

plifies the ability of neutral host to complex water via crown ether ligands. Furthermore, *cis*-1 is most likely to form intramolecular sandwich-type complexes with particular mono- and dicationic species by cooperative action of the two adjacent crown rings. The intrinsic chirality of the *cis* isomer may be of particular importance in selective complexation of enantiomeric cationic guests. The *trans*-1 isomer, which possesses two crown ether moieties, has the possibility of forming dinuclear complexes by placing two cations in close proximity. The characterization of such entities and the

design of other ligands based on the diphosphazane ring are currently under investigation.

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Registry No. *cis*-1, 121754-78-7; *cis*-1·H₂O, 121730-72-1; *trans*-1, 121754-80-1; *trans*-1·2CH₂Cl₂, 121754-81-2; 2, 73776-01-9; 3, 72583-76-7; 4, 121730-70-9; 5, 121730-71-0; 8, 121754-79-8; TsO(CH₂)₂O-(CH₂)₂O(CH₂)OTs, 19249-03-7; 2-nitrophenol, 88-75-5.

Supplementary Material Available: Listing of observed and calculated structure factors for *cis*-1·H₂O and *trans*-1·2CH₂Cl₂ (53 pages). Ordering information is given on any current masthead page.

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Functionalization of Saturated Hydrocarbons. 14. Further Studies on the Mechanism of Gif-Type Systems

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Abstract: The photolysis (W light) of acyl derivatives of *N*-hydroxy-2-thiopyridone in pyridine-acetic acid permits a study of the partitioning of secondary radicals between oxygen, pyridine, and the thione function. Comparison with the Gif^{IV} oxidation system for saturated hydrocarbons confirms that radicals are not involved in oxidation at secondary positions. On the contrary, radical behavior at the tertiary position in adamantane is again established. The two recently introduced Gif-type systems, GoAgg^I and GoAgg^{II}, have been shown to give the same overall selectivity in attack on adamantane with the usual coupling of the tertiary radical with pyridine.

The selective functionalization of saturated hydrocarbons is a subject of great topical concern.² Amongst the many approaches to the problem, we have developed several systems that oxidize and substitute saturated hydrocarbons with an unusual regioselectivity.^{3a} The system Gif^{III} consists of Fe⁰-O₂ in pyridine-acetic acid; Gif^{IV} is similar, with Zn⁰-O₂-Fe^{II} catalyst in the same solvent mixture. The Gif-Orsay system^{3b} is the same as Gif^{IV}, but the Zn⁰ is replaced by the cathode of an electrochemical cell. These systems attack saturated hydrocarbons in the order secondary > tertiary ≥ primary. This contrasts with the normal order of radical attack, such as is seen with P450 porphyrin models,^{4,5} of tertiary > secondary > primary. It is quite unlike the selectivity seen in cobalt catalyzed autoxidation reactions.⁶ In addition, ketones are the principal reaction product, not secondary alcohols as in other oxidation systems.^{2,7}

When the reaction is run in the presence of a large excess of hydrocarbon to a conversion of 10-15%, the yield of ketone is nearly quantitative. In the Gif-Orsay system,^{3b,8} the Coulombic yield is high (about 50% for cyclohexane). The electrochemical system does not involve the reduction of pyridine as does the Gif^{IV}(Zn⁰) procedure. Recent work⁹ has shown that FeCl₂-KO₂ (GoAgg^I) or FeCl₃-H₂O₂ (GoAgg^{II}) give the same selectivity as the earlier Gif and Gif-Orsay systems in the same solvent mixture. Hence, the reduction of pyridine has nothing to do with the mechanism of the oxidation. However, pyridine is an essential ligand, and acetic acid (or other acid) has to be present to buffer the system.

We have expended much effort on trying to establish the mechanism of this unusual oxidation process. An early obser-

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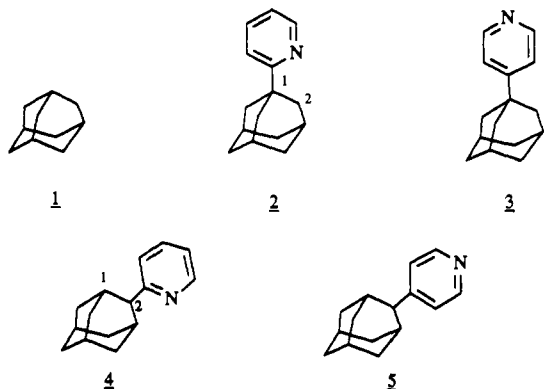
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(9) Barton, D. H. R.; Halley, F.; Ozbalik, N.; Young, E.; Balavoine, G.; Gref, A.; Boivin, J. *New J. Chem.* **1989**, *13*, 177. In the description of GoAgg^I and GoAgg^{II}, we use the same geographical connotations as before. G stands for Gif, O is for Orsay, and Agg is for Texas A&M, College Station, where the work described in this paper was carried out. This kind of nomenclature saves space.

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vation^{3a} of mechanistic significance concerned the hydrocarbon adamantane (**1**). Defining C² as the total of the products oxidized



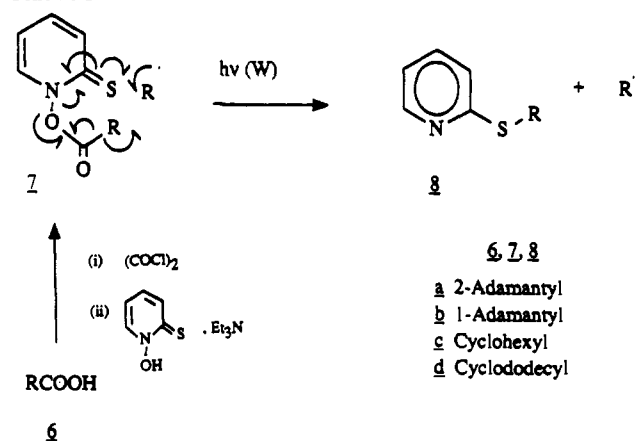
at the secondary position and C³ similarly for the tertiary position, the ratio of C²/C³, if all hydrogens were equally reactive, would be 3. In fact, in radical reactions, the tertiary position should be more reactive. For alkoxide radical attack, a reliable C²/C³ of 0.15 has recently been established.¹⁰ The same number has also been found for the oxidation of adamantane in acetone solution by ruthenium *tert*-butyl hydroperoxide. This is also regarded as a alkoxide radical reaction.¹¹ Groves,⁴ using a porphyrin derivative as catalyst, found a number of less than 0.15. A number of reactions involving *tert*-butoxide radical attack¹² on adamantane with subsequent carbon-carbon bond formation gave no significant attack on the secondary positions of the hydrocarbon or of its di-*tert*-methyl derivative. It is clear then that oxygen radical attack on the tertiary position of adamantane is a highly favored process. Noteworthy is a recent, thorough study of the substitution reactions of adamantane using tetraarylmetalporphyrins.¹³ The highest C²/C³ seen was 0.25, and the majority of the data gave numbers much less. The reactivity of the tertiary position in adamantane toward radical-type reagents in a range of solvents is thus confirmed.

In the Gif^{IV} system under atmospheric pressure, C²/C³ numbers of 10–20 are easily secured. Thus, the reaction appears to be highly selective for attack on the secondary position.³

However, the presence of *tert*-adamantyl radicals can be demonstrated. As the oxygen pressure is lowered, the reaction becomes apparently more and more selective and C²/C³ can be 100 or more. Inspection of the pyridine bases at the end of the reaction showed coupled products involving only the tertiary position of adamantane. Taking into account the pyridine derivatives gives a C²/C³ of about 1.15, which is invariant over a wide oxygen pressure range. This can only be true if an intermediate is formed at the tertiary position, which reacts competitively with oxygen and pyridine. Such an intermediate is accepted in all our publications as a tertiary radical. The ratio of C²/C³ of 1.15 is still far from that found for alkoxide radical attack.^{10–13} For the two reactions (i) R^{1•} + O₂ → R¹OO• and (ii) R^{2•} + O₂ → R²OO•, where R^{1•} is the tertiary radical and R^{2•} the hypothetical secondary radical, the ratio of the oxidation products cannot change with oxygen pressure. Clearly then, if oxidation at the tertiary position involves radicals, that at the secondary position must have a different mechanism.

Our first working hypothesis³ was that an iron-oxenoid species was formed, which reacted with the C–H bond to give an iron-carbon bond with the structure HO–Fe–C. For the tertiary position, the iron-carbon bond broke down to give radicals,¹⁴ whereas at the secondary position, it evolved into an iron carbene,

Scheme I

Table I. Photolysis of 7a in Pyridine–Acetic Acid Solution^{a,b}

entry	O ₂ , %	products, %							total
		8a	4	5	6a	10	11	12	
1	0	52	24	12	9.9	0	0	0	98
2	3	55	16	12	9.1	<0.5		12	104
3	6	39	7.5	5.9	8.6	10	5.9	31	108
4	10	16	4.5	4.5	13	15	22	31	102
5	21	15	<0.5	<0.5	9.4	15	23	38	100

^a A solution of 7a (1.0 mmol) in 8.0 mL of pyridine was added slowly with a syringe pump protected from light into a degassed pyridine (20-mL)–AcOH (2.3-mL) mixture, in the course of 6 h. The reaction vessel was a round-bottom flask (total volume = 300 mL) surrounded with a water jacket. It was initially filled up with N₂/O₂ mixture (by injection of a known volume of O₂ into pure N₂) and placed 25 cm from the light sources (two 300-W tungsten lamps). The photolysis was performed at 12 °C (temperature of circulating water) during 6 h. ^b See Table VIII for analysis of the reaction mixture.

Fe=C, which on cleavage with oxygen or superoxide would give a ketone. The unusual substitution pattern was then a compromise between carbon-hydrogen bond strength (tertiary < secondary < primary) and the steric bulk of the reagent seeking to impose the opposite order (primary < secondary < tertiary).

Could there be a fallacy in our argument? We have thought of two. Originally, we assumed that, if pyridine were bonded to the secondary position in adamantane, the product would not be oxidized further to ketone. At pH 6 in the pyridine-acetic acid medium, this seemed very probable. We had already prepared the tertiary-coupled pyridines **2** and **3** and identified them amongst the reaction products (see above).³ The secondary-coupled pyridines **4** and **5** were readily prepared from the *sec*-carboxylic acid¹⁵ **6** using our radical-generating system based on *N*-hydroxy-2-thiopyridone.¹⁶ This method also provided improved syntheses of the tertiary derivatives **2** and **3**.

The secondary-coupled pyridines **4** and **5** were not oxidized (no ketone formed) under Gif^{IV} conditions and were recovered unchanged (~80%). We also prepared 2-pyridylcyclohexane using the same radical chemistry based on cyclohexanecarboxylic acid. Again, no cyclohexanone was formed on Gif^{IV} oxidation.

The second fallacy was that *tert*- and *sec*-pyridyladamantanes might be inseparable on GC analysis. With the four compounds **2–5** now readily available, it was easy to demonstrate that they were separable by GC. Indeed, the addition of **4** and **5** to a Gif^{IV} system that was oxidizing adamantane in the usual way left **4** and **5** unchanged and produced **2** and **3** in normal amounts.

The development of the radical-generating system based on the acyl derivatives of thiohydroxamic acids¹⁶ permits a thorough study of the competition between oxygen and pyridine for the *tert*- and

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Table II. Photolysis of 7b in Pyridine–Acetic Acid Solution^{a,b}

entry	O ₂ , %	products, %						total
		8b	2	3	6b	13 + 14		
1	0	14	32	28	12	0.1	86	
2	2.5	15	31	27	11	1.5	86	
3	5	15	24	20	10	18	87	
4	21	8.8	7.7	6.5	6.9	51	81	
5	100	6.0	0	0	8.0	63	78	

^aA solution of 7b (1.0 mmol) in pyridine (28 mL)–AcOH (2.3 mL) was photolyzed for 2 h at room temperature under a flow of N₂/air mixture of known composition. Photolysis was carried out with two tungsten lamps (300 W) situated 25 cm from the reaction vessel. ^bSee Table VIII for analysis of the reaction mixture.

Table III. Photolysis of 7c in Pyridine–Acetic Acid Solution^a

entry	O ₂ , %	products, %							total
		8c	15a	16a	6c	17	18	19	
1 ^b	0	34	33	22	12	0	0	0	101
2 ^c	4	40	10	7.9	9.3	12	2.3	ND ^d	81
3 ^c	21	17	<0.5	<0.5	11	39	6	ND ^d	73

^aSee Table VIII for analysis of the reaction mixture. ^bExperimental conditions are as described for 7a (Table I), except that the reaction time was 4 h. ^cExperimental conditions as described for 7a (Table II) with the following modifications: 7a (1.0 mmol) dissolved in pyridine (28 mL)–AcOH (2.3 mL) was photolyzed for 4 h under a flow of N₂/air mixture of known composition. The flow rate of each gas was regulated separately with a needle valve and mixed before introducing into the reaction vessel. ^dNot detectable.

Table IV. Photolysis of 7d in Pyridine–Acetic Acid Solution^{a,b}

entry	O ₂ , %	products, %							total
		8d	15b	16b	6d	20	21	22	
1	0	61	14	9.7	8.7	2.6	0	0	96
2	4	47	4.7	5.3	7.9	17	8.6	6.8	97
3	21	14	0	0	8.3	40	23	10	95

^aA solution of 7d (1.0 mmol) in pyridine (28 mL)–AcOH (2.3 mL) was photolyzed for 4 h at 12 °C using two tungsten lamps (300 W) situated 25 cm from the reaction vessel. Premixed N₂/air mixture was blown over the stirred solution at a constant rate. ^bSee Table VIII for analysis of the reaction mixture.

for the *sec*-adamantyl radicals. As shown in Scheme I, a carboxylic acid 6 can be reacted with *N*-hydroxy-2-thiopyridone to furnish acyl derivatives 7. On photolysis with a W lamp, radicals are cleanly generated. In the absence of an added trap, the radical reacts with the thione function to give the decarboxylative rearrangement product 8 with reformation of the radical. In the presence of oxygen and pyridine, the radical can be trapped also by either of these reagents. Clearly, high oxygen pressures will favor oxygen-trapping products, and low oxygen pressures will favor pyridine or thione trapping.

Table V. Photolysis of Acyl Derivatives 7 under 4% Oxygen in Nitrogen (Flow System)^a

substrate (mmol)	photolysis products (% yield)								total	R(O)/R(Py)
	RCO ₂ H	RSPy	R(O)			R(Py)				
7a (1.0)	6a (13)	8a (45)	10 (3.1)	11 (8.7)	12 (21)	4 (5.4)	5 (2.4)	96	4.3	
7b (1.0)	6b (8.6)	8b (19)		13 + 14 (25)		2 (20)	3 (14)	87	0.74	
7c (1.0)	6c (9.3)	8c (40)	17 (12)	18 (2.3)	19 (ND) ^b	15a (10)	16a (7.9)	82	0.78	
7d (1.0)	6d (7.9)	8d (47)	20 (17)	21 (8.6)	22 (6.8)	15b (4.7)	16b (5.3)	98	3.2	

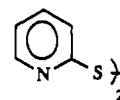
^aSee Experimental Section for reaction conditions and Table VIII for the method of analysis. ^bNot determinable.

Table VI. Gif^{IV} Oxidation under 4% Oxygen in Nitrogen (Flow System)^a

substrate (mmol)	Gif ^{IV} oxidation products (% yield)							total	R(O)/R(Py)
	R(O)			R(Py)					
1 (5.0)	10 (0.1)	12 (14)	13 (0.2)	2 (3.3)	3 (4.3)	4 (0.08)	5 (0.07)	96	94 (sec)/0.03 (tert)
cyclohexane (15)	17 (4.8)	18 (0.1)				15a + 16a (0.9)	ND ^c		5.4
cyclododecane (15)	20 (7.0)	21 (1.3)			15b (0.1)		16b (0.3)	95	21

^aSee Experimental Section for reaction conditions and Table VIII for the method of analysis. ^bRecovered hydrocarbon.

We studied first the photolysis of the *sec*-adamantanecarboxylic acid derivative 7a in a static system in pyridine–acetic acid at room temperature. The solvent mixture and temperature were as used in the Gif^{III} and Gif^V systems. The results are shown in Table I. In all cases, about 10% of derivative 7a was hydrolyzed back to acid 6a. In the absence of oxygen (entry 1), the rearrangement product 8a was the major product (52%), but the pyridine-coupled products 4 and 5 (36%) were also important. Thus, the large excess of pyridine competes with the thione function for the radical. As the oxygen pressure increases, the oxidation products 10, 11, and 12 become more important. At the 21% (air) oxygenation level, there is little rearrangement product 8a, only a trace of pyridine coupling, and the major products arise from capture of the radical by oxygen. The results show that the secondary radical does partition itself between oxidation and pyridine coupling. The thiopyridyl moiety was largely converted into dipyrindyl disulfide (9).

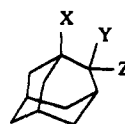


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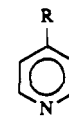


15

a Cyclohexyl
b Cyclododecyl

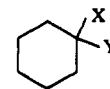


10 X,Y=H Z=OH
11 X,Y=H Z=OOH
12 Y,Z=O X=H
13 Y,Z=H X=OH
14 Y,Z=H X=OOH



16

a Cyclohexyl
b Cyclododecyl



17 X,Y=O
18 X=OH Y=H
19 X=OOH Y=H



20 X,Y=O
21 X=OH Y=H
22 X=OOH Y=H
23 X,Y = -CH₂O-
24 X=H Y=CHO

Some results for the tertiary radical are shown in Table II. This, and all the later results, refers to a flow system of defined composition. In the absence of oxygen, the tertiary radical is trapped efficiently by the pyridine. Even with air, a significant amount of trapping by pyridine is seen. It is clear that the tertiary radical is more reactive toward pyridine than the secondary radical.

We decided, therefore, to compare the reactivity of other secondary radicals toward pyridine and oxygen and to compare the ratios of oxidation to pyridine capture under radical conditions and under Gif^{IV} conditions.

Table III shows the reactivity of the cyclohexyl radical as the oxygen pressure is changed. At 4% oxygen concentration, the ratio of oxidation products to coupling products is 0.77. In contrast, for the Gif^{IV} oxidation at 4% oxygen pressure, this ratio is 5.5.

Cyclododecane is an excellent substrate for Gif^{IV} oxidation, and because of its lack of volatility, it is easy to obtain a good mass balance. Table IV summarizes data on the photolysis of the usual

Table VII. GoAgg^I and GoAgg^{II} Oxidations of Adamantane, (1)^a

exp	reagents (mmol)	Products, %					C ² /C ³ (overall)
		10	12	13	2	3	
GoAgg ^I	Py ₄ FeCl ₂ (2.55)	KO ₂ (4.5)	0.5	2.7	1.8	0.9	1.0
GoAgg ^{II}	FeCl ₃ ·6H ₂ O (1.12)	H ₂ O ₂ ^b (9.7)	0.5	7.7	4.0	4.0	0.82

^a Oxidations of adamantane (5.0 mmol) were performed in pyridine (30 mL)-acetic acid (5 mL) at room temperature. The solutions were stirred under nitrogen for 16 h. ^b 1.0 mL of 30% aqueous solution of H₂O₂ was used. ^c Analysis of the reaction mixtures was performed according to the method described in Table VIII.

derivative of cyclododecylcarboxylic acid.¹⁷ At 4% oxygen pressure, the ratio of oxidation to coupling is 3.24. In contrast, a Gif^V oxidation on cyclododecane gave a ratio of oxidation to coupling of 22.

These comparative data are summarized in Tables V and VI. Table V summarizes the ratio observed at 4% oxygen flow for oxidation versus coupling with pyridine for secondary radicals and for the tertiary radical in adamantane. In Table VI, the same ratio is calculated for Gif^V oxidation using the same flow rate of 4% oxygen. If radicals were involved in the Gif^V system, these ratios should be similar. Clearly they are not. For secondary positions, oxidation is much more efficient than coupling with pyridine. In contrast, coupling to pyridine is strongly preferred for the tertiary position in adamantane. The ratio for the radical from **7b** is 0.74, whereas in Gif^V, at the tertiary position, it is about 0.03. Thus, although we have convincing evidence for radicals at the tertiary position, there is another factor that promotes coupling with pyridine. If the iron-carbon bond is formed first, then pyridine is certainly coordinated to the iron. Thus, as the iron-carbon bond fragments into radicals, one or more pyridine residues are held close by and are probably activated by their coordination to iron toward radical attack.

Be this as it may, the results shown in Tables V and VI confirm that secondary radicals are not involved in Gif^V oxidation to any important extent.

The fact that Gif^{III}, Gif^V, Gif-Orsay, GoAgg^I, and GoAgg^{II} all have the same selectivity for hydrocarbon oxidation implies that all depend on an iron oxenoid species of the type HOFe(=O)₂ with pyridine and perhaps acetate as ligands. Of course, more than one iron center may be involved.¹⁸

We have recently studied the formation of pyridine-coupled products in the new systems GoAgg^I and GoAgg^{II}. Selected data are given in Table VII. The overall C²/C³ is not far from the normal Gif value, supporting our conclusion of a common Fe^V intermediate.

A different mechanism for the Gif-type system has been proposed by Geletii et al.¹⁹ It involves the idea that pyridine is oxidized to pyridine *N*-oxide radical cation, which then oxidizes the hydrocarbon to ketone without an intermediate. This interesting theory can hardly explain the remarkable reaction²⁰ between saturated hydrocarbons and diphenyl diselenide induced by the Gif^{III} system. The diphenyl diselenide captures the iron-carbon bond in a reaction that is almost quantitative in selenium. No products containing oxygen are formed.

However, there is agreement that the Gif system does not involve radical chemistry at the secondary positions.

During the course of these experiments, Prof. D. T. Sawyer kindly informed us of his important work²¹ on a modification of the GoAgg^{II} system. We, in turn, had provided him with a copy of our work⁹ on all variations of the Gif system. There is also a recent report by Geletii and his colleagues²² on the oxidation

of saturated hydrocarbons using an equivalent to GoAgg^{II}.

In conclusion, the present work has confirmed that the selective oxidation of saturated hydrocarbons to ketones in Gif-type systems does not involve secondary radicals. The arguments in favor of the iron-carbon bond, evolving by further oxidation to ketone, have been strengthened.

Experimental Section

General. ¹H NMR spectra were recorded with Varian XL-200E and Varian Gemini-200 spectrometers for CDCl₃ solutions (δ scale, TMS as internal standard). Some of the multiplicities were abbreviated as follows: br = broad, qnt = quintet, dd = doublet of a doublet. Mass spectra (70 eV, electron impact) were obtained with a Hewlett-Packard 5995C quadrupole GC-MS instrument. Exact mass measurements were carried out with a VG Analytical 70S high-resolution double-focusing magnetic sector mass spectrometer with attached VG Analytical 11/250J data system. The IR spectra were measured with a Perkin-Elmer 881 spectrometer; only the most significant absorptions were listed. The UV spectra were recorded on a Beckmann DU-7 spectrometer. Analytical GC was performed on a Chrompack 439 equipped with FID detector using a fused silica capillary column, CP-Sil-5 CB, 20- \times 0.22-mm i.d. (N₂ as carrier gas). Preparative TLC separations were performed using Analtech silica gel GF (1000- μ m) plates. Aldrich silica gel, 130-270 mesh, 60 \AA , was used for column chromatography. Melting points were determined on a Kofler hot stage and were uncorrected. *N*-Hydroxypyridine-2-thione was prepared from the 40% aqueous solution of its sodium salt (trade name: sodium omadine from the Olin Corp.)²³

Cyclododecanecarboxylic Acid (6d). Compound **6d** was prepared starting from cyclododecanone by adapting the method described for the synthesis of adamantane-2-carboxylic acid (**6a**).¹⁵ The epoxide (**23**, 87%) was rearranged to cyclododecanecarboxaldehyde (**24**) by boron trifluoride etherate at room temperature. Without isolation, the aldehyde **24** was oxidized (Jones reagent) to give the acid **6d** (68%), mp 95-97 °C (from pentane) (lit.¹⁷ mp 93-95 °C).

General Procedure for the Preparation of Acyl Derivatives 7 of *N*-Hydroxy-2-thiopyridone. A solution of the carboxylic acid (9.5 mmol) in dry benzene (40 mL) was treated with oxalyl chloride (2.6 mL, 29 mmol) and a drop of dimethylformamide. After the solution was kept at room temperature for 1 h, the solvent and excess oxalyl chloride were removed in vacuo. *N*-Hydroxypyridine-2-thione (1.4 g, 11 mmol) in methylene chloride (30 mL) was added with cooling (ice bath) followed by dropwise addition of pyridine (0.9 mL) in dichloromethane (5.0 mL). The cooling bath was removed after 5 min, and the mixture was kept at room temperature for 1 h. The reaction mixture was washed once with 20 mL of saturated NaHCO₃ solution and dried over MgSO₄. The solvent was evaporated under vacuum, and the residue was purified by chromatography on silica gel (CH₂Cl₂) to give the acyl derivative.

Acyl Derivative 7a. This had (68%) mp 138-140 °C (from CH₂Cl₂-ether). IR (CHCl₃): 1800 cm⁻¹. ¹H NMR: δ 7.57 (d, 1 H), 7.50 (d, 1 H), 7.17 (dd, 1 H), 6.60 (dd, 1 H), 3.10 (s, 1 H), 2.48 (s, 2 H), 1.5-2.2 (m, 12 H).

Acyl derivatives **7b**¹⁶ and **7c**²⁴ are known compounds.

Acyl Derivative 7d. This (75%) had mp 92-95 °C (from CH₂Cl₂-ether). IR (CH₂Cl₂): 1800 cm⁻¹. ¹H NMR: δ 7.68 (d, 1 H), 7.50 (d, 1 H), 7.17 (dd, 1 H), 6.60 (dd, 1 H), 2.90 (qnt, 1 H), 1.70-2.00 (m, 4 H), 1.25-2.50 (m, 18 H).

General Procedure for the Preparation of Alkyl 2-Pyridyl Sulfides (8). A solution of the acyl derivative **7** (0.35 mmol) in pyridine (6 mL) was irradiated with a 150-W tungsten lamp at room temperature for 40 min. The pyridine was removed under vacuum (30 °C). The residue was extracted with ether (25 mL). The ether extract was washed with sat-

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



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Table VIII. Analysis of Gif Oxidation and the Photolysis Products^a

oxygenated products			pyridine-coupled products		
			alkyl residue R = 		
10	NMR ^b	δ	2	NMR	δ
11^c	3.8	(s, 1 H)	3	3.07	(s, 1 H)
12	4.05	(s, 1 H)	8a	2.98	(s, 1 H)
	2.05	(s, 2 H)		4.25	(s, 1 H)
			alkyl residue R = 		
	GC (70 °C)			GC (105 → 205 °C, 15 °C/min)	
naphthalene ^d	<i>R_t</i> , min	<i>F</i> ^e	fluorene ^d	<i>R_t</i> , min	<i>F</i> ^e
13	1.31	1.0	4	1.32	1.0
	1.85	1.5	5	2.60	1.7
			8b	3.50	1.7
				4.51	1.7
			alkyl residue R = 		
	GC (30 °C)			GC (110 °C)	
cyclooctane ^d	<i>R_t</i> , min	<i>F</i> ^e	cyclododecane ^d	<i>R_t</i> , min	<i>F</i> ^e
17	1.67	1.0	15a	2.71	1.0
18	1.17	2.4	16a	4.57	1.8
	1.24	2.1	8c	1.27	1.9
				1.87	1.7
			alkyl residue R = 		
20^c	NMR ^b	δ	15b	NMR	δ
21	2.45	(m, 4 H)	16b	2.95	(qnt, 1 H)
22	3.78	(m, 1 H)	8d	2.75	(qnt, 1 H)
	4.05	(m, 1 H)		3.98	(qnt, 1 H)

^aThe reaction mixture was separated into its neutral, acidic and basic components by extractions from aqueous solution at different pHs. **Neutral Products.** A known portion of the homogeneous solution chilled in an ice-bath was acidified with 25% H₂SO₄ and extracted with ether. The combined extracts were washed with saturated Na₂CO₃ solution. The ether layer was then dried (MgSO₄) and analyzed. **Basic products.** Another portion of the reaction mixture was evaporated to dryness at room temperature using a dry ice cooled rotary evaporator. The residue was dissolved in ether and washed with saturated Na₂CO₃ solution. The ether layer was dried (MgSO₄) and analyzed. **Acidic Product.** The combined Na₂CO₃ washings from the photolysis experiment was acidified with 25% H₂SO₄ and extracted with ether. The ether extracts were washed once with dilute HCl, dried over MgSO₄, and evaporated to dryness. The residue was pure carboxylic acid **6** formed by hydrolysis of the thiohydroxamic ester **7**. The extent of error involved in the analysis methods described here could be estimated as $\pm 5\%$ in terms of mass balance, based on the data from the repetition of some of the experiments. ^bProducts were quantified by comparing the intensities of the peaks listed with that of trichloroethene (6.40 ppm, s, 1 H) used as an internal standard. ^cReady quantification of *sec*-hydroperoxides formed in the photolysis reactions was feasible by ¹H NMR. The *tert*-hydroperoxide **14** was detectable in the ¹H NMR of the neutral extracts from photolysis of **7b** under air and oxygen. A singlet at 1.76 ppm lost intensity with concomitant increase in the intensity of the peak of 1-adamantanol ($\delta = 1.68$, 6 β -H) upon addition of P(OCH₃)₃. The quantities of the *tert*-hydroperoxide **14** formed under oxygen and air were found to be 11% and 6.2%, respectively, by iodometric titrations. ^dA solution of known concentration of this compound was added as an internal standard to the combined ether extracts. ^ePercent yield of each product has to be multiplied by correction factor *F* to account for work-up losses as well as for the variation in GC detector response. It was determined by application of the work-up method on pyridine-AcOH solution or on a solution obtained from a Gif reaction without substrate, as appropriate, which contained a known quantity of the product.

urated NaHCO₃ solution (10 mL), dried (MgSO₄), and evaporated to dryness.

Sulfide 8a. This was crystallized from chloroform (98%), mp 40–42 °C. IR (film): 2908, 2850, 1577 cm⁻¹. UV: λ_{\max} (THF) 253 nm (ϵ 12900), 295 nm (ϵ 5070). ¹H NMR: δ 8.40 (d, 1 H), 7.40 (dd, 1 H), 7.12 (d, 1 H), 6.91 (dd, 1 H), 4.25 (s, 1 H), 1.52 (m, 14 H). MS: *m/z* 245 (M⁺), 135, 110. HRMS for C₁₅H₁₉NS (M⁺) calcd 245.1238, found 245.1214.

Sulfides **8b**¹⁶ and **8c**²⁴ are known compounds.

Sulfide 8d. This was a pale-yellow oil (97%). IR (CH₂Cl₂): 2937, 2850, 1577 cm⁻¹. ¹H NMR: δ 8.40 (d, 1 H), 7.45 (dd, 1 H), 7.12 (d, 1 H), 6.92 (dd, 1 H), 3.98 (qnt, 1 H), 1.2–1.9 (m, 22 H). MS: *m/z* 277 (M⁺), 244, 138, 125, 111. HRMS for C₁₇H₂₇NS (M⁺) calcd 277.1864, found 277.1865.

General Procedure for the Preparation of 2'- and 4'-Alkylpyridines. Acyl derivative **7** (0.5 mmol) in pyridine (8 mL) containing trifluoroacetic acid (0.12 mL, 1.55 mmol) was degassed with a stream of argon (10–15 min). The solution was then irradiated with a 150-W tungsten lamp at room temperature. The reaction was followed by TLC (CH₂Cl₂) until complete (disappearance of derivative **7**). To this solution, 20% (w/v) NaOH (20 mL) was added, and the mixture was extracted with ether (4 \times 30 mL). The combined ether extracts were dried (MgSO₄)

and evaporated under reduced pressure. The residue was purified by preparative TLC (CH₂Cl₂).

(a) Products from the Photolysis of 7a. (2-Pyridyl)-2-adamantane (4). Compound **4** was a light-yellow oil (27%). IR (film): 2904, 1598, 1449, 1429 cm⁻¹. UV (THF): λ_{\max} 256 nm (ϵ 2530). ¹H NMR: δ 8.59 (d, 1 H), 7.63 (dd, 1 H), 7.29 (d, 1 H), 7.09 (m, 1 H), 3.07 (s, 1 H), 2.63 (br s, 2 H), 2.08–1.50 (m, 12 H). MS: *m/z* 213 (M⁺), 134, 79. HRMS for C₁₅H₁₉N (M⁺) calcd 213.1517, found 213.1543.

(4-Pyridyl)-2-adamantane (5). This had mp 70–72 °C (from chloroform) (14%). IR (film): 2905, 1598, 1448, 1414 cm⁻¹. UV (THF): λ_{\max} 250 nm (ϵ 1780). ¹H NMR: δ 8.64–8.40 (br s, 2 H), 7.25 (dd, 2 H), 2.98 (s, 1 H), 2.45 (br s, 2 H), 2.17–1.51 (m, 12 H). MS: *m/z* 213 (M⁺), 134, 79. HRMS for C₁₅H₁₉N (M⁺) calcd 213.1517, found 213.1468.

2-Adamantyl 2-Pyridyl Sulfide (8a). This compound (12%) was compared with the authentic sample described above.

2,2'-Dipyridyl Disulfide (9). This was identical with the commercial (Aldrich) sample (15%).

(b) Products from the Photolysis of 7d. (2-Pyridyl)cyclododecane (15b). This was obtained as a white solid, mp 62–63 °C (from CH₂Cl₂) (16%). IR (CHCl₃): 2933, 2861, 1588, 1431 cm⁻¹. ¹H NMR: 8.52 (d, 1 H), 7.55 (dd, 1 H), 7.10 (d, 1 H), 7.05 (m, 1 H), 2.95 (qnt, 1 H),

2.00–1.70 (m, 4 H), 1.20–1.60 (m, 18 H). MS: m/z 245 (M^+), 162, 132, 106, 93. HRMS for $C_{17}H_{27}N$ (M^+) calcd 245.2144, found 245.2145.

(4-Pyridyl)cyclododecane (16b). This was a yellow oil (10%). IR ($CHCl_3$): 2920, 2860, 1595, 1520, 1445 cm^{-1} . 1H NMR: δ 8.45 (br s, 2 H), 7.09 (br d, 2 H), 2.75 (qnt, 1 H), 1.1–1.90 (m, 22 H). MS: m/z 245 (M^+), 146, 106, 93. HRMS for $C_{17}H_{27}N$ (M^+) calcd 245.2144, found 245.2143.

Cyclododecyl 2-Pyridyl Sulfide (8d). Compound **8d** isolated here (5.6%) was compared with the authentic sample.

General Procedure for Gif^{IV} Oxidation. A mixture of pyridine (28 mL), acetic acid (2.3 mL, 40 mequiv) containing $FeCl_2 \cdot 4H_2O$ (14.8 mg, 7×10^{-3} mmol), and hydrocarbon was placed in a 150-mL Erlenmeyer flask. Zinc powder (1.3 g; 20 mg) was added and kept suspended in solution by stirring. The mixture was stirred open to air at room temperature until the zinc powder disappeared (8–10 h). The resulting dark-brown solution was subjected to the work-up procedure described in Table VIII.

Stability of *sec*-Alkylpyridine-Coupled Products under Gif^{IV} Conditions. (a) For **2-(2-Pyridyl)adamantane (4)**. Compound **4** (213 mg, 1.0 mmol) was subjected to Gif^{IV} conditions. The chilled reaction mixture was acidified with 25% H_2SO_4 (v/v) and extracted with ether (4×25 mL). The combined ether layers were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated to dryness. The 1H NMR spectrum of the residue was compared with the spectra of 2-adamantanone and 2-adamantanol. Neither of these compounds was present. The IR spectrum did not show any carbonyl absorption.

The acidic aqueous layer was basified (20% NaOH) and extracted with ether (4×50 mL). The combined ether extracts were washed with water, dried ($MgSO_4$), and evaporated to dryness at room temperature using a dry ice cooled rotary evaporator. The recovery of **4** (82%) was determined by comparing the intensity of the 1H NMR peak representing the α -2-adamantyl proton with the protons of CH_2I_2 ($\delta = 3.8$ ppm) added as an internal standard.

(b) For **2-(4-Pyridyl)adamantane (5)**. A Gif^{IV} reaction was performed in the presence of **5** (158 mg, 0.75 mmol), and the reaction mixture was worked up as described for compound **4**. The neutral extracts did not contain any oxidation products (1H NMR and IR). A major proportion of **5** (73%) was found in the basic fraction as determined by 1H NMR using CH_2I_2 as internal standard.

(c) For **(2-Pyridyl)cyclohexane (15a)**.³ Compound **15a** (161 mg, 1.0 mmol) was incubated under Gif^{IV} conditions. The resulting solution was worked up as described for compound **4**. The neutral fraction was treated with 2,4-dinitrophenylhydrazine reagent. There was no detectable amount of cyclohexanone dinitrophenylhydrazone. The basic fraction was purified by column chromatography on silica gel using petroleum ether as eluent. 1H NMR of the fraction containing **15a** was recorded using CH_2I_2 as internal standard. The yield of **15a** was 50%.

Oxidation of Adamantane with and without *sec*-Adamantylpyridine-Coupled Products. (a) **Without *sec*-Adamantylpyridine-Coupled Products 4 and 5.** Adamantane (272 mg, 2.0 mmol) was oxidized by a Gif^{IV} oxidation reaction. The resulting residue was treated with 5% NaOH (50 mL) and extracted with ether (4×100 mL). The combined ether extracts were washed once with water, dried ($MgSO_4$), and concentrated to 20 mL. The analysis of this concentrate (GC) for the coupled products showed compounds **2** (5.66%), **3** (7.65%), **4** (<0.5%), and **5** (<0.5%).

(b) **With *sec*-Adamantylpyridine-Coupled Products 4 and 5.** A mixture of adamantane (272 mg, 0.17 mmol), (2-pyridyl)-2-adamantane (38.6 mg, 0.17 mmol), and (4-pyridyl)-2-adamantane (18.1 mg, 0.085 mmol) was subjected to Gif^{IV} oxidation conditions. The chilled (ice bath) mixture was acidified with 25% (v/v) H_2SO_4 and extracted with ether (4×50 mL). The combined ether extracts were dried ($MgSO_4$) and evaporated to dryness. The 1H NMR of the residue with CH_2I_2 as internal standard showed 10.5% of 2-adamantanone (**12**) and 3.5% of 2-adamantanol (**10**).

The acidic aqueous solution was basified (20% NaOH) and extracted with ether (4×50 mL). The combined ether extracts were washed with water, dried ($MgSO_4$), and concentrated to 20 mL. The concentrate contained **2** (5.55%), **3** (12.7%), **4** (97.7% recovery), and **5** (94.8% recovery) as determined by GC analysis.

Photolysis of Acyl Derivatives 7 under 4% Oxygen in Nitrogen. A steady stream of nitrogen (30 mL/min) and air (7.5 mL/min) was maintained with needle valves. Each gas, after being mixed in a flask, was blown over the surface of the stirred pyridine (28-mL)-acetic acid (2.3-mL) solution containing compound **7**. The photolysis was carried out with two W lamps situated 25 cm from the reaction flask for 2 h, at 12 °C. The reaction mixture was analyzed as described in Table VIII. The products and their quantities are given in Table V.

Gif^{IV} Oxidations of Hydrocarbons Adamantane (1), Cyclohexane, and Cyclododecane under a Flow of 4% Oxygen in Nitrogen. A stable stream of nitrogen (30 mL/min) and air (7.5 mL/min) was maintained with the aid of needle valves. Each gas was connected to inlets of a flask that served as a premixing chamber. The gas mixture was then blown over the surface of the stirred reaction mixture which was composed of hydrocarbon, $FeCl_2 \cdot 4H_2O$ (8 mg, 4×10^{-2} mmol), and zinc powder (1.3 g, 20 mg) in pyridine (28 mL)-acetic acid (2.3 mL, 40 mmol). The solution was stirred at a rate to keep the zinc in suspension for 24 h at room temperature. The resulting dark solution was worked up after combining with the contents of the cold trap (dry ice-acetone) attached to the outlet of the reaction vessel. The workup and method of analysis are described in Table VIII. The amount of hydrocarbon used and quantities of products found are listed in Table VI.

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Ylidions: A New Reactive Intermediate Prepared by Photosensitized One-Electron Oxidation of Phenacyl Sulfonium Ylides

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Abstract: The chemistry of a series of phenacyl sulfonium ylides was studied. Their photosensitized one-electron oxidation by 9,10-dicyanoanthracene generates ylidions, a new class of radical cation intermediates. In some cases, the ylidions cleave to form a free alkyl radical and a cation; in others, they are attacked by nucleophiles or by an alkene. The chemical properties displayed by the phenacyl sulfonium ylidions appear to be controlled primarily by the nature of the sulfur-bound alkyl groups. The direct photolysis and thermolysis of the phenacyl sulfonium ylides was examined for comparison with their one-electron oxidation. Some of the ylides undergo the Stevens rearrangement either when heated or photolyzed. Contrary to an earlier report, there is no evidence that direct photolysis of a phenacyl sulfonium ylide leads to formation of benzoylcarbene.

Ylides play important roles in both practical and theoretical organic chemistry.¹ Numerous studies of their chemical and

physical properties have related their unique bonding pattern to their characteristic reactivity.² Surprisingly, an aspect of the