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.

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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 $\mathbf{1}^{+\cdot}$ and anion radical $O_2^{-\cdot}$. $\mathbf{1}^{+\cdot}$ 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.

[2] Fox, M. A.; Chen, C.-C. *J. Am. Chem. Soc.* **1981**, *103*, 6757. Fox, M. A.; Lindig, B.; Chen, C.-C. *Ibid.* **1982**, *104*, 5829. Fox, M. A.; Chen, C.-C. *Tetrahedron Lett.* **1983**, *24*, 547. Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokurmaru, K. *Tetrahedron Lett.* **1980**, *21*, 467.

[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.

[7] Evans, D. F. *J. Chem. Soc.* **1953**, 345; **1957**, 1351. Tsubomura, H.; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966.

[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.

0022-3263/85/1950-0149$01.50/0

Table I. Photooxidation of Olefins Adsorbed on Inorganic Supports

compound	time, h	convrsn,[a] %	products distribution,[a] %
$(C_6H_5)_2C{=}CH_2$	48^b	$18\text{–}23^c$ $(75)^d$	$(C_6H_5)_2CO$, 98 (97);^{d} $(C_6H_5)_2CH(OH)CH_3$, 2 (1); $(C_6H_5)_2CHCHO$ (2)
	4^e	$17\text{–}25^f$ $(60)^d$	$(C_6H_5)CO$, 98 (96);^{d} $(C_6H_5)_2CHCHO$, 2 (1)
$C_6H_5C(CH_3){=}CH_2$	4^b	3^g $(41)^d$	$C_6H_5COCH_3$, 98 (71);^{d} $C_6H_5(CH_3)CHCHO$, 2 (6);^{d} $C_6H_5(CH_3)_2COH$ $(23)^d$
trans-p-$MeOC_6H_4CH{=}CHCH_3$	4^e	23^g	*p*-$MeOC_6H_4CHO$, 52; *p*-$MeOC_6H_4CH_2COCH_3$, 3; 45^h
1-phenylcyclohexene	22^e	85^g	$C_6H_5CO(CH_2)_4CHO$, 37; $C_6H_5CO(CH_2)_4COOH$, 46; 17^i
trans-$C_6H_5CH{=}CHCH{=}CH_2$	72^b	64^g	C_6H_5CHO, 8; $C_6H_5CH{=}CHCHO$, 92
trans,trans-$C_6H_5CH{=}CHCH{=}CHC_6H_5$	72^b	98^g	C_6H_5CHO, 53; $C_6H_5CH{=}CHCHO$, 42

[a] The yields were determined by calibrated gas chromatography and NMR using internal standards. [b] Illumination with laboratory light. [c] On silica gel (23%), Florisil (20%), neutral alumina (18%), and basic alumina (21%). [d] On acidic alumina. [e] Irradiation with 350-nm light. [f] On silica gel (17%), Florisil (25%), neutral alumina (22%), basic alumina (19%). [g] On silica gel. [h] *cis*-Anethole. [i] Allylic oxidation products.

72 h, in 25% conversion to a 1:1 mixture of cinnamaldehyde and benzaldehyde., In this case, the low oxidation potential of 1,4-diphenylbutadiene ($E_{1/2}$ = 1.18 V vs. SCE)[12] is sufficient to cause an electron transfer and formation of a cation radical without the intervention of light.

It is of interest that photoreactions of some electron-rich olefins in solution in the presence of oxygen, which serves as an electron acceptor, and in the absence of sensitizers lead mainly to dimerizations,[13] unlike the oxidations on the solid supports described here.

Registry No. $(C_6H_5)_2C{=}CH_2$, 530-48-3; $C_6H_5C(CH_3){=}CH_2$, 98-83-9; *trans-p*-$MeOC_6H_4CH{=}CHCH_3$, 4180-23-8; *trans*-$C_6H_5CH{=}CHCH{=}CH_2$, 16939-57-4; *trans,trans*-$C_6H_5CH{=}CHCH{=}CHC_6H_5$, 538-81-8; 1-phenyl cyclohexene, 771-98-2; alumina, 1344-28-1; Florisil, 1343-88-0.

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[12] Stanienda, A. *Z. Phys. Chem.* **1962**, *33*, 170.

[13] Kojima, M.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, *21*, 2831.

Additions and Corrections

Vol. 49, 1984

Tsutomu Fujita, Shoji Watanabe,* Kyoichi Suga, Yoshiki Higuchi, and Tsukasa Sotoguchi. A Convenient Preparative Method of [*m.n.*3]Propella-γ-lactones.

Page 1975. Column 2: the information given below is needed to identify structures **1**, **2**, and **3**.

1a, $m = 3; n = 4$
b, $m = 3; n = 5$
c, $m = 4; n = 4$
d, $m = 4; n = 5$
e, $m = 5; n = 4$
f, $m = 5; n = 5$

2a, $m = 3; n = 4; R^1 = R^2 = H$
b, $m = 3; n = 5; R^1 = R^2 = H$
c, $m = 4; n = 4; R^1 = R^2 = H$
d, $m = 4; n = 5; R^1 = R^2 = H$
e, $m = 5; n = 4; R^1 = R^2 = H$
f, $m = 5; n = 5; R^1 = R^2 = H$
g, $m = 4; n = 4; R^1 = Me; R^2 = H$
h, $m = 4; n = 4; R^1 = R^2 = Me$
i, $m = 4; n = 4; R^1 = Et; R^2 = H$
j, $m = 4; n = 4; R^1 = n\text{-Pr}; R^2 = H$

3a, $m = 3; n = 4; R^1 = R^2 = H$
b, $m = 3; n = 5; R^1 = R^2 = H$
c, $m = 4; n = 4; R^1 = R^2 = H$
d, $m = 4; n = 5; R^1 = R^2 = H$
e, $m = 5; n = 5; R^1 = R^2 = H$
f, $m = 4; n = 4; R^1 = Me; R^2 = H$
g, $m = 4; n = 4; R^1 = R^2 = Me$
h, $m = 4; n = 4; R^1 = Et; R^2 = H$
i, $m = 4; n = 4; R^1 = n\text{-Pr}; R^2 = H$

Seiji Shinkai,* Kenichi Inuzuka, Osamu Miyazaki, and Osamu Manabe*. Redox-Switched Crown Ethers. Cyclic–Acyclic Interconversion Coupled with Redox between Dithiol and Disulfide.

Page 3441. The abscissa for Figure 1 should be $[Cs^+ \text{tosylate}] \times 10^2$ (M).