CHEMISTRY LETTERS, pp. 775-778, 1991.

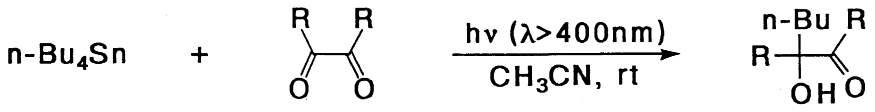
Photoalkylation of α-Diketones with Tetraalkylstannanes via Electron Transfer

Soichiro KYUSHIN, Shinju OTANI, Tomoyuki TAKAHASHI,
Yasuhiro NAKADAIRA, and Mamoru OHASHI*
Department of Applied Physics and Chemistry,
The University of Electro-Communications, Chofu, Tokyo 182

Irradiation of α-diketones in the presence of tetraalkylstannanes gave α-ketols via electron transfer. The analogy between the photo-induced electron transfer reactions and mass spectrometry exists in the fragmentation of the radical cation of the stannanes.

Allylation and benzylation using allylic and benzylic group 14 compounds in the presence of a Lewis acid[1)] or on irradiation[2)] are one of the most useful methods of the formation of a carbon-carbon bond. Recently, an electron-donating property of group 14 metal-carbon σ bond of simple tetraalkylsilanes, -germanes, and -stannanes has been reported,[3)] in which various alkyl groups can be introduced to electron acceptors such as aromatic nitriles and a pyrylium salt on irradiation.[3b)] We describe herein photoalkylation of α-diketones with tetraalkylstannanes via electron transfer.

Irradiation of benzil (0.015 mol dm^{-3}) or biacetyl (0.12 mol dm^{-3}) in deoxygenated acetonitrile containing tetrabutylstannane (0.027 or 0.015 mol dm^{-3}, respectively) with a 300 W medium-pressure mercury lamp through a filter gave an α-ketol in a good isolation yield.[4)] Similar alkylation did not take place and gentle decomposition of the ketones occurred when tetrabutylsilane or -germane was used instead of the stannane, or benzophenone was used instead of 2. These results indicate that a relatively strong electron donor and acceptor pair is necessary in the photoalkylation.

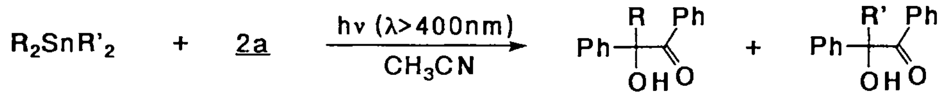


1

2a : R=Ph 4h 82% (conv. of 2a : 70%)
2b : R=Me 5h20min 58% (conv. of 1 : 100%)

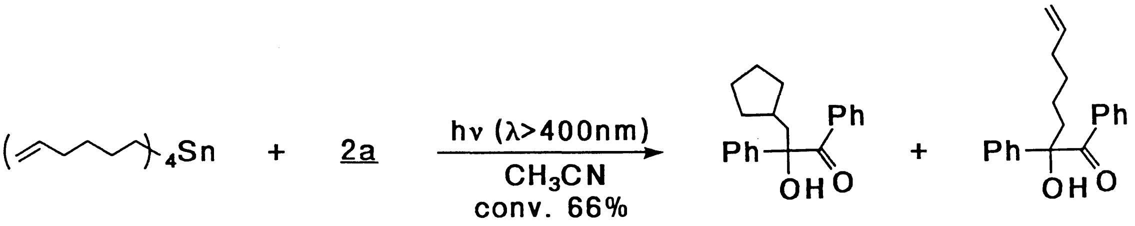
The photoalkylation was effectively quenched by anthracene. Since the singlet and triplet excitation energies are 59.0 and 54.3 kcal mol^{-1} (2a), 65.3 and 57.2 kcal mol^{-1} (2b), and 76.3 and 42.7 kcal mol^{-1} (anthracene), respectively,[5] anthracene acts as a quencher of the excited triplet states of 2a-b.[2b] Therefore, the photoalkylation proceeds via the excited triplet states of the α-diketones. The electron transfer process from tetrabutylstannane to the excited triplet states of the α-diketones is supported from the free energy changes calculated by the Rehm-Weller equation.[6] As a large structural change was reported in the electron transfer process of tetraalkylstannanes, where the reorganization energies were assumed to be about 41 kcal mol^{-1},[7] standard oxidation potentials[7,8] of stannanes were used in the calculation. Furthermore, the rate of the photoalkylation is very slow in benzene and only a trace amount of alkylation product was formed under the conditions. This result is in contrast with the photoreaction of polysilanes with benzophenone, in which solvent dependence is not found between acetonitrile and benzene and an electron transfer process plays a negligible role.[8] From these results, the electron transfer mechanism from stannanes to the excited triplet states of α-diketones is considered to be reasonable.

Selectivity of the alkyl group transferred to 2a was investigated using stannanes with two kinds of alkyl groups. In each case, two alkylation products were formed. From the product ratio, the reactivity of alkyl groups increases in the order of Me < n-Bu < i-Pr, t-Bu. Although the order is the same as those seen in the photoalkylation of aromatic nitriles and a pyrylium salt,[3b] the ratio of the two products is quite different, indicating that the Sn-C cleavage of the radical cations of stannanes is not necessarily a unimolecular process. The result is in accord with a recent study on nucleophile-assisted cleavage of radical cations of organosilanes.[9]



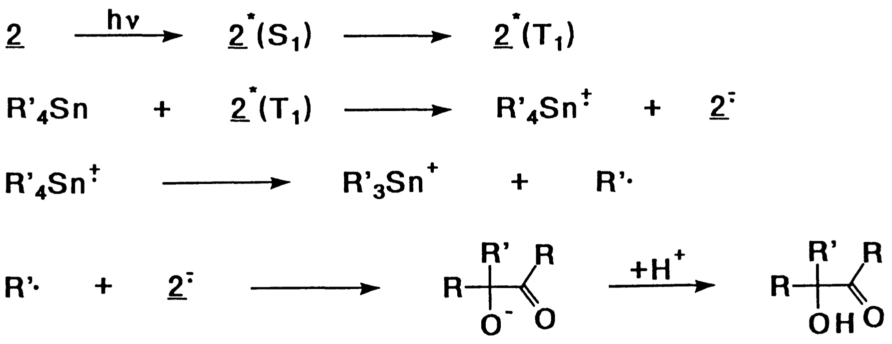
R=n-Bu, R'=Me :	54%	22%	(conv. of 2a : 37%)
R=i-Pr, R'=n-Bu :	66%	11%	(conv. of 2a : 78%)
R=t-Bu, R'=n-Bu :	50%	14%	(conv. of 2a : 52%)

In order to ascertain the participation of free radicals in the photoalkylation, tetra(5-hexenyl)stannane was used as a radical clock probe.[10] On irradiation of an acetonitrile solution of 2a containing the stannane, a cyclic product 3 was formed predominantly and a linear product 4 was a minor product. Apparently, the free alkyl radical is formed from the radical cation of the stannane, and the process is a main pathway in the photoalkylation.



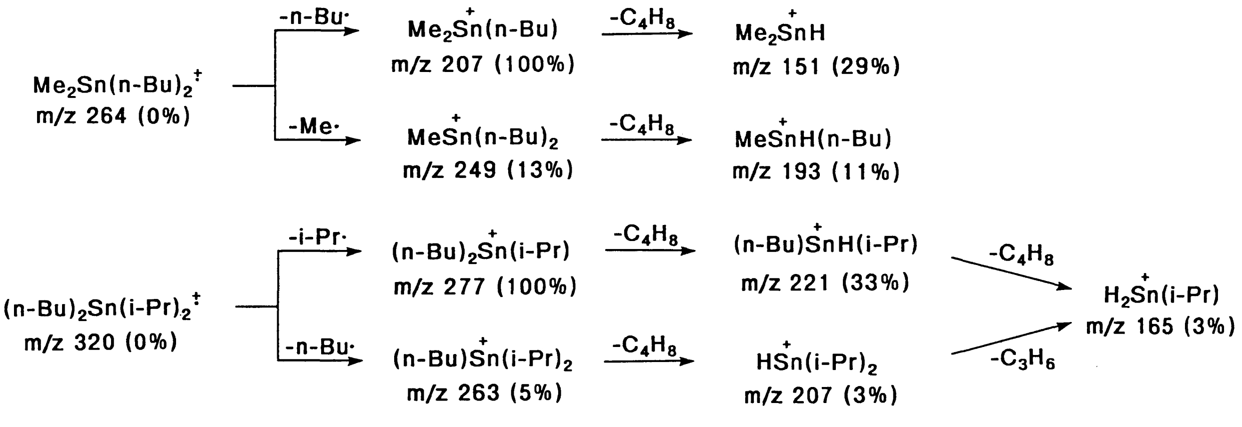
3 (57%) 4 (5%)

From these results, we propose the mechanism of the photoalkylation as shown in Scheme 1. Electron transfer from tetraalkylstannane to the excited triplet state of 2 forms the radical cation of the stannane and the radical anion of 2. The radical cation is cleaved to a trialkylstannyl cation and an alkyl radical probably by the assistance of a nucleophile.11) The alkyl radical attacks the carbonyl carbon and the subsequent hydrolysis affords an α-ketol.



Scheme 1.

It is interesting to compare the cleavage pattern of a radical cation generated in the photo-induced electron transfer with those in the mass spectrometry.12) In order to minimize the further fragmentation, mass spectra (EI) of dibutyldimethylstannane and dibutyldiisopropylstannane were measured with 10 eV of the ionization energy and followed with the linked-



Scheme 2.

scan method (B/E and B^2/E). Scheme 2 shows that the butyldimethylstannyl cation and the dibutylisopropylstannyl cation were formed preferentially. Although conditions in the gas phase and of photoreactions in the solution are rather different, fragmentations in Scheme 2 are in good accord with those observed in the photo-induced electron transfer reaction.

This work was partially supported by Grants-in-Aid on Priority Areas (Nos. 01648508 and 02230211) and a Grant-in-Aid for Encouragement of Young Scientists (No. 02854054) from the Ministry of Education, Science, and Culture. We thank Sankyo Organic Chemicals Co., Ltd. for a gift of stannanes.

References

1) H. Sakurai, Pure Appl. Chem., 54, 1 (1982).
2) a) D. F. Eaton, J. Am. Chem. Soc., 103, 7235 (1981); K. Ohga and P. S. Mariano, ibid., 104, 617 (1982); K. Mizuno, M. Ikeda, and Y. Otsuji, Tetrahedron Lett., 26, 461 (1985); b) A. Takuwa, Y. Nishigaichi, K. Yamashita, and H. Iwamoto, Chem. Lett., 1990, 639, 1761.
3) a) J. K. Kochi, Angew. Chem., Int. Ed. Engl., 27, 1227 (1988) and references therein; S. Fukuzumi, S. Kuroda, and T. Tanaka, J. Chem. Soc., Perkin Trans. 2, 1986, 25; b) S. Kyushin, Y. Masuda, K. Matsushita, Y. Nakadaira, and M. Ohashi, Tetrahedron Lett., 31, 6395 (1990); S. Kyushin, Y. Nakadaira, and M. Ohashi, Chem. Lett., 1990, 2191.
4) The yield of the product is calculated on the basis of consumed 1 or 2a.
5) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973).
6) D. Rehm and A. Weller, Isr. J. Chem., 8, 259 (1970).
7) S. Fukuzumi, C. L. Wong, and J. K. Kochi, J. Am. Chem. Soc., 102, 2928 (1980). Similar results were also reported in oxidation of permethylated catenates of group 14 elements. See, S. Fukuzumi, T. Kitano, and K. Mochida, Chem. Lett., 1990, 1741.
8) A. Alberti, S. Dellonte, C. Paradisi, S. Roffia, and G. F. Pedulli, J. Am. Chem. Soc., 112, 1123 (1990).
9) J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd, and S. L. Mattes, J. Am. Chem. Soc., 111, 8973 (1989).
10) D. Griller and K. U. Ingold, Acc. Chem. Res., 13, 317 (1980) and references therein.
11) Although the nucleophilic attack by the radical anion of carbonyl compounds on the radical cation of stannanes and intermediacy of a stannyl ether have been proposed in the photoallylation, we could not detect a stannyl ether in the course of the photoalkylation. See, A. Takuwa, H. Tagawa, H. Iwamoto, O. Soga, and K. Maruyama, Chem. Lett., 1987, 1091 and references 2b.
12) D. R. Arnold and A. J. Maroulis, J. Am. Chem. Soc., 98, 5931 (1976); M. Ohashi, S. Akiyama, and S. Yamada, Nippon Kagaku Kaishi, 8, 1386 (1989); Y. Nakadaira, S. Otani, S. Kyushin, M. Ohashi, H. Sakurai, Y. Funada, K. Sakamoto, and A. Sekiguchi, Chem. Lett., in press; M. Ohashi, S. Otani, and S. Kyushin, ibid., in press.

(Received February 12, 1991)