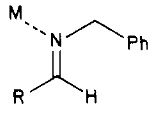
Quite surprisingly, the ratio of erythro to threo products proved essentially independent of the Lewis acid used; all Lewis acids which successfully promoted reaction gave ca. 4:1 mixtures of diastereomeric products in which the erythro product predominated. For the case of R = cyclohexyl, erythro:threo ratios were between 77:23 and 79:21 for all of the following Lewis acids (isolated yields in parentheses[7]) by using the reaction protocol previously described for allyl additions: $BF_3 \cdot OEt_2$ (82%), $TiCl_4$ (83%), $MgBr_2$ (71%), ZnI_2, Et_2AlCl (79%), $ZrCl_4$ (84%), CF_3CO_2H, and CH_3SO_3H.

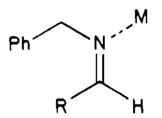
Fortunately, however, considerable improvement in stereoselectivity could be achieved by allowing sufficient time at −78 °C to effect complexation rather than employing the expedient of warming. Moreover, carefully controlled experiments with respect to time and temperature using $TiCl_4$ as Lewis acid revealed that *stereoselectivity is determined primarily by the history of the Lewis acid–aldimine complex.* Thus, the following results were obtained for experiments conducted by using the following protocol: 0.2 M in substrate at −78 °C in CH_2Cl_2, add 1 equiv of $TiCl_4$, warm to temperature T for the indicated period of time, recool to −78 °C, add 2.0 equiv of crotyltri-*n*-butylstannane, stir at −78 °C for 1 h, and warm slowly to 23 °C overnight.

T	time at T	erythro:threo ratio
23 °C	1.0 h	4.4:1
0 °C	1.5 h	6.7:1
-42 °C	1.0 h	11.3:1
-78 °C	2.5 h	23.6:1

These results quite strongly suggest that, at least for the case of $TiCl_4$, two different aldimine–Lewis acid complexes are undergoing reaction, that these complexes are interconvertible at elevated temperatures, and that the kinetically formed complex exhibits high erythro selectivity in its reaction with crotyltri-*n*-butylstannane, while the erythro selectivity of the other, thermodynamically favored, complex is low. These may be reasonably formulated as I and II, although the identity of which complex exhibits high erythro selectivity is not presently known. However, one would reasonably expect that species I should be formed initially from an aldimine and Lewis acid. If this is so, the equilibration to II suggests that the $TiCl_4$ moiety may be rather sterically demanding. However, using this hypothesis and the extended transition state proposed by Yamamoto[5] for additions to aldehydes the selectivities observed are not readily explained, since one would then expect higher erythro selectivity for addition to II than for $TiCl_4$-mediated addition to the corresponding aldehyde, which is not the case.[4] Similar difficulties are encountered upon attempting to rationalize the results via synclinal transition states as espoused by Denmark[8] for similar additions to aldehydes. It may be that I and II are not in fact the species undergoing reaction, or that factors other than simple steric interactions are important in controlling the reaction pathway. Efforts to develop a better mechanistic understanding of such reactions are in progress. For the present, however, we note that such organostannane additions to aldimines provide a useful route to homoallylamines and β-methylhomoallylamines with good stereocontrol in the bond construction for the latter case. Product ratios and isolated yields for the $TiCl_4$-mediated addition to other *N*-benzyl aldimines are included in Table I.



I



II

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Gary E. Keck,*† Eric J. Enholm
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

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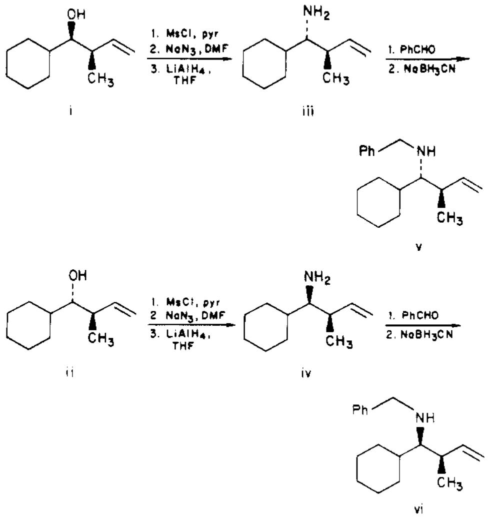
[6] Thus, the readily available[4] erythro and threo alcohols i and ii were subjected to mesylation, azide displacement, and reduction to afford amines iii and iv with clean inversion of configuration in each case. Imine formation[3] and sodium cyanoborohydride reduction then afforded the desired *N*-benzylamines v and vi.



[7] For cases where no yield is indicated, conversion to products was 50% or less after ca. 18 h at 23 °C.

† Fellow of the Alfred P. Sloan Foundation, 1981–1985.

[8] Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* 1983, *66*, 1655–1660.

Desulfurization and Carbonylation of Mercaptans

Summary: The first examples of the carbonylation of mercaptans are described: cobalt carbonyl catalyzes the desulfurization and carbonylation of mercaptans to carboxylic esters by means of carbon monoxide in aqueous alcohol.

Sir: Carbonylation reactions are an important class of organic reactions. Of industrial importance are those transformations utilizing olefins, alkynes, and halides as substrates.[1,2] For example, benzylic halides as well as vinylic mono- or dibromides can be carbonylated to acids by cobalt carbonyl (eq 1)[3] or palladium(0)[4] catalysts under

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[1] Wender, I., Pino, P., Eds. "Organic Synthesis via Metal Carbonyls"; Wiley-Interscience: New York, 1977; Vol. II.

[2] Falbe, J., Ed. "New Syntheses with Carbon Monoxide"; Springer Verlag: Berlin, 1980.

[3] Alper, H.; des Abbayes, H. *J. Organomet.* Chem. 1977, *134*, C11.

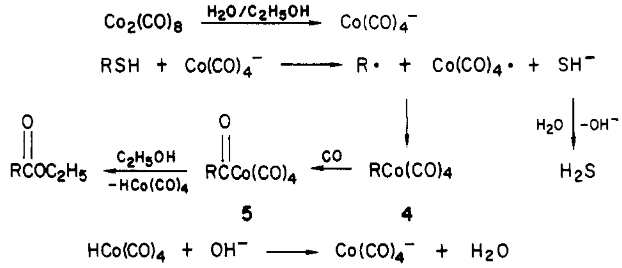
0022-3263/85/1950-0147$01.50/0

Table I. Desulfurization and Carbonylation of Mercaptans 1 Catalyzed by $Co_2(CO)_8$[a]

1, R =	2, R′ =	3	yield,[b] %
p-$CH_3C_6H_4CH_2$	C_2H_5	p-$CH_3C_6H_4CH_2COOC_2H_5$	75
	CH_3	p-$CH_3C_6H_4CH_2COOCH_3$	83
	$CH(CH_3)_2$	p-$CH_3C_6H_4CH_2COOCH(CH_3)_2$	74
	$C(CH_3)_3$	p-$CH_3C_6H_4CH_2COOC(CH_3)_3$	28
o-$CH_3C_6H_4CH_2$	C_2H_5	o-$CH_3C_6H_4CH_2COOC_2H_5$	51
p-$CH_3OC_6H_4CH_2$	C_2H_5	p-$CH_3OC_6H_4CH_2COOC_2H_5$	68
p-$ClC_6H_4CH_2$	C_2H_5	p-$ClC_6H_4CH_2COOC_2H_5$	67
	$C(CH_3)_3$	p-$ClC_6H_4CH_2COOC(CH_3)_3$	58
2,4-$Cl_2C_6H_3CH_2$	C_2H_5	2,4-$Cl_2C_6H_3CH_2COOC_2H_5$	25
2-naphthyl	C_2H_5	2-$C_{10}H_7COOC_2H_5$	50
C_6H_5	C_2H_5	$C_6H_5COOC_2H_5$	32
m-$CH_3C_6H_4$	C_2H_5	m-$CH_3C_6H_4COOC_2H_5$	77
$CH_3(CH_2)_7$	C_2H_5	$CH_3(CH_2)_7COOC_2H_5$	trace

[a] 20:1 $RSH/Co_2(CO)_8$; R′OH (30 mL); H_2O (2 mL); 850–900 psi, 190 °C 24 h. [b] Yields are of pure materials, identified by comparison of spectral data [IR, NMR (^1H, ^{13}C), MS] with those for authentic samples.

Scheme I



phase-transfer catalysis conditions, at room temperature and atmospheric pressure.

$$ArCH_2Br + CO \xrightarrow[C_6H_6,R_4N^+X^-,\ \text{r.t., 1 atm}]{Co_2(CO)_8,\ NaOH} ArCH_2COOH \qquad (1)$$

Another subject which has attracted attention in recent years is the water gas shift reaction, i.e., conversion of carbon monoxide and water to carbon dioxide and hydrogen.[5] Under such conditions one can, for example, reduce nitro compounds to amines[6] and polynuclear heteroaromatic nitrogen compounds.[7]

To our knowledge, no successful attempts to carbonylate mercaptans to esters have been reported in the primary or patent literature. We now report that cobalt carbonyl can catalyze the desulfurization and carbonylation of mercaptans to carboxylic esters.

Treatment of a benzylic or aromatic mercaptanl, in aqueous ethanol (2, R′ = C_2H_5), with carbon monoxide and a catalytic amount of cobalt carbonyl [20:1 ratio of 1/$Co_2(CO)_8$] for 24 h at 850–900 psi and 190 °C, affords carboxylic esters in 25–83% yields (Table I). Methanol, isopropyl alcohols and *tert*-butyl alcohol can be used instead of ethanol. Chloride and methoxy groups do not interfere with the reaction. No reaction occurs in the absence of cobalt carbonyl or, of course, in the absence of carbon monoxide. No ester was formed when p-methylbenzyl mercaptan was treated with carbon monoxide and anhydrous ethanol in the presence of cobalt carbonyl. Triiron dodecacarbonyl and rhodium carbonyl are incapable of catalyzing the conversion of 1 to 3.

$$\underset{1}{RSH} + CO + \underset{2}{R'OH} \xrightarrow[850\text{–}900\ \text{psi},\ 190\ ^\circ\text{C, 24 h}]{Co_2(CO)_8,\ H_2O} \underset{3}{RCOOR'} + H_2S$$

In Scheme I is outlined a possible pathway for the reaction [illustrated for ethanol]. Cobalt carbonyl undergoes disproportionation in aqueous ethanol, giving the cobalt tetracarbonyl anion.[8] single electron transfer from the latter to the mercaptan would generate the organic radical, cobalt tetracarbonyl radical, and SH^-. Protonation of the latter by the solvent liberates hydrogen sulfide (confirmed by mass spectrometric analysis). Coupling of the two radicals would afford 4, which on carbonylation to 5 and subsequent reaction with ethanol, gives the ester.

The following general procedure was used: a mixture of alcohol (30 mL), water (2 mL), mercaptan (10 mmol), and $Co_2(CO)_8$ (0.171 g, 0.5 mmol) was heated in an autoclave at 190 °C and 850–900 psi for 24 h. After being cooled to room temperature, the mixture was transferred to a round-bottomed flask and the solvents were removed using a rotary evaporator. Pure ester was obtained by silica gel column chromatography of the crude material.

In conclusion, benzylic and aryl mercaptans can undergo desulfurization and carbonylation to give primary, secondary, and tertiary esters by a process which is simple both in execution and workup. Since some mercaptans can be prepared from non-halide precursors [e.g., reaction of diazonium salts with SH^- or by the sulfurization of aromatic hydrocarbons],[9] this reaction constitutes a non-halide route to esters.

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Registry No. p-$CH_3C_6H_4CH_2SH$, 4498-99-1; o-$CH_3C_6H_4CH_2SH$, 25697-56-7; p-$CH_3OC_6H_4CH_2SH$, 6258-60-2; p-$ClC_6H_4CH_2SH$, 6258-66-8; 2,4-$Cl_2C_6H_3CH_2SH$, 59293-67-3; PhSH, 108-98-5; m-$CH_3C_6H_4SH$, 108-40-7; $CH_3(CH_2)_7SH$, 111-88-6; EtOH, 64-17-5; t-BuOH, 75-65-0; CH_3OH, 67-56-1; i-PrOH,

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(4) Galamb, V.; Gopal, M.; Alper, H. *Organometallics* **1983**, *2*, 801.

(5) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31.

(6) Pettit, R.; Cann, K.; Cole, T.; Maudlin, C. H.; Sleigeir, W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 101.

(7) Fish, R. H.; Thornodsen, A. D.; Cremer, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 5234. Note that cobalt carbonyl is a very poor catalyst for the water gas shift reaction.

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(9) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 481, 610–611.

67-63-0; p-$CH_3C_6H_4CH_2C(O)OEt$, 14062-19-2; p-$CH_3C_6H_4CH_2C(O)OMe$, 23786-13-2; p-$CH_3C_6H_4CH_2C(O)O$-i-Pr, 64450-64-2; p-$CH_3C_6H_4CH_2C(O)O$-t-Bu, 33155-60-1; o-$CH_3C_6H_4CH_2C(O)OEt$, 40291-39-2; p-$CH_3OC_6H_4CH_2C(O)OEt$, 14062-18-1; p-$ClC_6H_4CH_2C(O)OEt$, 14062-24-9; p-$ClC_6H_4CH_2C(O)O$-t-Bu, 33155-59-8; 2,4-$Cl_2C_6H_3CH_2C(O)OEt$, 41022-54-2; 2-$C_{10}H_7C(O)OEt$, 3007-91-8; $PhC(O)OEt$, 93-89-0; m-$CH_3C_6H_4C(O)OEt$, 120-33-2; $CH_3(CH_2)_7C(O)OEt$, 123-29-5; $Co_2(CO)_8$, 10210-68-1; 2-naphthalenethiol, 91-60-1.

Sang Chul Shim, Shlomo Antebi, Howard Alper*
Ottawa-Carleton Chemistry Institute
Department of Chemistry, University of Ottawa
Ottawa, Ontario, Canada K1N 9B4
Received August 24, 1984

Reactions in Dry Media: Oxidative Cleavage of Olefins Adsorbed on Inorganic Supports with Oxygen

Summary: Substituted phenylethylenes adsorbed on inorganic supports are oxidatively cleaved to ketones or aldehydes under illumination in the presence of oxygen. It is suggested that these oxidations involve the intermediacy of cation radicals whose formation is initiated by contact charge-transfer interactions between the olefins on the adsorbing phase and oxygen molecules.

Sir: In recent years, there have been numerous reports on photooxidative cleavage of electron-rich olefins with oxygen sensitized by 9,10-dicyanoanthracene[1] or by semiconductors[2] which occur via the intermediacy of cation radicals. We report here on a similar oxidative cleavage of such olefins adsorbed on inorganic supports in the absence of sensitizers.

We have observed that the exposure of 1,1-diphenylethylene (1) adsorbed on chromatographic grade silica gel (2% w/w) to air and laboratory light for 48 h leads to benzophenone (2) (23% conversion and 98% relative yield)[3] (Table I).

Similar results were obtained by replacing silica gel as a reaction matrix with neutral or basic alumina or with Florisil.[4] The rate of oxidation of 1 adsorbed on each of these four supports increased significantly when the irradiation was with 350-nm light[5] and the air was replaced by oxygen; the time required to achieve a similar conversion of 1 to 2 decreasing from 72 h to 4 h (Table I).

On the other hand, no reaction occurred when the adsorbed material was left in darkness while exposed to air, or when it was illuminated under argon. Also, almost all the starting material was recovered after illuminating an acetonitrile solution of 1 with laboratory or 350-nm light under oxygen for the same period as was used for the adsorbed phase.[6]

We assume that this oxidation is initiated by a contact charge-transfer interaction[7] between 1 and the (triplet) oxygen molecules at the surface of the adsorbent. The existence of such interactions, which was deduced from shifts in the absorption spectra of electron-rich unsaturated compounds, adsorbed on silica gel in the presence of oxygen derives from the close contact between the oxygen and the electron-rich substrate.[8]

Illumination of these contact charge-transfer assemblies of 1 and O_2 results in an electron transfer with the formation of cation radical $1^{+\cdot}$ and anion radical $O_2^{-}\cdot$. $1^{+\cdot}$ may either react with O_2 or recombine with $O_2^{-}\cdot$, leading to a dioxetane, the precursor of 2, as suggested previously.[1,2]

The use of acidic alumina as an adsorbent for 1 led to higher oxidation rates than those with the above four adsorbents, both on illumination with laboratory light and on irradiation with 350-nm light (Table I). This enhancement of rate on acidic alumina was observed also in the oxidation of α-methylstyrene. Thus, illumination with laboratory light of this compound adsorbed on silica gel, neutral alumina, or basic alumina yielded 3% of acetophenone as the main product, but on acidic alumina, the yield of this product increased to 45%. With the latter adsorbent, dimethylphenylcarbinol, an acid-catalyzed hydration product of α-methylstyrene was also isolated.

The enhancement of the oxidation rate on acidic alumina can be ascribed to its Brønsted or Lewis acidity which increases the electrophilicity of the adsorbed O_2 molecules, thus lowering the energy barrier for the electron transfer from the olefin to O_2.[9–11]

1-Phenylcyclohexene and anethole, possessing comparatively low oxidation potentials ($E_{1/2} < 1.5$ V vs. SCE), were also oxidatively cleaved with oxygen on silica gel, which was here preferred as an adsorbent over acidic alumina, since the latter can lead to undesired hydration products (Table I).

1,4-Diphenylbutadiene and 1-phenylbutadiene (which adsorb in the 350-nm region) were oxidized by illumination with laboratory light. After 72 h, the former resulted in a quantitative conversion to a 1:1 mixture of cinnamaldehyde and benzaldehyde, while the latter gave cinnamaldehyde as a major product (Table I).

Contrary to other olefins adsorbed on silica gel, which are inert to oxygen in the dark, 1,4-diphenylbutadiene undergoes oxidation under these conditions, resulting, after

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[1] Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. Spada, L. T.; Foote, C. S. *Ibid.* **1980**, *102*, 391. Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083. Steichen, D. S.; Foote, C. S. *Ibid.* **1981**, *103*, 1855. Ilang, Z. Q.; Foote, C. S. *Tetrahedron Lett.* **1983**, *24*, 461. Schaap, P. A.; Zaklika, K. A.; Kaskar, B.; Fung, L. W. M. *Ibid.* **1980**, *21*, 102, 389. Ando, W.; Kabe, Y.; Takata, T. *J. Am. Chem. Soc.* **1982**, *104*, 7314.

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[3] The substrate (ca. 0.25 g) was preadsorbed from CH_2Cl_2 solution into the solid adsorbent (12.5 g), and the solvent was evaporated to dryness under reduced pressure. The dry powder was then shaken in an open vessel under illumination with Westinghouse fluorescent light (F40, cool white light, 6 × 40 W, having adsorption onset at ca. 400 nm). The reaction products were eluted with CH_2Cl_2, analyzed by GC–MS, then isolated by column chromatography, and identified by comparison with authentic compounds (IR, GC, NMR, MS).

[4] Chromatographic grade Woelm aluminas activity I and Florisil (Floridin 100–200 mesh) were used.

[5] Oxygen was passed through the adsorbed substrate, placed in a Pyrex U-tube inside a Rayonet photochemical reactor, equipped with 8 × 15 W RUL-3500 Å lamps.

[6] Only traces of 2 and other products were detected by TLC.

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[8] Ishida, H.; Takahashi, H.; Sato, H.; Tsubomura, H. *J. Am. Chem. Soc.* **1970**, *92*, 275.

[9] It has been shown that adsorption of electron-rich hydrocarbons on activated aluminas leads, in the presence of O_2, to the formation of cation radicals and $O_2^{-}\cdot$. Flockart, B. D.; Scott, J. A. N.; Pink, R. C. *Trans. Faraday Soc.* **1966**, *62*, 730. Flockhart, B. D.; Leith, I. R.; Pink, R. C. *J. Catal.* **1967**, *9*, 45.

[10] Electron transfer was found to take place also between polyaromatic compounds and O_2 in strongly acidic solutions: Cf. Aalsberg, W. I.; Hoijtink, G. J.; Mackor, E. L.; Weijland, W. P. *J. Chem. Soc.* **1959**, 3049. Analsberg, W. I.; Gaaf, J.; Mackor, E. L. *Ibid.* **1961**, 905.

[11] An oxidation with O_2 of adamantylideneadamantene in acidic solution has recently been reported and explained by an electron transfer from the olefin to O_2, activated by the acidic medium: Cf. Akaba, R.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1984**, *25*, 665.

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