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Steric Effect of Alkylidene Groups of Furylfulgides on the Photochromic Behavior

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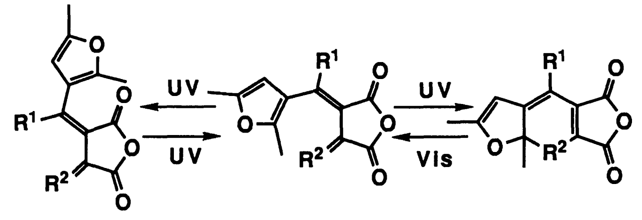
Photoreactions of furylfulgides having a large alkylidene group (7-norbornylidene or 2-adamantylidene) were investigated. An adamantylidene fulgide with [1-(2,5-dimethyl-3-furyl)-2-methyl]propylidene group recorded 0.51 and 0.26 for coloring and bleaching quantum yields, respectively.

Recently we have reported that the steric bulkiness of the alkyl group on the furylmethylidene group of furylfulgides greatly enhanced their coloring quantum yields.[1] This observation could be explained that the bulky alkyl group inhibited undesired olefinic E-Z isomerization and anchored the conformation of the furyl group in favor of the cyclization. However, the relatively small bleaching quantum yield was not affected. In 1983, Heller briefly mentioned that the 2-adamantylidene group (ADD) instead of isopropylidene group (IPD) of the prototype furylfulgide <u>1</u> greatly increased the bleaching quantum yield.[2] The steric repulsion inside the molecule accelerated the ring opening reaction.[3] In order to obtain a useful fulgide with high coloring as well as bleaching quantum yields, we undertook to combine Heller's concept with ours. In this communication, we would like to report the successful result to enlarge the bleaching quantum yield to a practically useful level, without loss of efficiency of the coloring cyclization.



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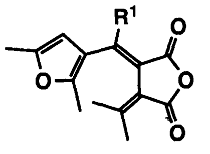
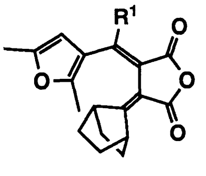
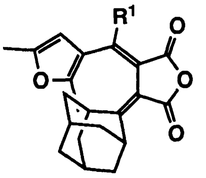


	R^1
1E	Me
2E	i-Pr



	R^1
3E	Me
4E	i-Pr



	R^1
5E	Me
6E	i-Pr

We chose fulgides <u>3</u> - <u>6</u>, with 7-norbornylidene[4] (NBD) or ADD groups as the bulky alkylidene group, and with methyl or isopropyl group on the furylmethylidene moiety. Table 1 shows the quantum yields of their photoreaction in toluene.

Table 1. Quantum yields of the photoreaction of the furylfulgides[a)]

Irradiation wavelength/nm			366				492
	R^1	R^2	ϕ_{EC}	ϕ_{EZ}	ϕ_{ZE}	ϕ_{CE}	ϕ_{CE}
1	Me	Isopropylidene	0.18	0.13	0.11	0.00	0.048[b)]
2	i-Pr	Isopropylidene	0.58	0.00	----	0.00	0.043
3	Me	7-Norbornylidene	0.20	0.30	0.42	0.01	0.057
4	i-Pr	7-Norbornylidene	0.56	0.01	0.01	0.00	0.049
5	Me	2-Adamantylidene	0.12	0.10	0.10	0.06	0.21[b)]
6	i-Pr	2-Adamantylidene	0.51	0.02	0.05	0.28	0.26

a) In toluene at room temperature. Determination of quantum yields; see Ref. 1.
b) Smaller than the values reported by Heller.[3)] The difference cannot be rationalized due to the lack of the detailed information about their experiments.

The fulgides 3 - 6 were prepared by condensing diethyl alkylidenesuccinate and the corresponding furylketone with lithium diisopropylamide as the base, followed by hydrolysis of the resulting ester and dehydrative cyclization to construct the acid anhydride moiety. Separation of the E- and Z-fulgides by column chromatography followed by recrystallization afforded pure materials. Structure determination including the assignment of the geometry of the newly introduced double bond was performed based on ^{1}H NMR, IR, UV, and HRMS, as well as the comparison of their chromatographic and photochemical behavior with those of 1E, 1Z, 2E, and 2Z.

While NBD group did not improve the bleaching process, ADD group, in compounds 5 and 6, increased it extremely. The compound 6, where R^1 was i-Pr and R^2 was ADD, recorded 0.51 for coloring quantum yield and 0.26 for bleaching quantum yield. The latter value is about fivefold of that of furylfulgides without ADD.

As we have reported, 2E did not isomerize to 2Z, because of the steric bulkiness of the isopropyl group.[1)] Contrary to the result, 4E and 6E, having the isopropyl group, slightly isomerized to the corresponding Z-form. As expected, compounds 3E and 5E showed certain E-Z and Z-E isomerization quantum yield values.

This study also clarified that, on irradiation with UV light, the bleaching quantum yields of the colored form of the fulgides with a bulky alkylidene group are not negligible. In the cases of coloring photoreaction of the compounds 3, 5, and 6, the open forms were detected by HPLC at the photostationary state. Fulgide 6 showed 0.28 for ϕ_{CE} with 366 nm light, and the molar ratio of E/Z/C at the photostationary state determined by HPLC was 6/2/92.

In conclusion, the steric bulkiness of both alkyl groups on the furylmethylidene moiety and the other alkylidene group worked almost independently, and the fulgide 6 recorded exceptionally large coloring and bleaching quantum yields.

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