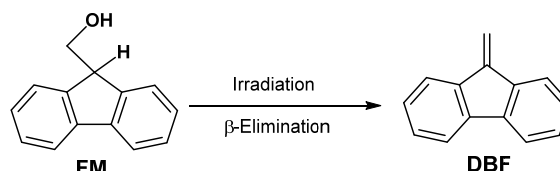




9-フルオレニルメタノールの光脱離によるジベンゾフルベンの合成 Photo-induced β -Elimination of 9-Fluorenylmethanol Leading to Dibenzofulvene

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Light promotes various reactions which are not driven by heat. Although various products have been obtained through photochemical reactions, effective photo induced β -elimination leading to olefin without any side reactions may be unprecedented. Because olefins can be used as monomers, their synthesis via alcohol dehydration through β -elimination is important



Scheme 1. Photo-induced β -elimination of 9-fluorenylmethanol (**FM**) leading to dibenzofulvene (**DBF**).

as well as the other methods including Aldol condensation, Wittig reaction, and McMurry reaction. In the ground state, dehydration of alcohol is achieved using base or acid through β -elimination.

Herein we introduce photo-induced β -elimination of 9-fluorenylmethanol (**FM**) leading to dibenzofulvene (**DBF**) (Scheme 1). **DBF** is an important olefin which leads through vinyl polymerization to poly(**DBF**) having a unique π -stacked conformation.^{1,2} On the basis of such a conformation, poly(**DBF**) exhibits characteristic photo electronic properties such as high charge mobility and remarkable hypochromism as well as charge delocalization over the stacked fluorene units. **DBF** monomer can be synthesized from 9-fluorenylmethanol (**FM**) in the presence of base such as *t*-BuOK where dehydration is considered to occur through an *E1cB* mechanism.³

Herein we report a new method of **DBF** synthesis through photo-induced dehydration of **FM** that does not require any base. The reaction was conducted in various solvents and was monitored by UV spectra. The spectra observed through the reaction comprised of **DBF** and **FM** contributions and exhibited isosbestic points, indicating the reaction is free from side reactions that may lead to any other ingredients in addition to **DBF** and **FM**. In order to obtain information on the reaction mechanism, effects of solvent, temperature and additives were studied. The reaction is proposed to occur through a β -elimination mechanism which may not be *E1cB* unlike the ground-state reactions.³

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