Tetrahedron Letters, Vol.31, No.44, pp 6395-6398, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

NOVEL ALKYLATION OF AROMATIC NITRILES VIA PHOTO-INDUCED ELECTRON TRANSFER OF GROUP 14 METAL-CARBON σ DONORS

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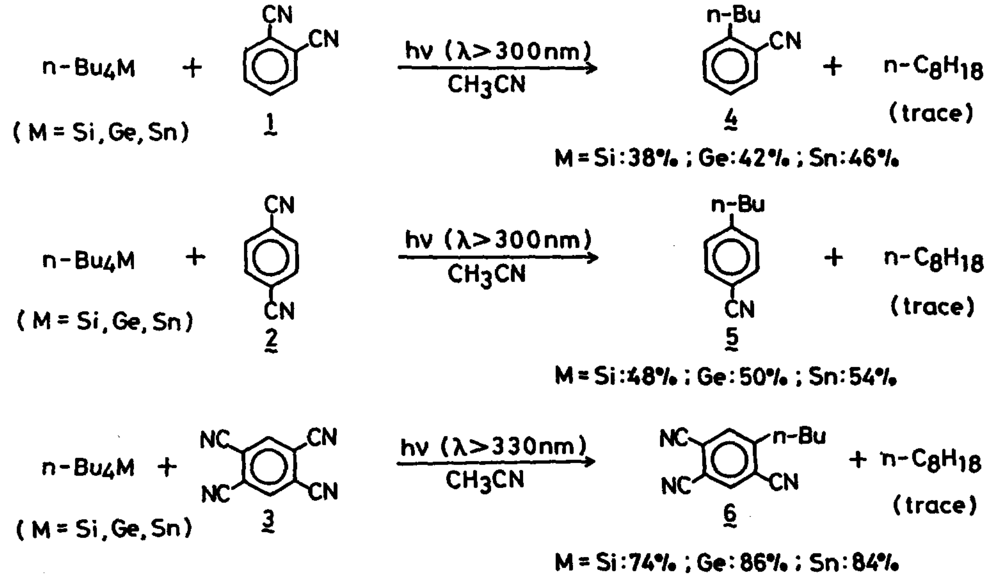
Summary: Photo-induced electron transfer reactions of tetraalkylsilanes, -germanes, and -stannanes with aromatic nitriles afforded alkylated products. The mechanism was investigated by use of a radical clock.

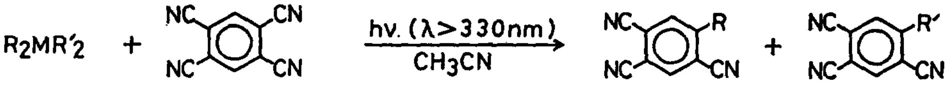
Although there are some detailed investigations on electron transfer of tetraalkylstannanes and -plumbanes,[1] studies of photo-induced electron transfer have been restricted rather to those of β-functionalized group 14 organometals such as allylsilanes and -stannanes,[2-7] which have relatively low ionization potentials due to σ-π conjugation. We describe herein novel photoalkylation of aromatic nitriles by tetraalkylsilanes, -germanes, and -stannanes, and show that M-C σ bonds (M=Si, Ge, Sn) act as effective electron donors to aromatic nitriles.

Acetonitrile solutions of tetra-n-butylsilane, -germane, and -stannane and aromatic nitriles (1-3) were irradiated with a medium-pressure mercury



lamp through an appropriate filter. In each case, one of the cyano groups of aromatic nitriles was displaced regioselectively by a n-butyl group to yield 4, 5, and 6, respectively, together with trace amounts of n-octane. The alkyl group was not introduced into other positions of aromatic nitriles in contrast with the photoalkylation with organoborates.[8] 5,5-Di-n-butylnonane failed to react with 1-3 under these conditions, indicating the poor electron-donating property of the carbon analogue.

Silanes and stannanes with two different kinds of alkyl groups were photolyzed in the presence of 3 under similar conditions. In every case,



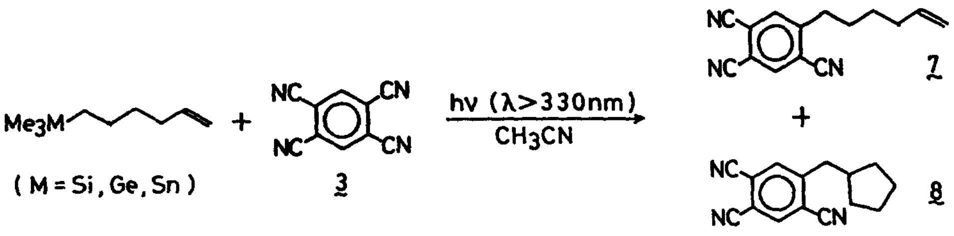
3

M=Si, R=n-Bu, R'=Me :	72%	0%
M=Si, R=i-Pr, R'=n-Bu :	88%	0%
M=Sn, R=n-Bu, R'=Me :	86%	0%
M=Sn, R=i-Pr, R'=n-Bu :	83%	0%
M=Sn, R=t-Bu, R'=n-Bu :	84%	trace

only one kind of possible photoalkylation products was formed and the selectivity indicates that the reactivity increases in the order of Me < n-Bu < i-Pr, t-Bu. This trend can be understood by considering that the cation radical of tetraalkylated group 14 metals releases more efficiently the alkyl group which is able to stabilize a radical more effectively.[1]

Operation of an electron transfer mechanism is evidenced by the nearly diffusion controlled fluorescence quenching of the aromatic nitriles with the group 14 organometals and exothemic free energy change for the electron transfer process calculated by the Rehm-Weller equation.[9] Hence, at the initial stage the electron transfer occurs from the tetraalkylated group 14 metals to the excited singlet state of the aromatic nitriles.

In order to learn more about the mechanism of these reactions by use of a radical clock,[10] 5-hexenyltrimethylsilane, -germane, and -stannane were photolyzed in the presence of 3. These reactions yielded both the acyclic product 7 and the cyclic product 8. The ratio of 7 to 8 decreases succesively as group 14 metal is varied from Si to Sn. The formation of 8 shows that free 5-hexenyl radical should be generated from the cation radical of tetraalkylated group 14 metals. On the other hand, the formation of 7 is explained either by considering that the radical cation attacks the radical anion with concomitant elimination of the group 14 metal cation or that 5-hexenyl radical combines the radical anion before the cyclization to cyclopentylmethyl radical. The formation of 7 cannot

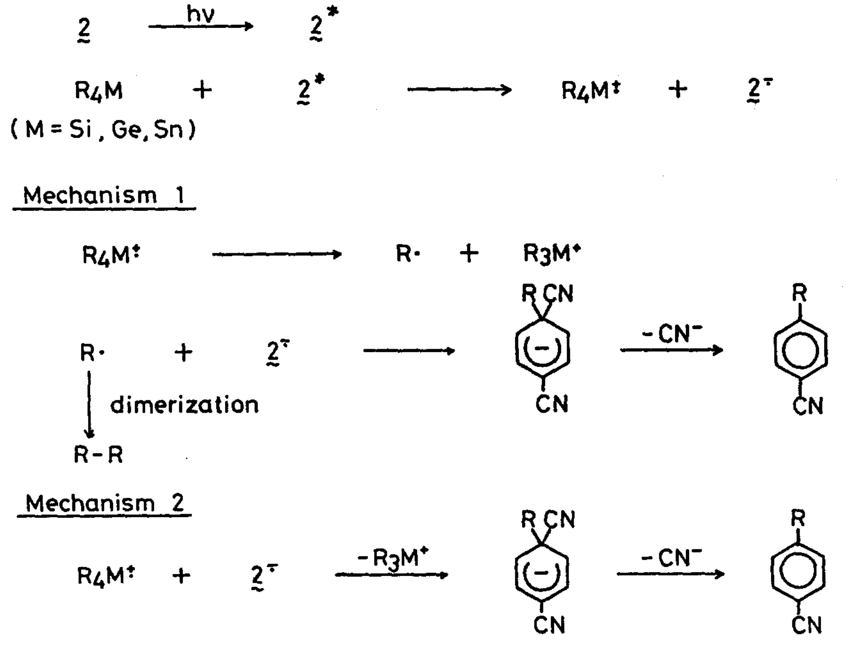


7 : 8 = 62 : 38 (M=Si, 61%), 49 : 51 (M=Ge, 78%), 29 : 71 (M=Sn, 84%)

be attributed only to the free 5-hexenyl radical because the ratios of 7 to 8 are quite different among the group 14 organometals. We conclude that the cation radical is responsible in part for the formation of 7, and the contribution is large in the case of silane and is small in the case of stannane.

From these results, we propose the electron transfer mechanism for the photoalkylation. In Scheme I, the mechanism is exemplified in the case of 2. Electron transfer from tetraalkylsilanes, -germanes, and -stannanes to the excited singlet state of aromatic nitriles gives a radical ion pair. The radical cation is dissociated to the group 14 metal cation and the alkyl radical probably by the attack of a nucleophile,[7] and the radical thus generated bonds to the radical anion at the ring carbon bearing a

Scheme I



cyano group where the spin density is at a maximum.[11] Then, elimination of a cyanide ion leads to the alkylated aromatic nitrile (Mechanism 1). Another mechanism assumes that prior to dissociation the cation radical attacks the radical anion of aromatic nitriles, followed by the elimination of a cation of group 14 metals either in a contact ion pair or in a solvent separated ion pair (Mechanism 2). From the result of the radical clock and the consideration of carbon-metal bond energy, Mechanism 1 may be preferred in stannanes, while Mechanism 2 may be favored in silanes.

Acknowledgement: The work was supported in part by Grants-in-Aid for Special Project Research (No. 01648508 and 01648509) from the Ministry of Education, Science, and Culture. We also thank Mitsubishi Metal Co. for a gift of tetrachlorogermane.

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(Received in Japan 16 July 1990)