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Photochemical Regioselective Addition of Alkylacylgermanes to Styrene

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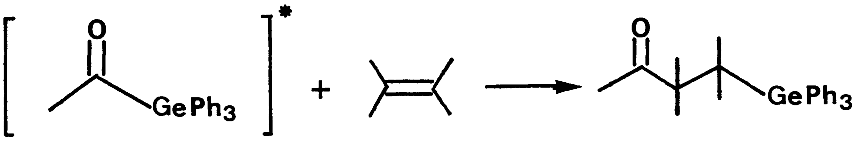
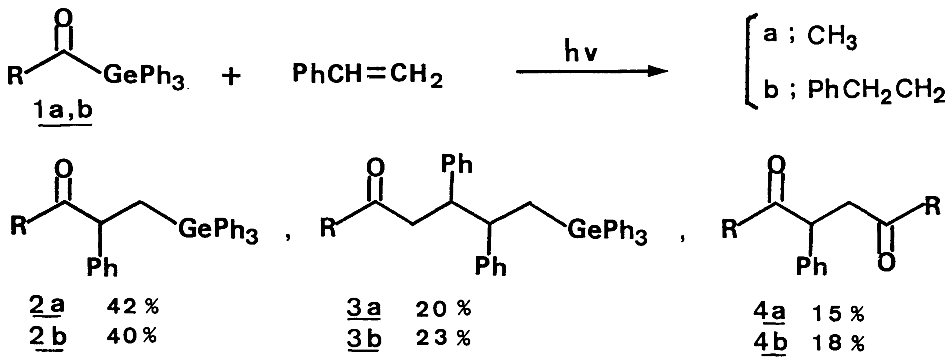
Photochemical addition of alkylacylgermanes to styrene has been achieved to give regioselective 1 : 1 and 2 : 1 adducts of acylgermanes to styrene in good yields.

Upon searching utilities of acylgermanes to organic synthesis, we became aware of the instability of acylgermanes dissolved in solvent toward sunlight.$^{1)}$ Concerning the photochemistry of acylgermane little is known in comparison with that of acylsilanes; acylsilanes show as a main process Norrish type II fragmentation on n,π^*-excitation and a siloxycarbene produced via rearrangement also is a significant species, but Norrish type I reaction is only minor process.$^{2)}$ Photochemical reaction of benzoyltriphenylgermane has been considered to proceed predominantly via Norrish type I cleavage on the S_1 state.$^{3)}$ We found that (α-arylacyl)triphenylgermanes, on irradiation, easily undergo decarbonylation to give the corresponding (α-arylalkyl)triphenylgermanes in solvent cage, presumably owing to the inherent stability of α-arylalkyl radical.$^{4)}$

Provided acylgermanes predominantly undergo Norrish type I cleavage contrary to the photochemical behaviors of acylsilanes, the resulting acyl radical can be captured with olefin and thus acylgermanes might be recognized as useful precursor carrying out addition to carbon - carbon double bond leading to novel carbon - carbon bond formation reaction. We report here the first photochemical addition of alkylacylgermanes to styrene.



Irradiation of a tetrahydrofuran solution (0.03 M) of acylgermanes (1a,b) prepared from the corresponding esters and triphenylgermyllithium,$^{1)}$ in the presence of styrene (1 - 3 mol equiv.) in a Pyrex flask was carried out by using light from a 400 W high-pressure Mercury lamp for 1 h under argon, followed by work-up and chromatography for the separation of products. Products (2,3,4) were obtained in a similar proportion regardless of the alkyl moieties of acylgermanes with a small amount of hexaphenyldigermane, as shown in Scheme 1.$^{5)}$ Main products (2a,b) are β-triphenylgermyl ketones corresponed to 1 : 1 adducts of the acylgermanes to styrene. The intermolecular photo-addition is characterized with



Scheme 1.

regard to its complete regioselectivity. This formal ${}_{\sigma}2 + {}_{\pi}2$ addition reaction might proceed via a transition state, minimized the steric repulsion between phenyl group of styrene and triphenylgermyl group of acylgermanes.

Products (3a,b) composed of a 2 : 1 adduct of acylgermanes to styrene have a quite interesting structure which can be considered to be made by a formal ${}_{\sigma}2 + {}_{\pi}2 + {}_{\pi}2$ addition reaction,[6] uniquely arranged by van der Waals interaction between the opposed phenyl groups of two styrenes. The observation of the regioselectivity in these photochemical addition reactions suggests that the addition takes place in solvent cage and may be initiated by the attack of triphenylgermyl radical. The lack of stereoselectivity of 3a and 3b (nearly 1 : 1 diastereoisomers), however, allows to exclude the possibility of concerted cycloaddition mechanism. Further diffusion of radicals from solvent cage results in trapping of olefin with acyl radicals to give products (4a,b) and recombination of triphenylgermyl radicals to give hexaphenyldigermane.

The continued exploration of the scope of the photochemical addition reaction of acylgermanes and the application are in progress.

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5) ^{1}H NMR data ($CDCl_3$) δ/ppm; 2a: 1.60 (s, 3H), 1.82 (dd, 1H, J= 5.5, 14.0), 2.52 (dd, 1H, J= 9.0, 14.0), 3.83 (dd, 1H, J= 5.5, 9.0), 7.05 - 7.67 (m, 20H). 3a: 1.87 (s, 3H), 1.64 - 3.80 (m, 6H), 7.0 - 7.8 (m, 25H). 4a: 2.11 (s, 3H), 2.16 (s, 3H), 2.55 (dd, 1H, J= 3.8, 16.0), 3.43 (dd, 1H, J= 9.9, 17.0), 4.22 (dd, 1H, J= 3.8, 9.9), 7.12 - 7.40 (m, 5H).
^{13}C NMR data ($CDCl_3$) δ/ppm, (except triphenylgermyl moiety); 2a: 17.6, 28.3, 56.1, 207.6. 3a: 17.7, 19.7, 30.2, 30.3, 46.3, 47.2, 48.0, 48.8, 50.2, 207.1. 4a: 28.9, 29.9, 46.4, 54.0, 206.4, 206.8. 2b: 17.6, 29.5, 42.6, 55.4, 208.4. 3b: 18.2, 18.7, 29.1, 29.3, 44.5, 44.7, 45.9, 47.1, 47.9, 48.1, 48.7, 50.2, 208.1. 4b: 29.5, 42.9, 44.1, 45.7, 53.2, 207.6, 207.8.
6) Other important 2 + 2 + 2 condensations: G. H. Posner and S. -B. Lu, J. Am. Chem. Soc., 107, 1424 (1985); T. R. Gadek and K. P. C. Vollhardt, Angew. Chem., Int. Ed. Engl., 20, 802 (1981).

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