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Photoalkylation of Pyrylium Salt with Group 14 Metal-Carbon σ Donors via Electron Transfer

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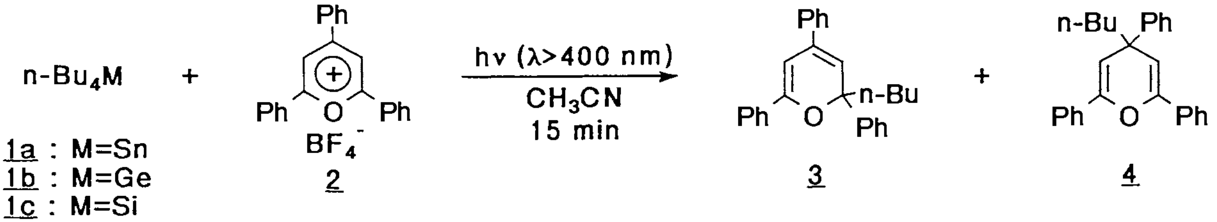
Tetraalkylsilanes, -germanes, and -stannanes reacted with a pyrylium salt to yield alkylated pyrans via photoinduced electron transfer.

Pyrylium salts have been used as sensitizers in various photoreactions such as cycloaddition,1) cycloreversion,2) isomerization,3) oxygenation,4) and other reactions.5,6) Photoreactions of pyrylium salts themselves, however, have not been studied in detail except for oxygenation.7) In this paper, we describe photoalkylation of a pyrylium salt with group 14 metal-carbon σ donors which have recently been shown as effective electron donors.8,9)

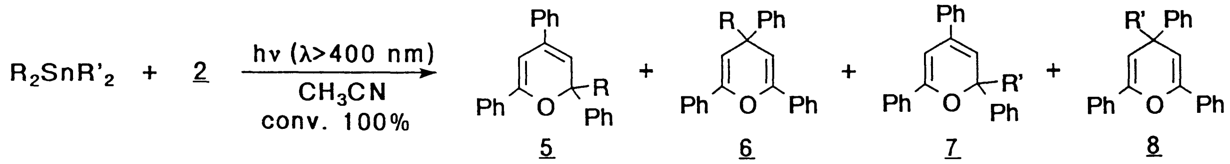
Irradiation of an acetonitrile solution of tetrabutylsilane, -germane, and -stannane (1a-c, 0.023 M) and 2,4,6-triphenylpyrylium tetrafluoroborate (2, 0.015 M) with a medium pressure mercury lamp through a filter gave 2-butyl-2,4,6-triphenyl-2H-pyran 3 and 4-butyl-2,4,6-triphenyl-4H-pyran 4.10) The reactivity of the photoalkylation is highly dependent on the group 14 elements. Thus, in 15 minutes, 1a reacted with 2 completely, but only 7% of 2 was consumed with 1c in the same time.



		3	4
M=Sn :	conv. 100%	58%	31%
M=Ge :	conv. 40%	16%	6%
M=Si :	conv. 7%	5%	trace

The fluorescence of 2 was quenched by 1 nearly at the diffusion controlled rate and the negative values of the free energy change for the electron transfer process from 1 to the excited singlet state of 2 were calculated by the Rehm-Weller equation.[11] Therefore, electron transfer occurs from 1 to the excited singlet state of 2 in the photoalkylation.

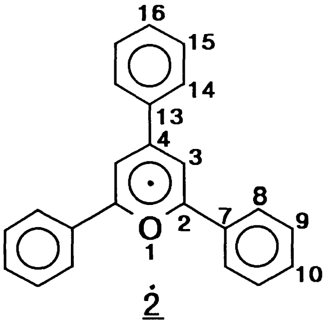
The selectivity of the alkyl group transferred to 2 was studied by use of stannanes with two kinds of alkyl groups. The competition among methyl, butyl, isopropyl, and t-butyl groups indicates that one kind of the alkyl groups is predominantly introduced to 2. We further used allyl- and benzylstannanes which are not simple metal-carbon σ donors but σ-π donors.[12] These results show that the selectivity of the alkyl group introduced to 2 increases in the order of Me < n-Bu < i-Pr, t-Bu < $CH_2=CHCH_2$ < $C_6H_5CH_2$. Since the order is the same as that of the stability of alkyl radicals, the cation radical of group 14 organometals releases the alkyl group which is the most stable as a radical.



			5	6	7	8
R=n-Bu,	R'=Me	:	55%	31%	trace	trace
R=i-Pr,	R'=n-Bu	:	68%	15%	3%	1%
R=t-Bu,	R'=n-Bu	:	78%	11%	0%	0%
R=CH_2=CHCH_2,	R'=t-Bu	:	40%	23%	16%	3%
R=$C_6H_5CH_2$,	R'=CH_2=CHCH_2	:	29%	14%	16%	12%

In order to obtain the information about the selectivity of the alkylated positions of 2, the spin densities of pyranyl radical formed by the electron transfer were calculated by the McLachlan method[13] using parameters reported earlier.[14a] The spin density is maximun in the positions of C-2 and C-4 (Table 1), which are just the positions alkylated in these reactions. Considering that $\dot{2}$ has two positions of C-2, the ratios of 5 to 6 (or 7 to 8) are in good accord with the spin densities in the cases of butyl, allyl, and benzyl groups. On the other hand, the ratios of 5 to 6 (or 7 to 8) were found to be considerably larger than that expected from the spin densities of $\dot{2}$ in the cases of bulkier alkyl groups such as iso-

Table 1. Spin Densities of Radical $\dot{2}$ Calculated by the McLachlan Method

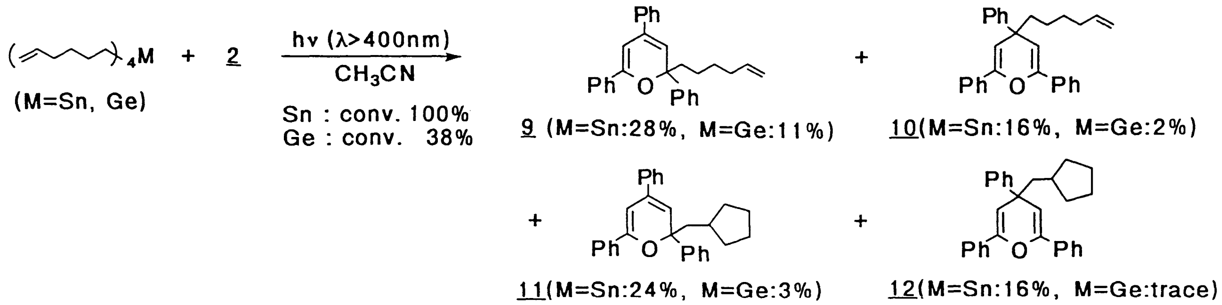


$\dot{2}$

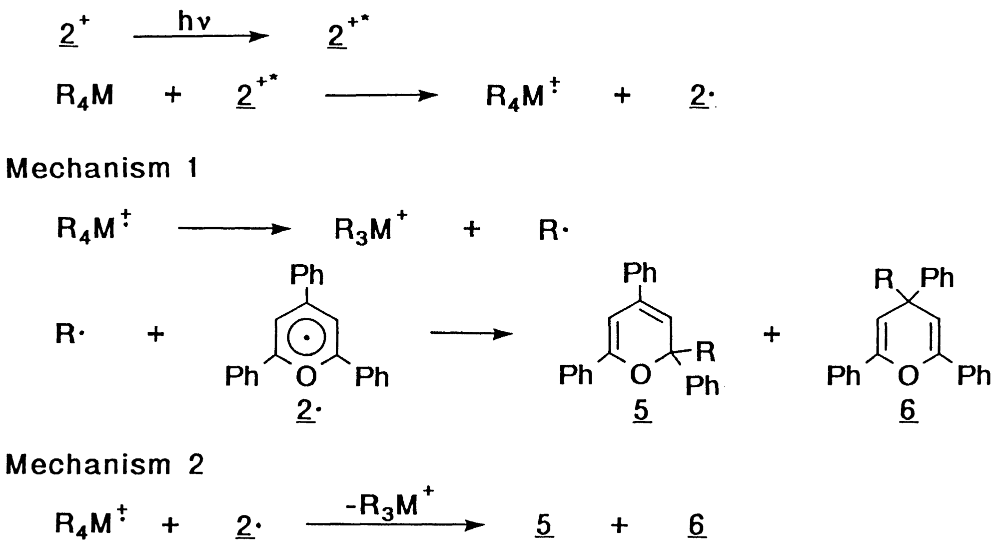
Position	ρ	Position	ρ
1	0.107	9	-0.012
2	0.204	10	0.042
3	-0.052	13	-0.006
4	0.259	14	0.066
7	-0.004	15	-0.022
8	0.037	16	0.075

propyl and t-butyl.

Photoalkylation of 2 with tetra(5-hexenyl)stannane and -germane afforded both linear products 9, 10 and cyclic products 11, 12. The ratio of (9+10):(11+12) is about 1:1 in the case of the stannane. On the other hand, the ratio is far larger in the case of the germane, although yields of the products are not good. Since the results have the same tendency as seen in the photoalkylation of aromatic nitriles,[9] a similar explanation is possible in these cases. The formation of 11 and 12 indicates that the free radical is formed from the cation radical of group 14 organometals. The difference of the ratios of linear products to cyclic products between the stannane and germane shows that the contribution of the cation radical which directly reacts with pyranyl radical cannot be neglected especially in the case of germane.



From these results, a mechanism for the photoalkylation is proposed in Scheme 1. Electron transfer from group 14 organometals to the excited singlet state of 2 gave the cation radical of organometals and pyranyl radical $\dot{2}$. In Mechanism 1, the cation radical dissociates to the cation of group 14 organometals and the free radical. The free radical attacks $\dot{2}$ at



Scheme 1.

the positions with maximum spin density to yield 5 and 6. On the other hand, Mechanism 2, in which the cation radical attacks $\dot{2}$ prior to dissociation, is operative to some extent and the contribution of Mechanism 2 increases as group 14 element is varied from Sn to Ge.

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