones or aldehydes. The oxidation of limonene afforded the ketone **24** resulting from methylene cleavage and racemic carvone **25**. The latter is considered to originate from a symmetrical  $\pi$ -allyl complex of iron.

We have devised a number of systems for the selective oxidation of saturated hydrocarbons to afford ketones.<sup>3</sup> Names, based on geography, have been given to five variants of the original Gif system. Thus, Gif<sup>111</sup> is iron powder suspended in pyridine-acetic acid with oxygen or simply open to the air.<sup>4</sup> Gif<sup>1V</sup> is the same with a catalytic amount of an iron species and suspended zinc dust to provide the electron input.<sup>5</sup> Gif-Orsay is the same as Gif<sup>1V</sup>, but with zinc dust replaced by the cathode of an electrochemical cell.<sup>1,6</sup> It is a much more efficient system with respect to electron input. Finally<sup>7</sup>, we have added GoAgg<sup>1</sup>(pyridine/acetic acid/stoichiometric <sup>11</sup>Fe-KO<sub>2</sub> under argon) and GoAgg<sup>11</sup>(pyridine/acetic acid/catalytic <sup>111</sup>Fe-H<sub>2</sub>O<sub>2</sub> under argon or air). The name comes from G for Gif, O for Orsay and Agg for Texas A&M. We believe that all these systems have a common <sup>V</sup>Fe=O species responsible for the chemistry.<sup>7</sup>

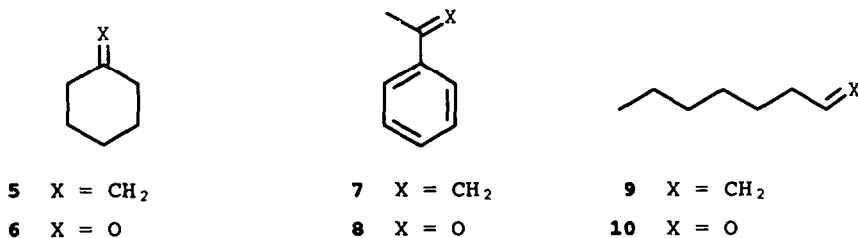
These systems show a remarkable selectivity for hydrocarbon oxidation even in the presence of large amounts of isopropyl alcohol, ethanol<sup>1,6</sup> or

even acetaldehyde.<sup>8</sup> Another curious fact is that cyclic hydrocarbons are oxidized at about the same rate as the corresponding olefins.<sup>9</sup>

The oxidation of cyclohexene affords cyclohexenone, not cyclohexene epoxide.<sup>3</sup> Various natural products behave in the same way.<sup>10, 11</sup> For example, oxidation of  $\gamma$ -eudesmol **1** under Gif<sup>IV</sup> conditions gave carissone **2**. However,  $\beta$ -eudesmol **3** behaved in a different way and the cleavage ketone **4** was the only product isolated. This paper is a more detailed study of these two different reactions.



We find that all olefins that contain the grouping C=CH<sub>2</sub> are cleaved by the Gif family of systems. In contrast, all the trisubstituted olefins are oxidized at the allylic position to unsaturated ketones or aldehydes. Some results are summarized in Table 1. Methylene cyclohexane **5** gave substantial yields of cyclohexanone **6**.  $\alpha$ -Methylstyrene **7** afforded nearly 30% of the corresponding ketone **8**.



Oct-1-ene **9** furnished the corresponding aldehyde **10**. A blank experiment showed that the aldehyde was further transformed under the oxidation conditions. Finally, 1,1-diphenylethylene gave excellent cleavage with Gif<sup>III</sup>, Gif<sup>IV</sup> and GoAgg<sup>II</sup> to afford benzophenone.

In relation with the results in Table 1 we carried out the appropriate

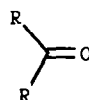
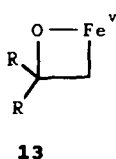
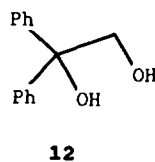
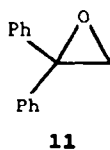
blank experiments to show that without iron, no reaction took place. Also, we showed that the epoxides, e.g. **11**, were not intermediates on the route to cleavage to ketone. We also showed that the 1,2-glycols, e.g. **12**, were not cleaved to a significant extent.

Table 1

OXIDATIVE CLEAVAGE OF THE METHYLIDENE GROUP  
BY GIF TYPE SYSTEMS

Entry	Oxidation System	Substrate (mmol)	Product (% Yield)	Percent of substrate recovered
1	Gif <sup>IV</sup>	<b>5</b> (1.9)	<b>6</b> (17)	n.d. <sup>a</sup>
2	GoAgg <sup>I</sup>	<b>5</b> (2.0)	<b>6</b> (3.1)	n.d.
3	GoAgg <sup>II</sup>	<b>5</b> (2.0)	<b>6</b> (9.2)	n.d.
4	Gif <sup>III</sup>	<b>7</b> (5.0)	<b>8</b> (27)	42
5	GoAgg <sup>II</sup>	<b>7</b> (5.0)	<b>8</b> (29)	36
6	Gif <sup>IV</sup>	<b>9</b> (2.0)	<b>10</b> (7.5)	40
7	Gif <sup>III</sup>	<b>9</b> (2.0)	<b>10</b> (8.1)	n.d.
8	GoAgg <sup>II</sup>	<b>9</b> (2.0)	<b>10</b> (4.4)	38
9	Gif <sup>IV</sup>	<b>15</b> (2.0)	<b>16</b> (45)	21
10	GoAgg <sup>II</sup>	<b>15</b> (2.3)	<b>16</b> (24)	46

<sup>a</sup> not determined



Recent work has shown<sup>7</sup> that all the Gif type systems depend for their selectivity on a common iron oxenoid species. We have postulated this to be an <sup>V</sup>Fe species on the basis of logical arguments. It is thus comparable to the radicaloid species <sup>IV</sup>Fe=O(+·) or <sup>III</sup>Fe-O·(+·) involved in P<sub>450</sub> model studies based on porphyrin ligands.<sup>12,13</sup> In terms of our theory, we would postulate the addition of the <sup>V</sup>Fe oxenoid species to the double bond 13 followed by cleavage to the ketone and a methylene carbene 14. We would expect the latter to be oxidized to formaldehyde. Table 2 summarizes a number of experiments which show that formaldehyde is indeed formed. Blank experiments demonstrated that formaldehyde was not formed without substrate,

**Table 2**

QUANTIFICATION OF CH<sub>2</sub>=O FORMED IN THE GIF REACTIONS IN THE FORM OF DIMEDONE ADDUCT<sup>a</sup>

Entry	Reaction Type	Substrate (mmol)	% Yield	Product mmol (N)	Dimedone Adduct mmol (M)	%CH <sub>2</sub> O [(M/N)x100]
1 <sup>b</sup>	Gif <sup>IV</sup>	5 (1.9)	17	6 0.33	0.054	16
2 <sup>c</sup>	Gif <sup>IV</sup>	15 (2.0)	27	16 0.54	0.084	15
3 <sup>b</sup>	GoAgg <sup>I</sup>	15 (2.3)	24	16 0.55	0.021	3.8
4 <sup>b</sup>	Gif <sup>IV</sup>	23 (6.0)	12	24 0.72	0.066	9.2
5 <sup>d</sup>	Gif <sup>IV</sup>	23 (6.0)	12	24 0.72	0.051	7.1

<sup>a</sup> Work-up procedure and quantification method are described in the experimental section.

<sup>b</sup> 1.0 mmol of dimedone was used.

<sup>c</sup> The Gif reaction was carried out under positive pressure (balloon) of oxygen; 5.0 mmol of dimedone was used.

<sup>d</sup> 2.0 mmol of dimedone was added after the reaction and stirring was continued for 3 more hours.

but that added in the same quantity as the ketone, it was only recovered, after conversion to the dimedone adduct, in 13% yield. Hence the data in Table 2 are compatible with the formation and cleavage of the iron-methylene carbene 14.

$\text{Ar}_2\text{C}=\text{CH}_2$	$\text{Ar}_2\text{C}=\text{O}$
15 Ar= Ph	16 Ar= Ph
17 Ar= <i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	18 Ar= <i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$
19 Ar= <i>p</i> - $\text{BrC}_6\text{H}_4$	20 Ar= <i>p</i> - $\text{BrC}_6\text{H}_4$
21 Ar= <i>p</i> - $\text{ClC}_6\text{H}_4$	22 Ar= <i>p</i> - $\text{ClC}_6\text{H}_4$

**Table 3**

GOAGG<sup>11</sup> OXIDATIONS OF *p*-SUBSTITUTED 1,1-DIARYLETHYLENES  
AND THEIR COMPETITION WITH 1,1-DIPHENYLETHYLENE<sup>a</sup>

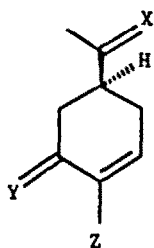
Entry	Substrate(s)	Products (%)	Substrate Recovery (%)	Mass Balance %	Reactivity Ratio <sup>b</sup>
1	15	16(11)	15(89)	15(100)	--
2 <sup>c</sup>	17	18(14)	17(87)	17(101)	--
3 <sup>c</sup>	15, 17	16(7.9), 18(12)	15(92), 17(83)	15(100), 17(95)	1.5
4	19	20(10)	19(89)	19(99)	--
5	15, 19	16(9.4), 20(6.2)	15(91), 19(88)	15(100), 19(94)	0.66
6	21	22(10)	21(86)	21(96)	--
7	15, 21	16(8.6), 22(5.9)	15(91), 21(94)	15(100), 21(100)	0.69

<sup>a</sup> 2.0 mmole of each substrate was oxidized using 27 mg (0.1 mmol)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.1 (0.9 mmol) 30% aqueous  $\text{H}_2\text{O}_2$ , 5.0 ml pyridine and 1.0 ml acetic acid.

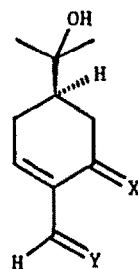
<sup>b</sup> Ratio of substituted ketone to benzophenone.

<sup>c</sup> 7.0 ml of pyridine instead of 5.0 was used due to limited solubility of compound 17.

The  $^V\text{Fe}$  oxenoid species postulated to explain Gif system reactivity is sensitive to steric hindrance and is weakly electrophilic in character. Thus, the introduction of one ketone into a cyclohexanone ring deactivates that ring, and also an adjacent one, toward further ketone formation.<sup>10</sup> The cleavage reaction that we have demonstrated here gave us another opportunity to examine the electrophilicity of the  $^V\text{Fe}$  oxenoid species. A series of 1,1-diarylethylenes was synthesized (17, 19 and 21) and oxidized separately under  $\text{GoAg}^{\text{I}}$  conditions. 1,1-Diphenylethylene 11 was also oxidized under the same conditions. The results are summarized in Table 3. The yield of the *p*-methoxybenzophenone 18 was superior to that of benzophenone, which in turn was superior to *p*-bromo- 20 and *p*-chloro- 22 benzophenones. The conclusion is that the most electron rich olefin is the most reactive toward the  $^V\text{Fe}$  oxenoid species.



- 23 X= CH<sub>2</sub>, Y= H<sub>2</sub>, Z= CH<sub>3</sub>  
 24 X= O, Y= H<sub>2</sub>, Z= CH<sub>3</sub>  
 25 X= CH<sub>2</sub>, Y= O, Z= CH<sub>3</sub>  
 26 X= CH<sub>2</sub>, Y= H<sub>2</sub>, Z= CHO



- 27 X= H<sub>2</sub> Y= H<sub>2</sub>  
 28 X= O, Y= H<sub>2</sub>  
 29 X= H<sub>2</sub> Y= O

This deduction was verified by a series of competitive oxidations in which each of the substituted olefins 17, 19 and 21 was mixed with an equimolar amount of 1,1-diphenylethylene 15 and oxidized together. The reactivity ratios in Table 3 confirm that the *p*-methoxy-substrate 18 is more reactive by 1.5 than the unsubstituted olefin 15. The *p*-bromo- and *p*-chloro- isomers 19 and 21 respectively are again shown to be less reactive than 15.

The oxidation of R-(+)-limonene 23 permitted us to study double bond cleavage and unsaturated ketone formation at the same time. The

Table 4

 OXIDATION OF R-(+)-LIMONENE **23** BY GIF SYSTEMS  
 UNDER VARIOUS CONDITIONS

Entry	Conditions	Products % Yield			Percent Recovery <b>23</b>	Mass Balance
		<b>24</b>	<b>25</b>	<b>26</b>		
1	Gif <sup>IV</sup> , RT 0.10 mmol FeCl <sub>2</sub>	7.7	3.7	0.9	88	100
2	Gif <sup>IV</sup> , RT 0.05 mmol FeCl <sub>2</sub>	9.7	4.9	1.3	83	99
3	Gif <sup>IV</sup> , RT 0.01 mmol FeCl <sub>2</sub>	10	5.3	1.5	80	97
4	Gif <sup>IV</sup> , 0°, 0.05 mmol FeCl <sub>2</sub>	12	5.4	n.d. <sup>a</sup>	68	~86
5	Gif <sup>IV</sup> , -25° 0.05 mmol FeCl <sub>2</sub>	13	5.2	n.d.	63	~82
6	GoAgg <sup>I</sup> 0.5 ml H <sub>2</sub> O <sub>2</sub>	2.1	4.3	n.d.	88	~95
7	GoAgg <sup>I</sup> 2.0 ml H <sub>2</sub> O <sub>2</sub>	6.0	6.1	n.d.	61	~73
8	GoAgg <sup>I</sup> 1.0 ml H <sub>2</sub> O <sub>2</sub>	2.5	4.5	n.d.	69	~76

<sup>a</sup> Not determined

results are summarized in Table 4. The ketone **24** was the major product in all the Gif<sup>IV</sup> oxidations. Its yield increased as the temperature was lowered to -25°. This ketone **24** was, as expected, fully optically active with no racemization. With the GoAgg<sup>I</sup> system the yield of **24** was not dominant.

The formation of carvone **25** was significant in all experiments. It was racemic. The third compound **26** was (+)-perillaldehyde with identical physical data (except for sign of rotation) when compared with (-)-perillaldehyde. The formation of racemic carvone **25** could well be explained by the intervention of the symmetrical allylic radical. So, we

repeated a  $\text{Gif}^{\text{IV}}$  experiment using an isopropanol-pyridine mixture (1:4 by volume). We expected this to lead to radical trapping to reform limonene, which would, of course, be racemic. So we expected the yield to fall and the recovered limonene to be partly racemic. Table 5 shows that the former prediction was true, but not the latter.

**Table 5**

OXIDATION OF R-(+)-LIMONENE.  
OPTICAL ROTATION RESULTS UNDER  $\text{GIF}^{\text{IV}}$  CONDITIONS

Solvent	<b>23</b> <sup>a</sup> [ $\alpha$ ] <sub>D</sub>	<b>23</b> <sup>b</sup> [ $\alpha$ ] <sub>D</sub>	<b>24</b> [ $\alpha$ ] <sub>D</sub> (%)	<b>25</b> [ $\alpha$ ] <sub>D</sub> (%)	<b>26</b> [ $\alpha$ ] <sub>D</sub> (%)
Pyridine	+122°	+121°	+116°(10)	+0.8°(5.3)	+119°(1.5)
Pyridine (80%)- Isopropanol (20%)	+122°	+119°	+114°(2.0)	+0.2°(1.3)	+111°(0.3)

<sup>a</sup> [ $\alpha$ ]<sub>D</sub> before oxidation. All [ $\alpha$ ]<sub>D</sub> in  $\text{CHCl}_3$ .

<sup>b</sup> [ $\alpha$ ]<sub>D</sub> of recovered **23**. Recovered only in pyridine : 80%. Mass balance 97%.

(-)- $\alpha$ -Terpineol **27** was oxidized to two major products. The first was carvone hydrate **28** (6.3%) which was 90% racemic. The second was the aldehyde **29** (1.4%).

We recently reported<sup>14</sup> competition experiments between oxygen and pyridine for carbon radicals generated by photolysis<sup>15</sup> of the appropriate acyl derivatives of *N*-hydroxypyridine-2-thione. In a flow system at 4% oxygen in nitrogen there was, as expected, partitioning of radicals between oxidation products and pyridine coupling. In contrast,  $\text{Gif}^{\text{IV}}$  oxidation of the hydrocarbons corresponding to the formally reduced radicals produced little coupling to secondary positions. There was clear partitioning between oxidation and coupling at the tertiary position in adamantane. The formation of the tertiary adamantyl radicals had been demonstrated much earlier<sup>3</sup> and explained by the fragmentation of an iron-carbon bond.

We therefore repeated this kind of  $\text{Gif}^{\text{IV}}$  experiment with R-(+)-limonene



and with (-)- $\alpha$ -terpineol at 4% oxygen - in nitrogen and at higher oxygen concentrations. There was no coupling to pyridine as judged by the sensitive procedure of g.c./m.s.

Clearly, then, allylic radicals are not present. In terms of the iron-carbon bond theory<sup>14</sup>, this means that the iron-carbon bond initially formed evolved into a  $\pi$ -allyl complex which, being symmetrical, naturally gave racemic products.

The recent publication<sup>16</sup> by Sawyer *et al.* has shown that if an Fe<sup>II</sup> species is present in the same concentration as the hydrogen peroxide in a GoAgg<sup>II</sup> type system, then radicals are formed by conventional Fenton type chemistry. They can be trapped easily by pyridine (as well as by diphenyldiselenide). In the case of cyclohexane, up to 77% of cyclohexylpyridine was formed, whereas in the GoAgg<sup>II</sup> system, the amount of cyclohexylpyridine formed is minute.

In conclusion, we have shown that a number of methyldene olefins are cleanly cleaved into ketone (or aldehyde) plus formaldehyde by the <sup>V</sup>Fe oxenoid present in the Gif type oxidation systems. At the same time the allylic oxidation to unsaturated ketones, seen with more substituted olefins, has been shown to have a symmetrical intermediate considered to be a  $\pi$ -allyl iron species.

Professor D. T. Sawyer of this department has kindly given us copies of two important papers<sup>17</sup> which will appear shortly. The first of these papers deals with Gif type reactivity. The results reported are in good agreement with those that we have found. In addition, the GoAgg<sup>II</sup> system has been modified by chelating the iron to picolinic acid. This makes for even more efficient hydrocarbon oxidation. So far as olefin oxidation is concerned, Sawyer *et al.*<sup>17</sup> agree that cyclohexene is converted to cyclohexenone and that no epoxide is formed. The cleavage of *cis*-stilbene to benzaldehyde was observed, a reaction also seen in acetonitrile<sup>18</sup>, but none of the methyldene olefins examined in this paper were studied.

We welcome this strong reinforcement of the effort devoted to Gif-type chemistry.

### Experimental Section

Melting points were determined with a Kofler hot stage apparatus and are uncorrected.  $^1\text{H-NMR}$  spectra were determined for solutions in deuteriochloroform with TMS as internal standard on Varian XL-200E and Varian Gemini-200 instruments. I.R. spectra were recorded on a Perkin Elmer 881 Spectrophotometer. Mass spectra (70 ev.; electron impact) were obtained using a Hewlett-Packard 5995C quadrupole gc-ms instrument. Analytical g.l.c. was performed on a Chrompack 439 equipped with FID detector using a fused silica capillary column CP-Sil-5 CB, 20 x 0.22 mm. i.d. ( $\text{N}_2$  as carrier gas). Preparative g.l.c. separations were carried out on a Shimadzu 8A instrument equipped with a TCD detector. The column used was a 0.6 cm x 2.9 m Carbowax 20M TPA on Chromosorb W AW. Optical rotation measurements were run using a JASCO Model DIP 140 Digital Polarimeter.

### Substrates and Authentic Samples of Oxidation Products

Methylenecyclohexane 5,  $\alpha$ -methylstyrene 7, 1-octene 9, heptanal 10, 1,1-diphenylethylene 15, 4,4'-dimethoxybenzophenone 19, 4,4'-dichlorobenzophenone 22, R-(+)-limonene 23, R-(-)-carvone 25,  $\alpha$ -terpineol 27 and S-(-)-Perillaldehyde 26 were purchased. 4,4'-Dibromobenzophenone 20 was prepared by bromination of diphenylmethane followed by  $\text{CrO}_3$  oxidation.<sup>19</sup> 1,1-Diphenylethylene epoxide 11 was readily available from benzophenone by treatment with trimethylsulfonium iodide in presence of  $\text{NaH}$ .<sup>20</sup>

The 1,1-diarylethylenes 17, 19 and 21 were obtained by methylenation of the corresponding ketones with the Wittig reagent. The purity of the compounds 17, 19 and 21 was verified (g.l.c., NMR) before being used as substrates in Gif oxidations. The melting points were compared with the reported values: 1,1-Bis(4-methoxyphenyl)ethylene 17, mp. 139-140°; lit.<sup>21</sup> 142°; 1,1-Bis(4-bromophenyl)ethylene 19 mp. 82-83°; lit.<sup>22</sup> 84°; 1,1-Bis(4-chlorophenyl)ethylene 21 mp. 80-82°; lit.<sup>23</sup> 84-85°.

### General Procedures for Gif Type Reactions.

1) Gif<sup>IV</sup> Reaction (Pyr/AcOH/Zn/Fe<sup>2+</sup>/Air). A solution of the substrate (2.0 mmol) in pyridine (28 ml) containing  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (20-40 mg; 0.1-0.2 mmol) and zinc powder (1.31 g; 20 mg-at) was placed in a 125 ml Erlenmeyer flask open to air. The reaction was started by adding glacial acetic acid (2.3 ml; 40 mmol) and the solution was stirred for 16-20 hrs. at such a rate

as to keep the zinc in suspension.

2) Gif<sup>III</sup> Reaction (Pyr/AcOH/Fe<sup>0</sup>/Air). The procedure was the same as Gif<sup>V</sup> except the zinc powder and iron catalyst (FeCl<sub>2</sub>.4H<sub>2</sub>O) were replaced by iron powder (1.12 g; 20 mg-at) and 1 ml of 1N H<sub>2</sub>S in pyridine was added to initiate the reaction at room temperature.

3) GoAgg<sup>I</sup> Reaction (Pyr/AcOH/Fe<sup>2+</sup>/KO<sub>2</sub>). To a solution of the substrate (2.0 mmol) and Py<sub>4</sub>FeCl<sub>2</sub> (886 mg; 2.0 mmol) in pyridine (28 ml)-acetic acid (5 ml), KO<sub>2</sub> (143 mg 2.0 mmol) was added slowly in the course of 4 hrs. under an argon atmosphere with the aid of a powder dispensing funnel. The reaction mixture was stirred vigorously for a total of 10-12 hrs.

4) GoAgg<sup>I</sup> Reaction (Pyr/AcOH/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>). A solution of the substrate (2.0 mmol) and FeCl<sub>3</sub>.6H<sub>2</sub>O (270 mg; 1 mmol) in pyridine (28 ml)-acetic acid (5 ml) was placed in a 125 ml Erlenmeyer Flask open to air. The solution was stirred for 16 hrs. at room temperature after addition of 1 ml of 30% H<sub>2</sub>O<sub>2</sub> (9.8 mmol).

**General Work-Up Procedure. Method A:** The reaction mixture was chilled in an ice-salt mixture and 60 ml of 25% (v/v) H<sub>2</sub>SO<sub>4</sub> was slowly added with stirring. Then the acidic aqueous layer (pH 2-3) was extracted with ether (4 x 75 ml). The combined ether layers were washed succesively with 75 ml of 5% (w/v) NaHCO<sub>3</sub> solution and brine. The dried (MgSO<sub>4</sub>) ether layer was mixed with a solution of an internal standard and analyzed by g.l.c.

**Method B:** 2 ml of The reaction mixture was placed in a test tube. Ether (5.0 ml) and the solution of an internal standard were added. Then the solution was chilled and acidified by dropwise addition of 25% (v/v) H<sub>2</sub>SO<sub>4</sub>. The mixture was shaken vigorously and left aside for separation of layers. The ether layer was drawn with a pipet, dried over MgSO<sub>4</sub> and injected into the g.l.c. apparatus.

The oven temperature and the retention times (min) for each substrate and its oxidation products were as follows: At 30° (isothermal), 0.91 for methylenecyclohexane **5**, 2.02 for ethylbenzene (internal standard), 2.32 for cyclohexanone **6**,; at 60 to 110° (20 deg/min), 1.26 for α-methylstyrene **7**, 1.80 for acetophenone **8**, 2.31 for adamantane (internal standard); at 40 to 120° (20°/min), 0.98 for 1-octene **9**, 1.68 for cyclohexanone (internal standard), 1.95 for 1-heptanal **10**; at 120 to 210° (10°/min), 1.70 for 1,1-diphenylethylene **15**, 2.25 for fluorene (internal standard), 2.56 for benzophenone **16**; at 160 to 210° (32°/min) with an initial time of 0.8 min,

1.07 for benzoin (internal standard), 1.83 for 1,1-bis(4-methoxyphenyl)ethylene **17**, 2.31 for 4,4'-dimethoxybenzophenone **18**; at 160 to 200° (3°/min) with an initial time of 0.8 min, 1.69 for benzoin (internal standard), 4.39 for 1,1-bis(4-bromophenyl)ethylene **19**, 5.18 for 4,4'-dibromobenzophenone **20**; at 150 to 210° (8°/min) with an initial time of 0.8 min, 1.42 for benzoin (internal standard), 2.05 for 1,1-bis(4-chlorophenyl)ethylene **21**, 2.41 for 4,4'-dichlorobenzophenone **22**.

**Quantification of Formaldehyde Formed in the Gif Reactions as the Dimedone Adduct.** To the Gif reaction mixture, 1.0-5.0 mmol of dimedone (see Table 2) was added, and the solution was stirred for an additional 3 hrs. at room temperature. The resulting solution was worked up according to method A. The ether solution obtained was evaporated to dryness. A known quantity of CH<sub>2</sub>I<sub>2</sub> was added as an internal standard. The mixture was then dissolved in CDCl<sub>3</sub> and its <sup>1</sup>H-NMR was recorded. The quantity of the dimedone adduct was determined by comparing the intensities of singlets at 3.84 ppm (CH<sub>2</sub>I<sub>2</sub>, 2H) and 3.12 ppm (2H).

**Blank Experiments for the Recovery of Formaldehyde.**

a) The authentic dimedone adduct (0.14 mmol) was added to the solution of a Gif<sup>I<sup>V</sup></sup> reaction run without substrate. Work-up method A followed by <sup>1</sup>H-NMR in presence of CH<sub>2</sub>I<sub>2</sub> (internal standard) showed 101% recovery of the dimedone adduct.

b) Formaldehyde (1 ml of 0.027 M solution in pyridine) was subjected to Gif<sup>I<sup>V</sup></sup> oxidation conditions. After 16 hrs. 1.0 mmol of dimedone was added and the solution was stirred for an additional 3 hrs. The <sup>1</sup>H-NMR of the concentrate obtained by work-up method A indicated 13.2% of dimedone adduct.

c) Formaldehyde solution in pyridine (1 ml of 0.027 M) was added to the solution of a Gif<sup>I<sup>V</sup></sup> reaction which had been performed without substrate and then treated with dimedone (1.0 mmol). After 3 hrs. of stirring, the solution was worked up (method A) and analyzed by <sup>1</sup>H-NMR. The recovery of the dimedone adduct was 85%.

**The Extent of Benzophenone Formation from 1,1-Diphenylethylene Oxide **11** under Gif<sup>I<sup>V</sup></sup> Conditions.** The epoxide **11** was used as a substrate in a Gif<sup>I<sup>V</sup></sup> reaction. Half of the resulting mixture was used to quantify the unreacted epoxide **11** (78%, <sup>1</sup>H-NMR) by comparing the intensity of the peak at 3.22 ppm

(CH<sub>2</sub> of **11**) with that of the singlet at 2.51 ppm (CH<sub>3</sub> of  $\alpha$ -picoline as an internal standard). The other half was subjected to work-up method A. The analysis of the ether layer (g.l.c.) showed 4.0% of benzophenone.

**The Extent of Benzophenone Formation from 1,1-Diphenylethylene Glycol 12 Under Gif<sup>IV</sup> Conditions.** The diol **12** (1.0 mmol) was incubated under Gif<sup>IV</sup> conditions. Half of the reaction mixture was evaporated to dryness under vacuum (dry ice rotary evaporator) at room temperature. <sup>1</sup>H-NMR of the residue recorded in presence of  $\alpha$ -picoline (internal standard;  $\delta_{\text{CH}_3}$ =2.51) showed recovery of the diol **12** ( $\delta_{\text{CH}_2}$ =4.14). The other half of the solution was acidified and extracted with ether (method A) and analyzed by g.l.c. for benzophenone. The yield was 3.8%.

**Oxidation of R-(+)-Limonene 23 by Gif Systems.** R-(+)-Limonene (817 mg, 6.0 mmol) was oxidized by Gif<sup>IV</sup> and GoAgg<sup>I</sup> systems under various conditions (Table 4). The resulting mixtures were treated according to method A. The ether solutions thus obtained were used in preparation of derivatives of the oxidation products **24-26**. The isolation of **24-26** in pure form was by preparative g.l.c. and their quantification was by analytical g.l.c. In the case of the latter, the retention times (min) at a temperature program of 60 to 90° (3°/min) was 2.30 for R-(+)-limonene **23**, 2.89 for adamantane (internal standard), 3.63 for 4-acetyl-1-methyl-cyclohexene **24**, 6.22 for carvone **25** and 7.02 for perillaldehyde **26**.

**R-(+)-Limonene 23, Oxidation Products 24-26 and Their Derivatives.** R-(+)-Limonene **23**, recovered from a Gif<sup>IV</sup> reaction in pure form had  $[\alpha]_D = +120.5^\circ$  (c=2.16, CHCl<sub>3</sub>). Thus, the R-(+)-limonene had not undergone any racemization during the Gif<sup>IV</sup> reaction [before Gif<sup>IV</sup>,  $[\alpha]_D = +123^\circ$  (neat)]. The optical activity of R-(+)-limonene was also conserved in a Gif<sup>IV</sup> reaction performed in pyridine-isopropanol mixture (80:20),  $[\alpha]_D = 119^\circ$  (C=1.6, CHCl<sub>3</sub>).

**4-Acetyl-1-Methylcyclohexene 24**, purified from a Gif<sup>IV</sup> reaction mixture, had  $[\alpha]_D = +116.3^\circ$  (c=4.9, CHCl<sub>3</sub>), lit.<sup>24</sup>  $[\alpha]_D$  for the R-enantiomer =  $+122.3^\circ$  (C=1.157, CHCl<sub>3</sub>). Its 2,4-dinitrophenylhydrazone derivative had  $[\alpha]_D = +98.1^\circ$  (c=0.32, CHCl<sub>3</sub>), melted at 133-134° (lit.<sup>25</sup> 143°), and showed a molecular ion peak (m/z=318) in its mass spectrum. The oxime was an oil,  $[\alpha]_D = +75^\circ$  (c=0.37, EtOH). <sup>1</sup>H-NMR:  $\delta$  9.3 (br.s., 1H), 5.4 (s, 1H), 1.8-2.4 (m, 6H), 1.8 (s, 3H), 1.6 (s, 3H), 1.55 (m, 1H); Mass: m/z 153 M<sup>+</sup>. It was

also compared with an authentic specimen of the racemic compound.

**Carvone 25**, isolated from Gif<sup>IV</sup> oxidation of R-(+)-limonene, did not show any optical activity. The <sup>1</sup>H-NMR of carvone from Gif<sup>IV</sup> and the commercial sample were identical. Its 2,4-dinitrophenylhydrazone derivative melted at 189-191°; lit.<sup>26</sup> 189°.

**Perillaldehyde 26** purified from Gif<sup>IV</sup> reaction mixture had  $[\alpha]_D = +120^\circ$  (C=0.32, CHCl<sub>3</sub>). The commercial sample of S-(-)-perillaldehyde (Aldrich) had  $[\alpha]_D = -121^\circ$  (c=10, EtOH). The <sup>1</sup>H-NMR and mass spectrum of the commercial sample and of the Gif<sup>IV</sup> oxidation product were compared. The 2,4-dinitrophenylhydrazone derivative melted at 192-194°, lit.<sup>27</sup> mp for the racemic mixture 199-200°.

**Oxidation of  $\alpha$ -Terpineol 27** The solution from Gif<sup>IV</sup> oxidation of 27 (0.92 mg; 6 min) was worked up according to Method A. The concentrated ether solution contained unreacted 27 and two major oxidation products 28 and 29. They were isolated in pure form by preparative g.l.c.

(-)- $\alpha$ -Terpineol 27 recovered after Gif<sup>IV</sup> oxidation had  $[\alpha]_D = -27^\circ$  (c=2.2, CHCl<sub>3</sub>). The commercial sample used as substrate had  $[\alpha]_D = -29.1^\circ$  (c=2.0, CHCl<sub>3</sub>).

**Carvone Hydrate 28** was isolated in 6.3% yield;  $[\alpha]_D = -4.74^\circ$  (c=1.62 CHCl<sub>3</sub>), lit.<sup>28</sup>  $[\alpha]_D$  for the 4S enantiomer =  $-42^\circ$  (c=6.9, EtOH); IR (CHCl<sub>3</sub>) 3500, 1660 cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta = 1.23$  (s, 3H), 1.24 (s, 3H), 1.38 (s, 1H), 1.78 (s, 3H), 1.97-2.15 (m, 1H), 2.2-2.3 (m, 2H), 2.4-2.7 (m, 2H), 6.7 (m, 1H).

**8-Hydroxy-p-Menth-6-en-7-al 29** was isolated in 1.4% yield;  $[\alpha]_D = -34.7^\circ$  (c=0.74, CHCl<sub>3</sub>), lit.<sup>29</sup>  $[\alpha]_D$  for the 4S enantiomer =  $-147^\circ$  (c=10, EtOH); IR (CHCl<sub>3</sub>) 3500, 2720 and 1670 cm<sup>-1</sup>; <sup>1</sup>H-NMR  $\delta = 1.22$  (s, 3H), 1.24 (s, 3H), 1.38 (m, 1H), 1.98-2.27 (m, 3H), 2.4-2.6 (m, 2H), 6.84 (m, 1H), 9.44 (s, 1H). We have no explanation for the difference in optical rotation.

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