

Photochromism in Fulgides and Anhydrides

SUJATA S. DESHMUKH* and SHUBHRA BANERJEE

Department of Chemistry, Institute of Science, Nagpur-440 001, India

Fulgides (1) and anhydrides (2) obtained from the products of Stobbe condensation, were irradiated when a photochemical change was observed showing their photochromic nature.

INTRODUCTION

Fulgides are of interest for their photochromic properties.^{1–4} Synthesis of fulgenic acid with varying substituents is achieved with different aldehydes and ketones by stepwise Stobbe condensation.⁵ They are converted into fulgides (1a–f) by treatment with acetyl chloride under dry conditions. Similarly, the mono-stobbe condensation products give anhydrides (2a–f) which together with fulgides (1) have been studied for their photochromic properties which are reported here.

Analysing the mechanism of photochemical changes, Santiago and Becker⁶ observed that one of the substituents must be aromatic in nature for recording such photochromic properties. The fulgenic acids are pale to deep yellow in colour while the fulgides are yellow to orange which change to deeper orange red or reddish brown upon irradiation.

EXPERIMENTAL

The UV irradiation was done in an Iwq 1 immersion well photochemical reactor at 254 nm from low pressure lamp of 6 W capacity. Samples in specanol were irradiated for 20 min at room temperature through which nitrogen gas was bubbled.

Spectral scanning was done on Varian DMS 80 spectrophotometer before and after irradiation in the range 200–500 nm. All samples were purified before study.

RESULTS AND DISCUSSION

For anhydrides (2a–f) obtained from the products of monostobbe condensation the best results have been observed in case of 4-ethyl-4-methyl-3-carboxyl-but-3-enoic acid anhydride (2a) where a shift of 40 nm is observed after irradiation.

Also *p*-methoxyitaconic anhydride (2f) and 4-(2-naphthyl)-but-3-en-1,3-dicarboxylic acid anhydride (2d) show considerable shifts in the λ_{\max} values (22 and 25 nm) respectively. There is a visible shift for the rest of these anhydrides ranging from 5 to 10 nm. In fulgides, the strongest photochromic effects involving a shift of 35 nm in λ_{\max} values is observed in 1,1,4,4-tetraphenyl butadiene-2,3-dicarboxylic acid anhydride (1a). All other fulgides show shift of 10–15 nm (Table-1).

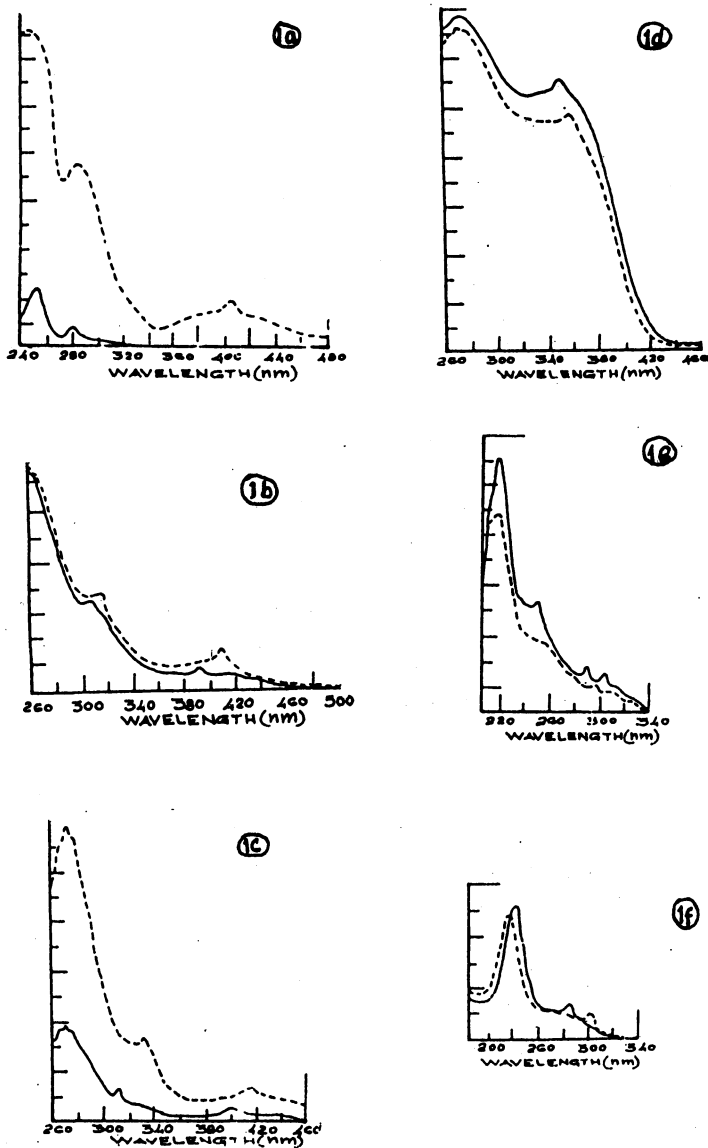


Fig. 1. UV* spectra of samples 1a-1f on spectrophotometer
[—] UV spectrum before irradiation.
[----] UV spectrum after irradiation by Photochemical Reactor

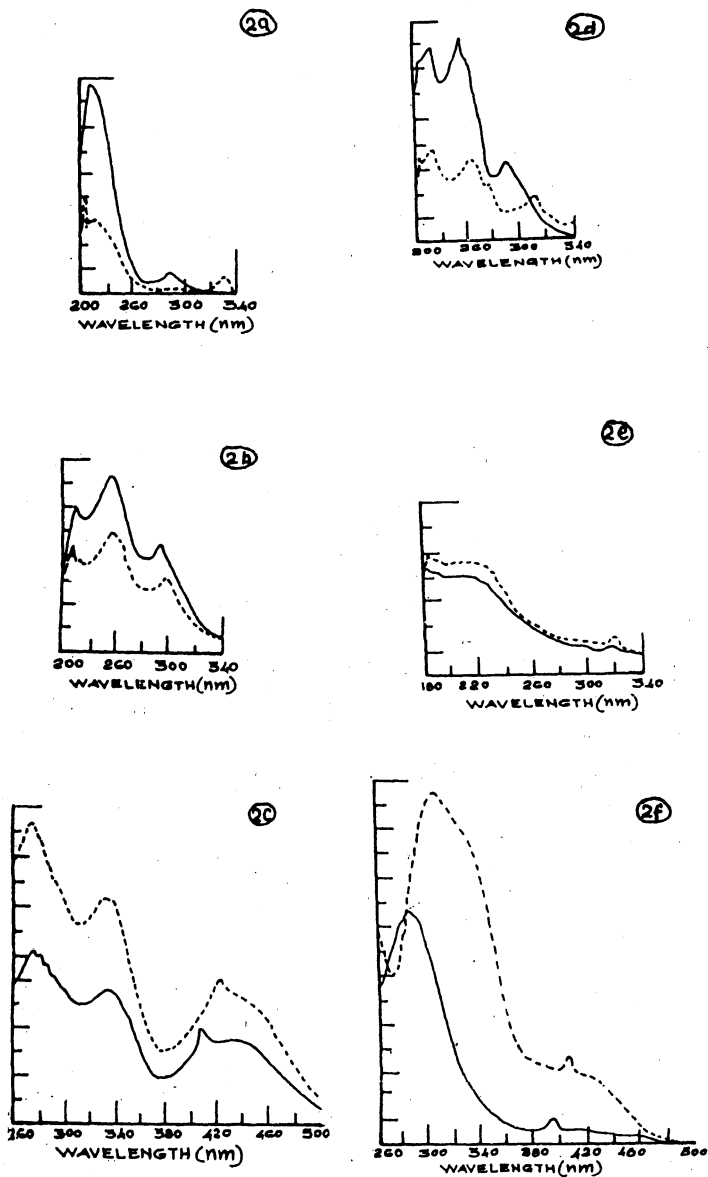


Fig. 2. UV* spectra of samples 2a-2f on spectrophotometer
 [————] UV spectrum before irradiation.
 [-----] UV spectrum after irradiation by Photochemical Reactor

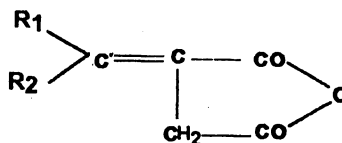
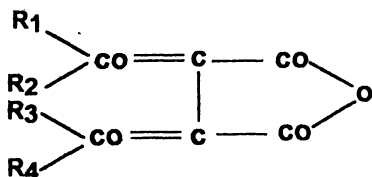
(1a) $R_1 = R_2 = R_3 = R_4 = \text{Ph}$ (1b) $R_1 = R_2 = \text{Ph}$, $R_3 = 2\text{-naphthyl}$, $R_4 = \text{H}$ (1c) $R_1 = R_2 = \text{Ph}$, $R_3 = p\text{-Cl Ph}$, $R_4 = \text{Ph}$ (1d) $R_1 = R_3 = p(\text{OMe})$, $R_2 = R_4 = \text{Ph}$ (1e) $R_1 = R_3 = 2\text{-naphthyl}$, $R_2 = R_4 = \text{H}$ (1f) $R_1 = \text{PhMe}$, $R_2 = \text{H}$, $R_3 = p(\text{Cl})$, $R_4 = \text{Ph}$ (2a) $R_1 = \text{Et}$, $R_2 = \text{Me}$ (2b) $R_1 = \text{Ph}$, $R_2 = \text{H}$ (2c) $R_1 = R_2 = \text{Ph}$ (2d) $R_1 = \text{naphthyl}$, $R_2 = \text{H}$ (2e) $R_1 = \text{Ph}$, $R_2 = \text{Me}$ (2f) $R_1 = p(\text{OMe})$, $R_2 = \text{Ph}$

TABLE-1
UV IRRADIATION DATA OF FUNGICIDES AND ANHYDRIDES

Compd.	R_1R_2	R_3R_4	Longest wavelength before irradiation	Longest wavelength after irradiation	Colour change
1a	Ph, Ph	Ph, Ph	370	405	Intense
1b	Ph, Ph	Naphthyl	303sh & 390	315sh & 405	–
1c	Ph, Ph	<i>p</i> (Cl)-Ph, Ph	315 & 400	330 & 418	–
1d	<i>p</i> (OMe)-Ph, H	<i>p</i> (OMe)-Ph, H	350sh	360sh	–
1e	Naphthyl, H	Naphthyl, H	262, 290 & 310	270 & 295 & 320	–
1f	Ph, Me, H	Ph, <i>p</i> (Cl), Ph	285	300	Moderate
2a	Et, Me	–	212 & 290	218 & 330	Intense
2b	Ph, H	–	295	300	–
2c	Ph, Ph	–	405	420	Moderate
2d	Naphthyl, H	–	290	315	Moderate
2e	Ph, Me	–	310	320	–
2f	<i>p</i> (OMe)-Ph, H	–	255 & 395	278 & 405	Moderate

ACKNOWLEDGEMENT

The authors are grateful to UGC for providing funds for these studies and photochemical reactor.

REFERENCES

1. S. Banerjee, *Indian J. Chem.*, **15B**, 487 (1977).
2. G.H. Brown, *Techniques of Chemistry*, Vol. III, John Wiley, New York, p. 595 (1971).
3. K. Ulrich and H Purst, *J. Mol. Struct.*, **218**, 45 (1990).
4. Hibino Junichi and Ando Eiji, *Jpn. Kokai Tokkyo Koho*, **3**, 72 (1987).
5. Saba Jabbar, Ph.D. Thesis, Nagpur University (1949).
6. A. Santiago and R.S. Becker, *J. Am. Chem. Soc.*, **90**, 3654 (1968).

(Received: 15 September 2000; Accepted: 4 December 2000)

AJC-2207