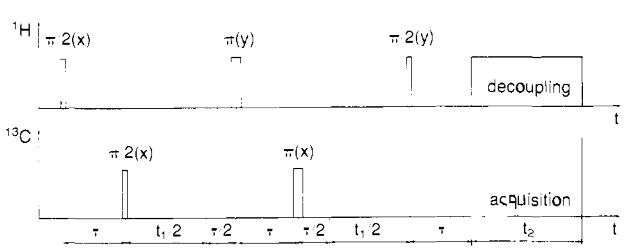

Figure 1. Schematic representation of the pulse sequence that utilizes correlated motion of ^{13}CH spin pairs for indirect detection of long-range J coupling constants.

Subsequent motion of ^{13}CH spin pairs becomes correlated.[3] If one of H_a spins flips over, the attached carbon C_a must also have flipped over and the proton spin starts to behave exactly as a H_b spin. Because of this mutual flipping, the net magnetization vectors should not change during the evolution period t_1.

The above conclusion holds only for "isolated" spin pairs which experience one-bond coupling $^1J_{CH}$ used to establish correlated motion.[3] In most real molecules long-range couplings are present, and they have a small but steady influence on both ^{1}H and ^{13}C spins.[4] The effect becomes apparent when the $\pi/2(y)$ pulse turns protons back into the $\pm z$ directions. The correlated motion is quenched and ^{13}C components establish phase coherence during the last period.[6] Signals are detected if (i) ^{13}C magnetization is present ($\vec{M}_{C_a}$ and $\vec{M}_{C_b}$) and (ii) attached protons are found with suitable orientations ($\vec{M}_{H_a}$ and $\vec{M}_{H_b}$).

As an illustration *cis*-dichloroethylene is described. It contains two chemically equivalent hydrogens that give rise to a single sharp peak in the ordinary ^{1}H NMR spectrum. Equivalence is removed in ^{13}C spectroscopy, which detects signals from $ClH^{13}C{=}^{12}CHCl$ molecules, and the ^{13}CH spin pairs are coupled to the proton spin in the ^{12}CH group.

During the evolution period t_1 magnetization of ^{1}H spins oscillates along $\pm x$ as

$$M_{H_a} = M^0_{H_a} \cos(\pi\,{}^3J_{HH}t_1) \tag{1}$$

$$M_{H_b} = M^0_{H_b} \cos(\pi\,{}^3J_{HH}t_1) \tag{2}$$

where $^3J_{HH}$ denotes coupling between ^{1}H spins and t_1 is the effective evolution period in the pulse sequence (Figure 1). ^{13}C spins also experience two-bond coupling $^2J_{CH}$ and

$$M_{Ca} = M^0_{Ca} \cos(\pi\,{}^2J_{CH}t_1) \tag{3}$$

$$M_{Cb} = M^0_{Cb} \cos(\pi\,{}^2J_{CH}t_1) \tag{4}$$

therefore, the signal $s(t_1)$ is proportional to

$$s(t_1) = s_0 \cos(\pi\,{}^2J_{CH}t_1) \cos(\pi\,{}^3J_{HH}t_1) \tag{5}$$

where $s_0 = s(t_1 = 0)$ denotes signal amplitude. After rearrangement

$$s(t_1) = \tfrac{1}{2}s_0\{\cos[\pi({}^2J_{CH} + {}^3J_{HH})t_1] + \cos[\pi({}^2J_{CH} - {}^3J_{HH})t_1]\} \tag{6}$$

it becomes evident that Fourier transformation with respect to t_1 reveals resonances at frequencies $\pm{}^1/_2({}^2J_{CH} + {}^3J_{HH})$ and $\pm{}^1/_2|{}^2J_{CH} - {}^3J_{HH}|$, while $^1J_{CH}$ has been eliminated by the correlated motion.[3]

Equation 6 was used to calculate $^2J_{CH} = 15.8 \pm 0.1$ Hz and $^3J_{HH} = 5.2 \pm 0.1$ Hz from Figure 2. The same experiment on *trans*-dichloroethylene gave $^3J_{HH} = 12.1 \pm 0.1$ Hz and $^2J_{CH} < 0.2$Hz. The results are in agreement with previous measurements via ^{13}C satellites in ^{1}H NMR spectra.[1,7,8]

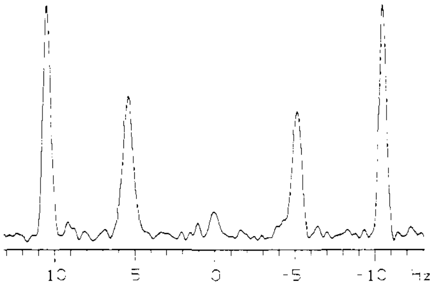

Figure 2. Cross section of the NMR spectrum of *cis*-dichloroethylene as obtained by the pulse sequence from Figure 1 and after the Fourier transformation with respect to the evolution time t_1 which has been incremented in steps of 38 ms. Presaturation[9] of the ^{13}C spin system and phase alternations[10] of the last proton pulse [$\pi/2(y)$ add and $\pi/2(-y)$ subtract] ensured that all signals were due to polarization transfer.

The new method has serious disadvantages, because it needs detection of weaker ^{13}C signals, two-dimensional data processing, and ^{13}CH spin pairs as "probes"; therefore, it can not become a universal way for measuring J coupling between chemically equivalent hydrogen nuclei. On the other hand two very important advantages must be pointed out:

(i) π pulses refocus precession resulting from inhomogeneous magnetic field, and resolution of the experiment is limited only by natural line widths.

(ii) Overlap of satellite and main peaks occurs very often in complex ^{1}H NMR spectra, and determination of the J coupling becomes impossible. The new pulse sequence solves this problem.

Acknowledgment. The Nicolet NT-300 spectrometer was purchased through a grant from the National Science Foundation (PCM-8115599).

Registry No. *cis*-Dichloroethylene, 156-59-2; *trans*-dichloroethylene, 156-60-5; carbon-13, 14762-74-4.

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Photocatalytic Formylation of Primary and Secondary Amines on Irradiated Semiconductor Powders

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Received December 22, 1982

Although amines have been often used as sacrificial single-electron donors in many photoinduced redox studies, little is known of the chemical fate of the oxidized species so generated. We report here the identity of products formed by photocatalytic oxidation of a primary and a secondary aliphatic amine on irradiated TiO_2 powders suspended in oxygenated acetonitrile. These experiments represent the first characterizations of solution-phase aliphatic amine photooxidations sensitized by a heterogeneous metal oxide catalyst.

By use of previously described procedures,[1] *N*-methyl-4-phenylbutylamine (**1a**) and its demethylated analogue **1b** were catalytically photooxidized. The major products obtained were the respective N-formylation (**2**) and α-C–N oxidative cleavage (**3**) products (eq 1 and 2). Smaller amounts of other cleavage products were also formed.[2] The relative amounts of the two

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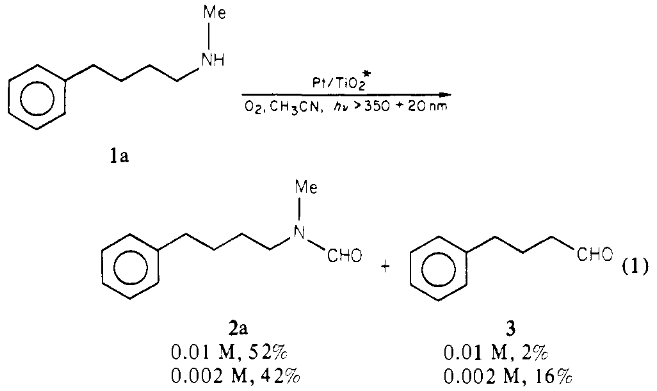
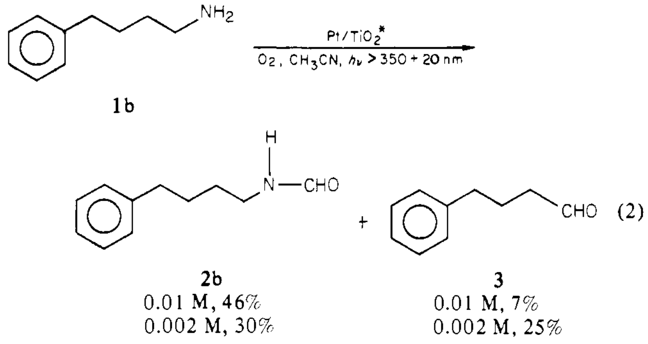
(1) Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 6757.



1a

2a
0.01 M, 52%
0.002 M, 42%

3
0.01 M, 2%
0.002 M, 16%



1b

2b
0.01 M, 46%
0.002 M, 30%

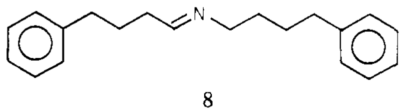
3
0.01 M, 7%
0.002 M, 25%

major products were controlled by the initial concentration of the oxidizable amine. Nearly identical product distributions were observed in neat acetonitrile or in alcoholic (trifluoroethanol) acetonitrile suspensions. Similarly, partial platinzation[3] of the TiO_2 photocatalyst did not significantly affect the product distribution. Analogous products were obtained upon preparative electrolysis of **1** at a single-crystal TiO_2 anode, although, as in previous studies of 1,1-diphenylethylene,[1] in much lower yield than in this photocatalytic route.

Although both **1a** and **1b** display tailing absorption bands in the region of the excitation (350 ± 20 nm), the formation of oxidation products is at least 5 times more rapid in the presence of the heterogeneous photocatalyst than in its absence. Furthermore, products and/or distributions of products obtained upon direct irradiation are different than in our photocatalytic conditions.[4] No reaction is observed when the amine is exposed to the reaction suspension mixture unless photoexcitation and oxygen are also present.

Previous studies in this laboratory have implicated the photocatalytic single-electron oxidation of adsorbed organics on irradiated semiconductor surfaces as the primary photoprocess in catalytic oxygenation of olefins and arenes.[1,5-7] A parallel route capable of explaining the observed products is shown in Scheme I.

In this scheme, photoexcitation effects an electron–hole pair separation at the surface of the metal oxide particle. Since the oxidation peaks for both primary and secondary aliphatic amines[8] lie at less positive potentials than the valence band of TiO_2 (ca. +2.4 V), the adsorbed amine can capture the photogenerated hole to form an aminium cation radical. Such species will rapidly deprotonate to form a stabilized α-amino radical **4**.[9] If **4** is captured by oxygen, a chain process involving the hydroperoxy radical **5** can ultimately lead to the observed aldehyde **3**. Alternatively, **4**, formed in a highly polar environment in which electron exchange is expected to be facile, can lose a second electron, perhaps reversibly, to form an iminium cation, **6**. Nucleophilic attack on this intermediate by superoxide (generated in situ by capture of the photogenerated electron on the irradiated particle surface) provides an alternate route to **5**. A similar reaction with starting material leads to a coupled iminium ion, **7**, deprotonation of which gives either the imine found in the photocatalytic oxidation of **1a** (**8**) or an enamine, **9**. Since electron-rich olefins are known to suffer chemically efficient oxidative cleavage on irradiated TiO_2, further photocatalytic oxidation of **9** to the observed N-formylation product **2** is reasonable.



8
0.01 M, 28%
0.002 M, 0%

The requirement for oxygen for the induction of photoreactivity follows from the nature of the electron transfer from **1** to the electron–hole pair. In the absence of oxygen (to inhibit back-electron transfer), the aminium cation radical, held at the negatively charged surface of the particle, will be rapidly reduced back to **1**, effectively quenching the sensitization. This scheme also provides a rationale for the observed dependence of the initial concentration of amine, since the ratio of **2** and **3** obtained will depend on the rate of the bimolecular capture of **6** by **1** or **3**. That **3** results from oxygenation of **4**, rather than from oxidative cleavage of **8**, is supported by two observations: **3** is still detected from **1a** where imine formation is alkylatively blocked, and no N-oxygenated products expected to accompany the oxidative cleavage of **8** could be detected.[10]

The possibility that the observed amine oxidation proceeds not through radical cation formation but rather through a dark chemical reaction of photogenerated hydrogen peroxide requires evaluation. While the photoinduced formation of hydrogen peroxide by capture of the photogenerated conduction band electron by adsorbed oxygen is viable, the cleaner formation of oxidation products on our photocatalyst compared with reported radical reactions[11,12] weigh against its involvement as the primary oxidant.

The N-formylation products obtained in this heterogeneous photooxidation are not complicated by the formation of α-hydroxy ketones or diones, which have sometimes been observed upon singlet oxygenation of enamines.[13] That similar formylation products can be formed with singlet oxygen and with this redox photocatalyst, however, may provide supporting evidence for the involvement of electron transfer in the singlet oxygen reaction, a phenomenon that has been reasonably documented for the

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(2) Chemical yields of all products were determined by gas chromatography (5 ft × 1/4 in. 20% SE-30 on Chromosorb P, 150–270 °C, 6 °C/min) against a calibrated internal standard. Reported yields are based on the expected consumption of 2 mol of reactant for each mole of formylation product and were determined after 4 h of irradiation when nearly complete consumption of starting material had occurred. The major products were identified by isolation and comparison of spectral properties with known samples. Minor products were identified by comparison of mass spectral fragmentation patterns with library standards. Besides the major products shown in eq 1 and 2, the following compounds were detected: from **1a**, $Ph(CH_2)_4NHCHO$ (3%), $Ph(CH_2)_3CO_2H$ (2%), $Ph(CH_2)_3OH$ (1%), $Ph(CH_2)_2CHO$ (8%), PhCHO (8%); from **1b**, $Ph(CH_2)_4NCHPh$ (4%), $Ph(CH_2)_3CN$ (6%), $Ph(CH_2)_3CHO$ (6%), PhCHO (10%).

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(4) The products of the direct photolysis were obtained by using the same irradiation conditions as in the photocatalytic oxygenations,[1] except that the powdered catalyst was omitted. After 4 h of irradiation of a 0.01 M solution (ca. 35% consumption of starting material), two products were detected from **1a** (**2a** (10%) and **2b** (28%)). After 13 h of irradiation (ca. 80% consumption of starting material), $Ph(CH_2)_4N{=}CHCH_3$ (47%) was formed from **1b**.

(5) Fox, M. A.; Lindig, B. A.; Chen, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 5828.

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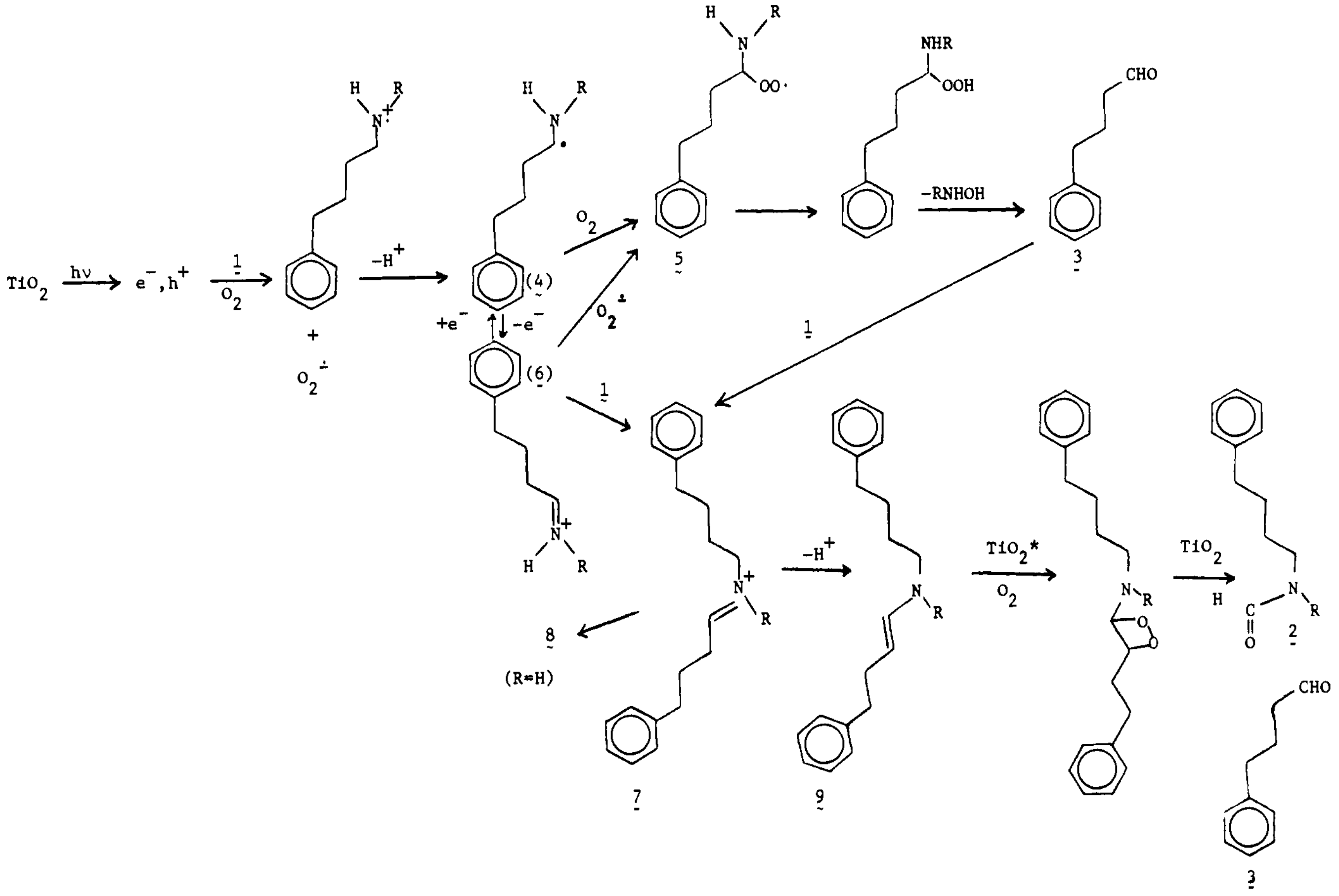
Scheme I. Proposed Mechanism for Photocatalytic Amine Oxidation



interaction of singlet oxygen with other electron-rich functional groups.[14] In fact, the concurrent operation of radical and charge-transfer mechanisms in the photooxygenation of tributylamines has already been suggested.[15]

This work is not the first description of heterogeneous photooxidation of nitrogen-containing compounds. Pichat and coworkers have previously reported, for example, that the TiO_2-photocatalyzed oxidation of gaseous ammonia gives rise to N_2 and N_2O.[16] Similarly, the photocatalyzed oxidation in aqueous suspensions of TiO_2 of toluidines to azo coupling products[17] and of amides to imides[18] have been described. The experiments reported here, however, are the first attempts at controlling the mode of photooxidation of aliphatic amines on a heterogeneous photocatalyst suspended in a nonaqueous solvent.

Although one photochemical route to the N-formylation of aliphatic amines (the photooxygenation of enamines) has been previously described,[13,19] this work represents the first demonstration that the formyl carbon can be derived from the amine itself. Hence, in addition to expanding the arsenal of redox reactions that can be accomplished on irradiated semiconductor powders, this study provides an alternate synthetic route to formylated products as well as a mechanistically important characterization of electron-transfer-induced amine oxidations. Future work will address the comparison of these semiconductor surface-mediated photocatalytic oxidations with those initiated by photexcited electron-transfer sensitizers in homogeneous solution.

Acknowledgment. This work was supported by the National Science Foundation and the Robert A. Welch Foundation. M.A.F. is grateful for support as a Alfred P. Sloan Research Fellow and as a Camille and Henry Dreyfus Teacher–Scholar.

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Stereospecific Synthesis of Acyclic Unsaturated Amino Alcohols. A New Approach to *threo*- and *erythro*-Sphingosine

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Received March 14, 1983

The discovery of new methodology for efficient genesis of relative stereochemistry in acyclic systems has continually been of major importance in synthetic organic chemistry.[1] The recent elegant and extensive work on stereocontrol in aldol and related reactions[2] has not been matched to data by the development of methods for stereoselectively preparing nitrogen-containing acyclic molecules.[3] We now describe a conceptually new route to vicinal amino alcohols containing unsaturation that allows total control of both relative configuration and double-bond geometry.

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