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PHOTOCHEMICAL INCORPORATION OF PROTIC SOLVENTS BY OPEN CHAIN OLEFINS

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Few examples are known with respect to the title reaction (1), while BTX-sensitized ionic additions to cycloolefins are well documented (2). We wish to report anomalously smooth reaction which has been observed with o-anethole (I_a), o-anol (I_b) and o-(1-propenyl)aniline (I_c). The results are summarized in Table 1.

When an acetic acid soln of I_a (67.5 mM concn) was irradiated externally (200 W high press Hg arc, Pyrex filter, room temp), most of the olefin disappeared within 20 hr to give a quantitative yield of the adduct II_{ax} (R = OMe, R' = Ac) (3). The formate II_{ay} (R' = CHO) (3) was obtained similarly, whereas the photoaddition of methanol required the presence of a trace of conc HCl. No positional isomers of II have been isolated and this indicates that the benzylic cation is a possible intermediate.

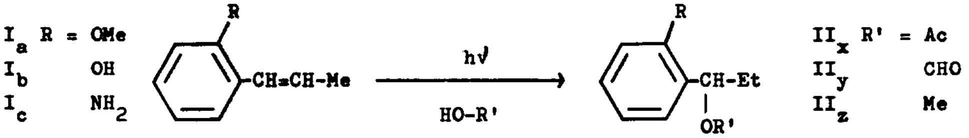


Table 1. Photoreactions of o-anethole, o-anol and o-propenylaniline in acidic solvents

	solvent	adduct	bp (°/mm) or mp | °|	yield [e] in %	dimer [f] yield in %	reaction time hr
I_a[a]	AcOH	II_{ax}	110-111/6	quant	nil	20
	HCOOH	II_{ay}	84-85/3	quant	nil	20
	MeOH [d]	II_{az}	74-75/3	quant	nil	20
I_b[b]	AcOH	II_{bx}	|66-67|	quant	nil	50
I_c[c]	AcOH	II_{cx}	110-113/15	quant	nil	50
m-I_a	AcOH	m-II_{ax}	110-115/4	8	92 [g]	72
p-I_a	AcOH	p-II_{ax}	92-95/2	7	93 [h]	72

[a] The starting material I_a contained 94% trans and 4% cis. [b] I_b was pure trans. [c] I_c contained 89% trans and 11% cis. [d] A drop of conc HCl was added. [e,f] The yields were determined by GLC (HVSG 10% on Celite). [g] Two dimers of unknown structure were produced. [h] See ref. (4).

The photoreaction was followed by determining the distribution of trans-, cis-I_a and II_{ax} by means of GLC (HVSG 10% on Celite) of samples taken out periodically during the reaction. Fig. 1 shows the results. The fast trans to cis isomerization was

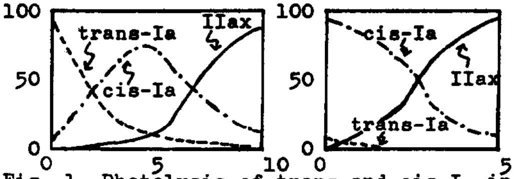
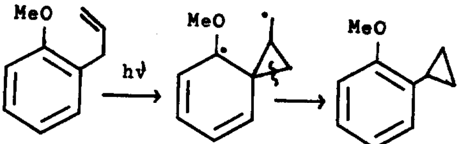


Fig. 1. Photolysis of *trans* and *cis*-I_a in AcOH. Distribution in % *vs* irradiation time in hr.



III Fig. 2 IV

observed in the early stage of the reaction. The supposed intermediacy of *cis*-I_a in the photoaddition was supported by similar monitoring of the reaction of *cis*-Ia itself, which is considered to be the precursor of the adduct II_{ax}.

The multiplicity of the reactive species was then investigated. A soln of *trans*-I_a (33.7 mM) and benzophenone (67.5 mM) (or triphenylene (67.5 mM)) in acetic acid was irradiated under N_2 through $CuSO_4$ filter at room temp for 12 hr. GLC of the recovered I_a showed that the *cis/trans* ratio was 90:10 (benzophenone) and 88:12 (triphenylene), respectively. No trace of II_{ax} at all was detected in each case. These results may indicate that the species responsible for the polar addition is the exited singlet state of *cis*-I_a in sharp contrast to the similar reaction of cycloalkenes (2). Irradiation of an acetic acid soln of *trans*-I_a (33.7 mM) and benzophenone (33.7 mM) with Pyrex-filtered light for 5 hr gave II_{ax} (8%) and a *cis-trans* mixture of I_a (95:5, 92%). Apparently, benzophenone is not an effective singlet quencher for Ia (5) but a sensitizer.

The reaction of *p*-anethole (p-I_a) in acetic acid soln under similar conditions gave the corresponding photoadduct *p*-II_{ax} (3) in much inferior yield, the photodimer being a major product. *m*-Anethole behaved similarly (Table 1).

Irradiation of *o*-anol (I_b) (75.0 mM) in acetic acid with Pyrex-filtered light for 50 hr gave the acetate I_{bx} (3) quantitatively. When *o*-(1-propenyl)aniline (I_c, 75.0 mM) was irradiated under the same condition as I_b, quantitative incorporation of the solvent occurred to afford II_{cx} (3). Obviously the salt of I_c is reacting here.

Meanwhile, a novel type of photorearrangement has been observed. A soln of *o*-allylanisole (III) (67.5 mM) in acetic acid was photolyzed with quartz-filtered light for 120 hr. Preparative GLC gave *o*-cyclopropylanisole (IV) (3) as a sole isolable product in an 11% yield possibly *via* vinyl-di-pi-methane rearrangement (6, 7).

REFERENCES AND REMARKS

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