

PHOTOREACTION OF N-(ω -INDOL-3-YLALKYL)PHTHALIMIDES
 INTRAMOLECULAR OXETANE FORMATION OF THE AROMATIC IMIDE SYSTEM ¹

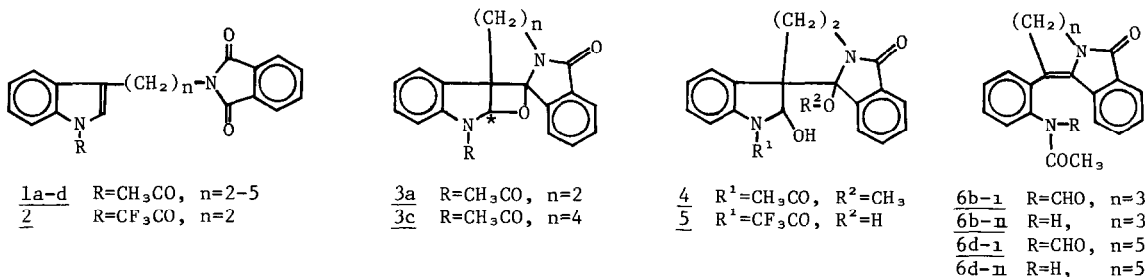
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Summary Photoreaction of N-(ω -indol-3-ylalkyl)phthalimides (1a and 1c) gave oxeto[2,3-b]indoles (3a and 3c), the first example of oxetane formation of the aromatic imide carbonyl in the Paterno-Buchi reaction

There are remarkable differences between the photochemistry of the alicyclic imides and the aromatic cyclic imides (i.e., phthalimides) ² In photoreactions with alkenes, aliphatic cyclic imides undergo efficient inter- or intra-molecular Paterno-Buchi reactions, ^{2b} whereas phthalimides undergo photoadditions ^{2b} and photocyclizations, ³ not oxetane formation Recently possible involvement of the Paterno-Buchi reaction in phthalimide systems has been reported, ⁴ but the Paterno-Buchi product (oxetane) was not isolated We now wish to report the first unambiguous example of the oxetane formation in the phthalimide system

In a typical run, a solution of 1a in acetone (10 mM) was irradiated with a Pyrex-filtered 500 W high-pressure mercury lamp in a nitrogen atmosphere for 12.5 h Structures of the products were assigned on the basis of analytical and spectral data ⁵ As listed in Table 1, compounds 1a,c underwent cycloaddition to give oxetane 3a,c, while 1b and 1d gave the ring opening products 6b,d On treatment with methanolic hydrochloric acid, the oxetane 3a was quantitatively converted to spiro compound 4 In fact, upon irradiation of a N-trifluoroacetyl derivative 2, a similar spiro diol 5 was isolated in a moderate yield Since the imide oxetane 3a was very sensitive to solvolysis and lost even on silica gel treatment, products 6b,d are probably generated from the



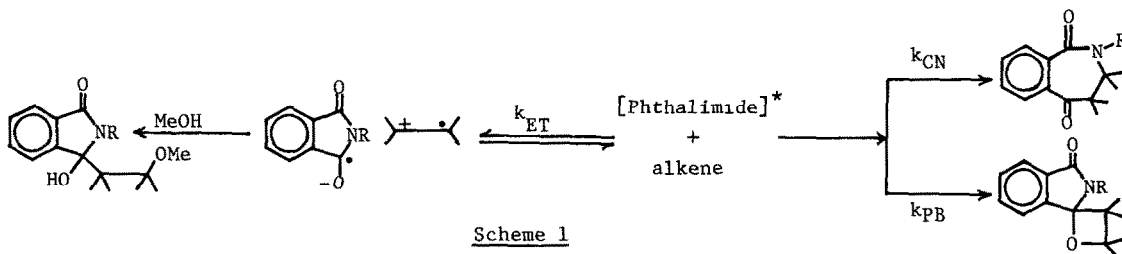
initially formed oxetane by hydrolysis followed by ring opening ($\underline{3} \rightarrow$ spiro-diol such as $\underline{4}$, $R^2=H \rightarrow \underline{6}$).

From many studies by Mazzocchi et al,^{2,4} Maruyama et al,^{2,3a,b} and our group,^{2,3b-d} it has become increasingly clear that the characteristic feature of the photoadditions of phthalimides with alkenes is associated with electron transfer process. Mazzocchi discussed the competition of the addition (k_{CN} , addition to the C(O)N bond) and electron transfer (k_{ET}) in terms of the ionization potentials.^{2b,4} The occurrence of the Paterno-Büchi reaction (k_{PB}) in the phthalimide photoaddition has now been verified by trapping the imide-oxetane using the *N*-acylindole group, a good Paterno-Büchi acceptor.⁶ Thus the general aspect of the photoaddition of the aromatic cyclic imides with alkenes may now be summarized as shown in Scheme 1.

Table 1 Photoproducts from $\underline{1}$ and $\underline{2}$.

Substrate	n	mp °C	Time (h)	Product	mp °C	Yield (%)	Recovery of $\underline{1}$ (%)
$\underline{1a}$	2	197-198	12	$\underline{3a}$	181 - 182	27	
			5	$\underline{4^*}$	193 - 194.5	38	32
$\underline{1b}$	3	136.5-137	7	$\underline{6b-1}$	161 - 162	11	20
				$\underline{6b-11}$	238.5-240	13	
$\underline{1c}$	4	109-110.5	6	$\underline{3c}$	187.5-188.5	69	19
$\underline{1d}$	5	87 - 89	4	$\underline{6d-1}$	200 - 200.5	28	19
$\underline{2}$	2	172-172.5	7	$\underline{6d-11}$	271.5-272.5	6	
				$\underline{5}$	178 - 179	52	

* After irradiation the photolysate was treated with MeOH-HCl



References and Notes

- 1) a) Photochemistry of the Phthalimide System. 32. Part 31. M. Wada, H. Nakai, K. Aoe, K. Kotera, Y. Sato, Y. Hatanaka, and Y. Kanaoka, submitted, b) Photoinduced Reactions 65 Part 64, see ref. 1a).
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- 3) a) K. Maruyama, Y. Kubo, M. Machida, K. Oda, Y. Kanaoka, and K. Fukuyama, *J. Org. Chem.*, **43**, 2303 (1978), b) M. Machida, K. Oda, K. Maruyama, Y. Kubo, and Y. Kanaoka, *Heterocycles*, **14**, 779 (1982), c) M. Machida, K. Oda, and Y. Kanaoka, *ibid.*, **17**, 425 (1982), d) *ibid.*, **18**, 211 (1982).
- 4) P.H. Mazzocchi, S. Minamikawa, P. Wilson, M. Bowen, and N. Narayan, *J. Org. Chem.*, **46**, 4846 (1981).
- 5) a) $\underline{3a}$ 1H -NMR, 6.40 ppm (a methine* proton adjacent to the nitrogen and oxygen atoms), ^{13}C -NMR, 62.9 (s), 109.1 (s), and 92.4 (d) (two quaternary carbons and a methine carbon* on the oxetane ring), $\underline{3c}$ 1H -NMR, 6.65 (s) ppm (a methine* proton), ^{13}C -NMR, 63.9 (s), 103.3 (s), and 90.5 (d) ppm (two quaternary carbons and a methine carbon* on the oxetane ring), b) The chemical shift value is close to that (6.20 ppm) of the methine proton adjacent to the nitrogen and oxygen atoms in oxeto[2,3-b]indole system.⁶
- 6) D.R. Julian and G.D. Tringham, *J. Chem. Soc. Chem. Comm.*, 1973, 13.