

SYNTHESES OF SPIRO-NITROGEN MULTICYCLIC SYSTEMS BY
PHOTOCYCLIZATION OF N-CYCLOALKENYLPHthalIMIDES¹

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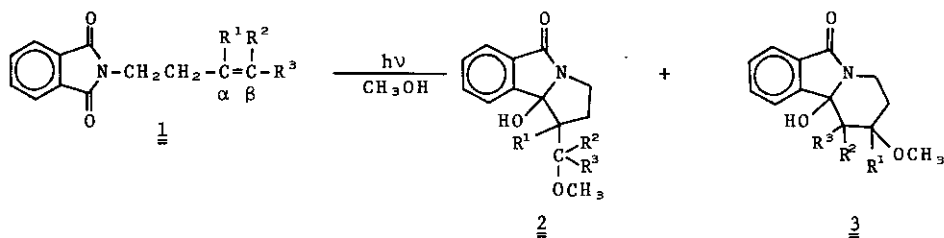
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Abstract----- Photolysis of the N-cycloalkenylphthalimide 4 ($m > 1$) in methanol gave spiro-nitrogen multicyclic products 5. In the case of $m=1$, pyrrolo[2,1-a]isoindole derivatives (6,7) were obtained. This support a mechanism involving an electron transfer followed by the anti-Markownikoff addition of methanol.

The photochemical reactions of phthalimides have been studied extensively.² The system undergoes a variety of photoreactions common to carbonyl compounds including inter- and intramolecular photoaddition of olefins.³ We have recently reported⁴ that photolysis of N-3-alkenylphthalimides 1 in methanol gave pyrrolo[2,1-a]isoindole 2 and/or pyrido[2,1-a]isoindole 3 systems depending on the degree of substitution at the olefin carbons (α, β) of 1, and an electron transfer mechanism was proposed.



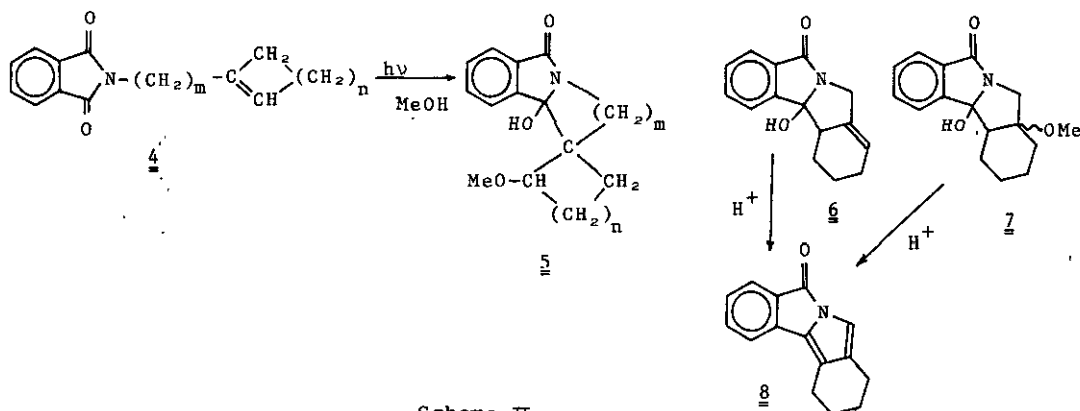
Scheme I

Based on the formulation given in Scheme I together with the mechanism proposed,⁴ it was anticipated that N-cycloalkenylphthalimides (1; R¹-R²=ring, R³=H) will lead to a photochemical synthesis of spiro-ring systems (2; R¹-R²=ring), which are otherwise rather difficult to access. In the present work we have examined this idea and found that this was really the case.

A series of N-cycloalkenylalkylphthalimides 4 were prepared and their photolysis was performed with a 500 W high-pressure mercury lamp in methanol in an atmosphere of nitrogen. The results are summarized in Table I and Scheme II.

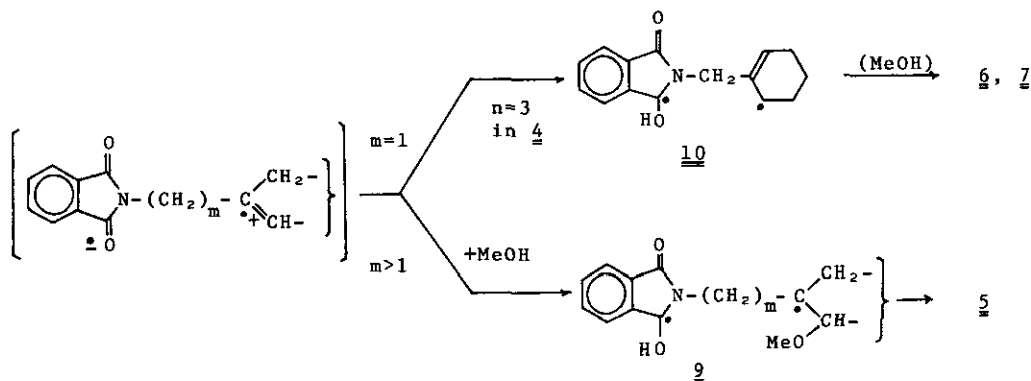
Table I. Photoproducts from 4

Substrates <u>4</u>		Products		SM (%)
m	n	<u>5</u> (%)	(mp °C)	
<u>a</u>	1	—	<u>6</u> 28 (213 - 214)	32
			<u>7</u> 16 (183 - 185)	
<u>b</u>	2	α 25 (114 - 116)		21
		β 22 (111 - 114)		
<u>c</u>	2	α 23 (190 - 194)		20
		β 18 (213 - 214)		
<u>d</u>	3	α 18 (195 - 198)		28
		β 16 (192 - 194)		
<u>e</u>	3	α 15 (181 - 182)		32
		β 12 (188 - 190)		



Irradiation of 4a afforded, after silica gel TLC, two products, 6 and 7, whose tetracyclic structures were assigned based on the elemental analysis and spectral properties. On the treatment with a trace of hydrochloric acid, both of them were converted into a pyrroloisindole 8 (mp 113-115°C) in a quantitative yield in support of their structures.

However, photolysis of the other substrates 4b-e proceeded to give the desired cyclized spiro compounds 5b-e, respectively (Table I). For example, two isomers 5ba and 5bg were isolated from the reaction of 4b. Their ¹H-NMR spectra were in agreement with the assigned structures. Also in the ¹³C-NMR spectra, all the peaks were reasonably assigned for the carbons; e.g.; 5ba, quaternary C 59 ppm (s), MeOCH 91 ppm (d); 5bg, quaternary C 53 ppm (s), MeOCH 83 ppm (d). The isomerism is apparently due to different configuration of the MeO groups with respect to the hydroxyl group, but the stereochemistry is not yet determined. Likewise, similar multicyclic spiro structures were assigned for all of the photoproducts 5c-d. The reaction is rationalized by the same mechanism as previously proposed.⁴ Thus the electron transfer from the double bond to the imide is mainly followed by anti-Markownikoff addition of methanol,^{3a,4,5} forming a more stabilized biradical 9, which, with the tertiary branched carbon of the side chain ring involved, will ultimately lead to 5 (Scheme III). The reason for the formation 6 and 7 from 4a is uncertain. Presumably with the substrate 4a, in which the double bond carbon is relatively closed to the imide carbonyl, a competing intramolecular proton transfer becomes preferred to the addition of methanol, and the resulting biradical 10 would lead to 6 and 7, with or without the participation of methanol. Minor involvement of an oxetane intermediate,³ however, can not be excluded.



Scheme III

ACKNOWLEDGEMENT

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