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SEMICONDUCTOR-CATALYZED PHOTOCYCLOREVERSION, VALENCE ISOMERIZATION AND [1,3]-SIGMATROPIC REARRANGEMENT[1]

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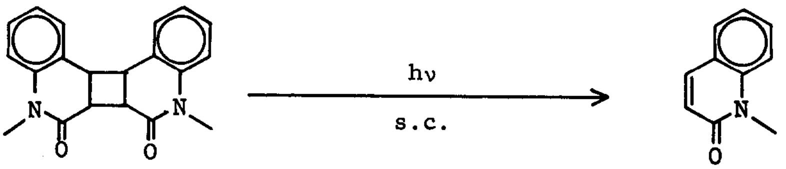
Summary: The semiconductor-catalyzed photochemical [2+2]cycloreversion of N-methylquinolone dimer, valence isomerization of hexamethyl(Dewar)benzene, and [1,3]-sigmatropic rearrangement of 2,2-bis(4-methoxyphenyl)-1-dideuteriomethylenecyclopropane gave N-methylquinolone, hexamethylbenzene, and 2,2-bis(4-methoxyphenyl)-3,3-dideuterio-1-methylenecyclopropane, respectively.

Photocatalytic action of semiconductors is one of the current topics in organic photochemistry.[2] Relatively simple molecules such as water,[3] carbon dioxide,[4] and cyanide or sulfite ion[5] have been studied from the view point of the conversion of solar energy to fuels and polution problems. The application of the unique character of semiconductors to the photooxygenation of organic molecules were recently studied.[6] Although the application other than photooxygenation is in principle possible, little attention has been focused on this subject. Recent observations, photo[2+2]cycloreversion of a cage molecule, photo[4+4]cycloreversion of anthracene dimer, and photo[2+2]cyclodimerization of phenyl vinyl ether reported by us[7] and de Mayo[8] are limited examples.[9] We report here additional three examples, i.e., a [2+2]cycloreversion, a valence isomerization, and a [1,3]-sigmatropic rearrangement.

When a suspension of the semiconductor (15 mg) in acetonitrile containing an anti-head-to-head dimer of N-methylquinolone (**1**) or hexamethyl(Dewar)benzene (**2**) was irradiated with 300 W xenon lamp through Corning filter 3-74 (for CdS) or 0-52 (for ZnO or TiO_2), the product, N-methylquinolone (**3**) or hexamethylbenzene (**4**) was formed in high yields (see Table). In the absence of the semiconductor or light, the starting substrates were recovered quantitatively. From the table, the common observations for these two compounds are that adding an electron donor such as 1,2,4,5-tetra-methoxybenzene efficiently quenched the reaction and that degassing the sample drastically reduced the yield.

These results can be accounted for by the following explanations. Irradiation of the semiconductor surface produces a hole-electron pair that separates



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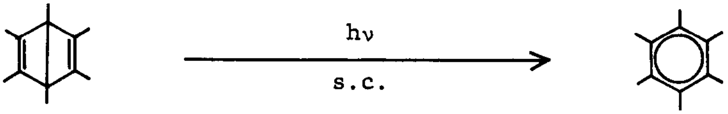

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Table. The Yields of (3) and (4) and The Irradiation Conditions

Substrate[a]	Semiconductor	Yield (%)[b]	Irradiation Conditions
1	CdS	34	aerated---180 min
1	CdS	0	degassed---180 min
1	ZnO	100	aerated---180 min
1	ZnO	0	aerated---180 min with TMB[c]
1	ZnO	42	degassed---180 min
1	TiO_2	28	aerated---180 min
1	TiO_2	0	degassed---180 min
2	CdS	62	aerated---180 min
2	CdS	0	aerated--- 30 min with TMB[c]
2	CdS	7	degassed--- 30 min
2	ZnO	35	aerated--- 30 min
2	ZnO	0	aerated--- 30 min with TMB[c]
2	ZnO	3	degassed--- 30 min
2	TiO_2	7	aerated--- 30 min
2	TiO_2	3	degassed--- 30 min

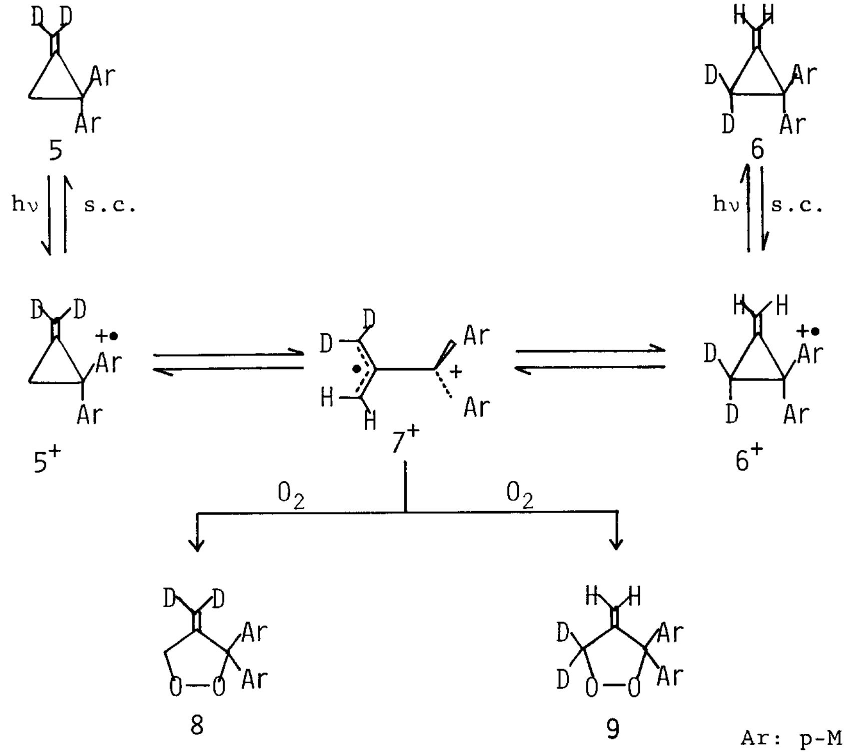
a)The concentration was ca. 0.1 M; b)The yields were determined by NMR for (3) and GLC for (4); c)1,2,4,5-Tetramethoxybenzene (0.074 M)

under influence of the electric field in space charge region. The photogenerated hole in semiconductors is swept to the surface and has an enough energy (+1.6, +2.4 and +2.2 V vs. SCE for CdS, ZnO, and TiO_2, respectively)[10,11] to oxidize the substrates ($E^{ox}_{1/2}(1)=+1.62$ and $E^{ox}_{1/2}(2)=+1.58$ V vs. SCE)[12,13] or can be quenched by 1,2,4,5-tetramethoxybenzene ($E^{ox}_{1/2}=+0.75$ V vs. SCE).

The effect of oxygen may be explained by either or both of the following reasons: 1) the band bending in the depletion layer occurs when the redox potential of the solution is positive of the flat band potential (-0.85, -0.76, and -1.2 ∿ -1.3 V vs. SCE for CdS, ZnO, and TiO_2, respectively).[10,11] Dissolved oxygen in the solution apparently serves a suitable redox couple O_2/O_2^{-}. ($E^{red}_{1/2} \cong -0.8$ V vs. SCE)[14] for the band bending and consequently accelerates the charge separation of a hole-electron pair; 2)the photogenerated electron diffuses to depletion layer with competing recombination with the hole. If oxygen removes the electron from depletion layer, the hole may have a long lifetime enough to oxidize the substrates.

Similar irradiation of a suspension of 2,2-bis(4-methoxyphenyl)-1-dideuteriomethylenecyclopropane (5) with CdS or TiO_2 in argon saturated acetonitrile (10 hr/ 2 KW xenon lamp) resulted in the formation of 2,2-bis(4-methoxyphenyl)-3,3-dideuterio-1-methylenecyclopropane (6) (20 % for CdS and 5 % for TiO_2) via a [1,3]-sigmatropic rearrangement. The rearrangement was, however, not efficient probably because the initially formed radical cation (5+) is quenched by the back electron transfer much faster than the bond cleavage of (5+) giving timethylenemethane cation radical (7+)[15] which serves as a key intermediate in this degenerate rearrangement. If this is correct, the similar oxygen effect to that observed in the [2+2]cycloreversions of (1) and (2) would be expected to retard the neutralization of (5+) to (5) by the back electron transfer and result in the acceleration of the bond cleavage of (5+) to (7+) which is known to undergo the very efficient oxygen trapping to give dioxolanes as we previously reported.[16] In fact, upon irradiation of (5) with CdS for 15 min in oxygen saturated acetonitrile a 1:1 mixture of (8) and (9) was obtained in 96 % yield. Similarly a 60 min irradiation of (5) with TiO_2 gave a mixture of (8) and (9) in 43 % yield.

The results described here thus provide a useful application of semiconductors to simple organic reactions such as cycloreversion, valence isomerization and sigmatropic reactions other than photooxygenation reactions.



Ar: p-$MeOC_6H_4$

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