acetate (II) or *m-tert*-butylphenyl acetate (III) reactions (the aromatic ring is pulled somewhat out of the cavity). In line with this, the ester V shows a K_d of 10 mM but V_{max} of only 4.1×10^{-3} s^{-1} in our Me_2SO buffer system. In this medium the pseudo-first-order rate constant for hydrolysis of V is 6.5×10^{-6} s^{-1}, so the acylation of β-cyclodextrin by V is only 630 times faster than hydrolysis. The *tert*-butylphenyl and ferrocene system have comparable binding constants, as we have seen previously[3] (while the binding constant of the *p*-nitrophenyl group shows that it would not be bound in this concentration range). V_{max} for V *should* be smaller than for IV, since models show that, with V, the conversion to a tetrahedral intermediate pulls the *tert*-butylphenyl group partly out of the cavity. Studies on other related substrates[9] will be needed to clarify all this, and even to show whether IV is yet the optimal substrate. However, it now seems clear that cyclodextrin-based catalysts have the potential to act as artificial enzymes with accelerations of enzymatic magnitudes.

Acknowledgment. This work was supported by the National Institute of Health.

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(2) R. L. Van Etten, J. F. Sebastian, G. A. Clowes, and M. L. Bender, *J. Am. Chem. Soc.*, **89**, 3242 (1967).
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(4) At this stage of the development of artificial enzymes, it seems best to optimize the *substrate* for a given catalyst. In a later stage the catalyst would be modified to fit a substrate of particular interest.
(5) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 906 (1957); the authors do not name the compound. We propose that ferrocinnamic acid is appropriate. Our NMR studies establish that the double bond is trans.
(6) Prepared by titrating KH_2PO_4 with NaOH. The solvent change alters pH's and p*K*'s as part of the total solvent effect.
(7) This plot excludes in particular a 2:1 cyclodextrin–substrate transition state involving both aromatic groups even if one cyclodextrin were fully bound throughout our concentration range. Known binding constants[1,3] also exclude such possibilities.
(8) H. Gutfreund and J. M. Sturtevant, *Biochem. J.*, **63** 656 (1956).
(9) As one example, we have already looked at the *N*-acylimidazole of ferrocinnamic acid as a substrate for β-cyclodextrin. It shows an acceleration of only 1200-fold over hydrolysis in the same 60% Me_2SO medium.
(10) National Science Foundation Postdoctoral Fellow.

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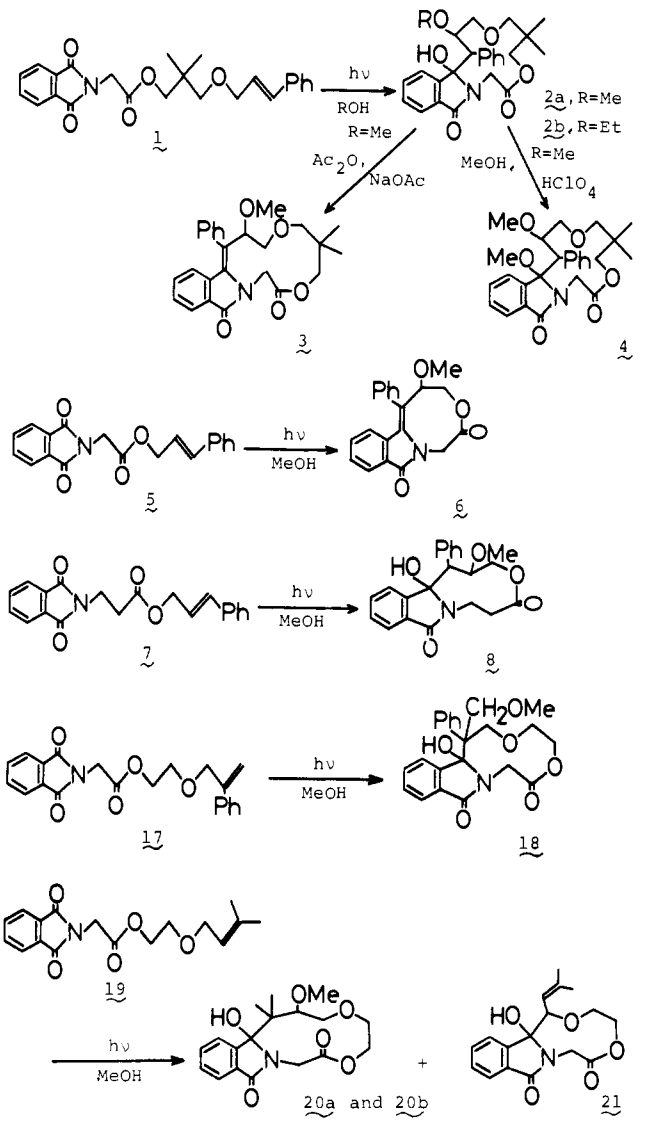
Solvent-Incorporated Medium to Macrocyclic Compounds by the Photochemical Cyclization of *N*-Alkenylphthalimides

Sir:

During recent years some examples of intramolecular photochemical cyclomerization between two chromophoric units bridged by more than four bonds have been reported by a few groups.[1] Compound formation between internal chromophores separated by 17–35 bonds has been successfully studied by Ors and Srinivasan in the cases of α,ω-dicinnamates.[1a,b] De Schryver and his co-workers were also successful in the cases of 7 7′-polymethylenedioxycoumarins with separation up to 14 bonds.[1c]

We report, for the first time, the photochemical solvent-incorporated medium to macro ring cyclomerizations between two chromophores separated by 6–13 bonds in the cases of *N*-alkenylphthalimides. A methanol solution of **1**[2,2] (2 mM) was irradiated for 3 h with a Eiko Sha PIH 300-W high-pressure Hg lamp through quartz. After evaporation of the solvent, a product (**2a**) crystallized (65%) (Scheme I). **2a:** mp 174–176 °C (from methanol); ^1H NMR ($CDCl_3$) δ 0.83 (s, 3 H), 1.05 (s, 3 H), 2.41 (s, 3 H, OMe), 2.8–3.1 (m, 3 H), 3.2–3.6 (m, 4 H), 3.78 and 4.30 (AB q, J = 12 Hz, 2 H), 3.98 and 4.26 (AB q, J = 16 Hz, 2 H), 7.2–7.8 (m, 9 H); IR (KBr) 3270 (OH), 1739 (ester), 1694 (amide) cm^{-1}; *m/e* (rel intensity) (20 eV) 439 (M^+, 6), 407 (M^+ − MeOH, 100), 273 (74); satisfactory elemental analysis for $C_{25}H_{29}NO_6$. Confirmatory evidence for the structure of **2a** was obtained by dehydration and methyl etherification as follows. The product **2a** was dehydrated by refluxing in acetic anhydride with a trace of sodium acetate to give **3** (30%). **3:** mp 157–159 °C; ^1H NMR ($CDCl_3$) δ 0.88 (s, 6 H), 3.1–3.5 (m, 4 H), 3.46 (s, 3 H, OMe), 3.80 and 4.49 (AB q, J = 12 Hz, 2 H), 4.41 and 5.78 (AB q, J = 18 Hz, 2 H), 5.00 (dd, J = 6, 8 Hz, 1 H), 5.68 (d, J = 8 Hz, 1 H), 6.9–7.9 (m, 8 H); IR (KBr) 1732 (ester), 1705 (amide) cm^{-1}; *m/e* (rel intensity) (20 eV) 421 (M^+, 59), 305 (94), 246 (100). On treatment with a trace amount of $HClO_4$ in methanol, **2a** was converted to its methyl ether **4. 4:** mp 175–176 °C; ^1H NMR ($CDCl_3$) δ 0.84 (s, 3 H), 1.11 (s, 3 H), 2.46 (s, 3 H, OMe), 2.60 (s, 3 H, OMe), 2.8–4.0 (m, 8 H), 4.54 (d, J = 12 Hz, 1 H), 4.61 (d, J = 17 Hz, 1 H), 7.2–8.1 (m, 9 H); IR (KBr) 1756 (ester), 1710 (amide) cm^{-1}; *m/e* (rel intensity) (20 eV) 453 (M^+, 3), 305 (100). Similar chemical manipulations were applied to the photoproducts of *N*-2-alkenylphthalimides.[4] Irradiation of **1** in ethanol gave the corresponding product **2b,** mp 200–203 °C (65%).

Scheme I



The photochemical solvent-incorporated cyclomerization was quite general in the cases of *N*-alkenylphthalimides with

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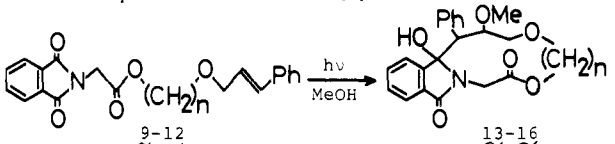
Table I. Photoproducts from *N*-Alkenylphthalimides **9-12**



9-12 **13-16**

substrate	*n*	product[a]	yield, %[b]	mp, °C	ring size	rel efficiency[c]
9	2	**13**	68	184-186	11	1.0
10	4	**14**	55	144-147	13	0.4
11	5	**15**	65	187-190[d,f] 197-200[e,f]	14	0.2
12	6	**16**	35	oil	15	0.1

[a] In methanol (2 mM) for 5-8 h at ambient temperature. [b] Based on the consumed imide. [c] Disappearance of imide with **9** as a standard. Using a Pyrex filter on a merry-go-round. [d] **15a.** [e] **15b.** [f] **15a:15b,** 3:1.

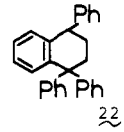
N-alkenyl group attached by β-styryl group at the end. Irradiation of **5** in methanol gave **6,** mp 237-239 °C (64%). In this case, the primary product seems to be unstable and results in the formation of the dehydrated product **6.** Photolysis of **7** in methanol afforded **8,** mp 217-219 °C (55%). A series of examples is summarized in Table I.

Irradiation of a methanol solution of **17** possessing the α-styryl moiety in the *N*-alkenyl group gave product **18,** mp 167-169 °C (68%). Photolysis of **19** having the 2-methyl-1-propenyl group instead of the α-styryl group afforded a mixture of the corresponding products **20a** (mp 168-169 °C) and its isomer (**20b**) as a mixture (total 35%). In this case, a hydrogen-abstraction product **21** was also obtained.[5] **21:** mp 169-171 °C; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.83 (s, 3 H), 3.2-3.5 (m, 1 H), 3.6-4.5 (m, 5 H), 4.7-5.1 (m, 2 H), 5.05 (br d, 1 H), 7.3-7.8 (m, 4 H) (the decoupling examination clearly demonstrated the presence of $Me_2C{=}C(H)CH{<}$ unit); IR (KBr) 3285 (OH), 1748 (ester), 1694 (amide) cm^{-1}; *m/e* (rel intensity) (20 eV) 317 (M^+, 7), 231 (100).

In recent years, radical ion pair formation in bimolecular photochemical reactions has been paid great interest.[6-9] In some cases olefins behave as electron donors. Arnold and his co-workers reported anti-Markownikoff methanol addition to some aromatic olefins photosensitized by methyl *p*-cyanobenzoate.[7] Similarly, photochemically induced methanol addition (substitution) reactions have been reported in the photoreaction of several cyanated aromatics with olefins,[8] and in the photoreaction of phthalimides with olefins.[4,9]

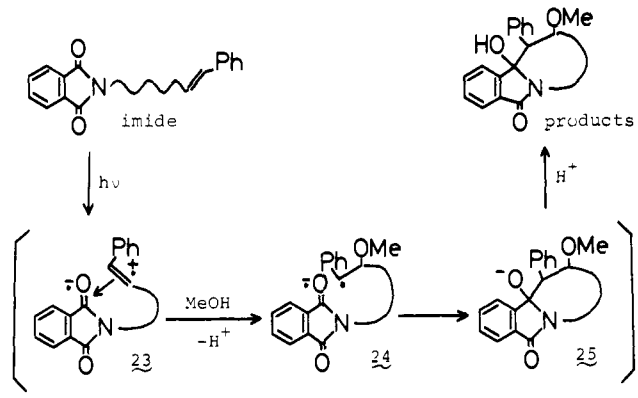
Photochemical intramolecular cyclomerization between two chromophoric units bridged by more than four bonds requires a certain interaction between the two remote chromophores in their excited state. Kanaoka and his co-workers reported the interesting "remote" photochemical hydrogen abstraction reaction of acceptor (phthalimide)-donor (S or N atom) systems, in which charge interaction in the excited state could play an important role to achieve the highly regioselective "remote" photoreaction.[5] Thus, the present reaction may be regarded as an application of the photoinduced methanol addition between electron acceptor (phthalimide) and donor (olefin) to the synthesis of "remote" cyclomerization products.

In our reaction initial one-electron transfer from the *N*-alkenyl double bond to the phthalimide moiety may be involved. Such an electron-transfer process is supported by the fact that photolysis of an acetonitrile solution containing *N*-methylphthalimide and 1,1-diphenylethylene gave 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (**22**); **22** is known to be derived from the radical cation of 1,1-diphenylethylene.[7a] Formation of the solvent-incorporated medium to macrocyclic products may be rationalized as shown in Scheme II.



22

Scheme II



The synthetic utility of this reaction has to be emphasized. Its scope, limitation, and mechanism are being studied.

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Selectivity Features of Polystyrene-Based Triphase Catalysts[1]

Sir:

Triphase catalytic methods serve as a compliment to phase-transfer catalysis.[2-6] Recently it occurred to us that triphase catalysts might possess inherent selectivity toward reactants. In particular, polystyrene resins are known to impose a modest size selectivity to attached catalysts and reagents in solid/liquid biphase reactions.[7,8] This effect has been attributed to the restriction in size of solvent channels by random cross-links in the polymer.[7] We reasoned that, not only would similar selectivity be found with certain of the polystyrene-based triphase catalysts, but, in addition, for those polymers that function as cosolvents,[6] a more pronounced degree of selectivity would be present owing to the relative solubility (ab-

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