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SYNTHESIS OF SPIRO-NITROGEN MULTICYCLIC SYSTEMS CONTAINING MACROCYCLES BY PHOTOCYCLIZATION OF N-(ω-INDEN-3-YLALKYL)PHTHALIMIDES[1]

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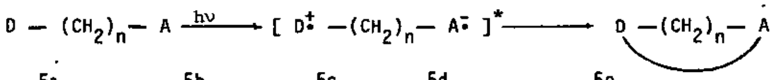
Abstruct----- Photolysis of the N-(ω-inden-3-ylalkyl)phthalimides **1** in methanol gave spiro-nitrogen multicyclic systems **3** containing macrocycles up to 13-membered in good yields.

From the systematic studies on the imide photochemistry,[2] it has become clear that there are remarkable differences between the photochemistry of the alicyclic imides and the aromatic cyclic imides (phthalimides). For example, whereas aliphatic cyclic imides undergo efficient inter- or *intramolecular Paterno-Büchi reactions*,[2,3] phthalimides undergo electron transfer,[2,4] as extensively studied by Mazzocchi et al.[2b,4]

We have been studying the application of a common working hypothesis,"photolysis of donor-acceptor pair systems" for general synthetic purposes[2a] (Scheme I). Several donors have been used such as



Scheme I

Sulfides,[5a] aromatics,[5b] anilines,[5c] amines,[5d] and olefins,[5e] with the phthalimide as a typical acceptor. Maruyama et al. have reported an interesting solvent-incorporated medium system for such syntheses.[5e] In an direct extention of these lines of studies, indene is now shown to be an especially useful donor group in constructing spiro-nitrogen macrocycles.[6]

A series of N-(ω-inden-3-ylalkyl)phthalimides **1** were prepared from potassium phthalimide and 3-(ω-bromoalkyl)indenes. These bromides were synthesized from indene and dibromoalkanes in the presence of tetraethylammonium chloride as a phase transfer catalyst. A methanol solution of **1** (10 mM) was irradiated with a 500w high-pressure mercury lamp in an atmosphere of N_2, and the products were purified by silica gel column chromatography. The results are summarized in Table I and Scheme II.

The photolysis gave rise to the desired spiro compounds **3**[7]. It is worth noting that spiro systems, including macrocycles up to 13-membered, wewe prepareed in very good chemical yields. Probably the

Scheme II

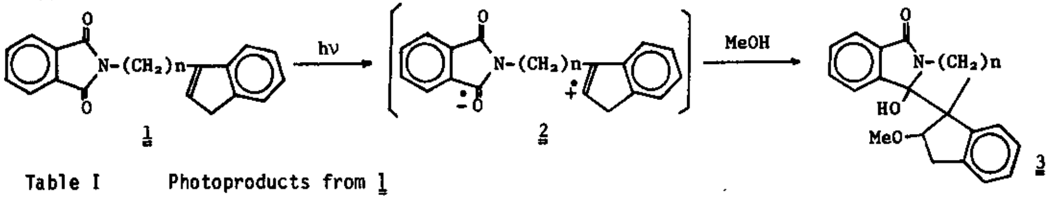


Table I Photoproducts from **1**

Substrates **1**		Conditions	Products **3**		Starting Materials
n	(mp °C)	time (hr)	(%)	(mp °C)	(%)
a	117-119	0.5	14	248-249	84
		5	82		8
b	88-90	2	37	228-230	58
		8	76		8
c	78-79	2	15	185-187	72
		8	86		6

reaction is rationalized by the electron transfer mechanism, with the indene as an excellent donor, involving the anti-Markownikoff addition of methanol as previously proposed[4,5e,6]. Recently much attention has been centered at the macrocyclic syntheses in view of the important chemistry of various natural and synthetic macrocyclic compounds. The present examples would encourage the participation of the photochemical methods in such synthetic challenge.

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7. All products gave satisfactory elemental analyses and showed reasonable spectral properties (UV, IR, Mass, ^{1}H-NMR, ^{13}C-NMR). The stereochemistry of **3** is unknown yet. Since methanol would add to the intermediate **2** from the opposite side of the imide carbonyl, however, a plausible configuration of the methoxyl would be *cis* to the hydroxyl.

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