noradamantane were obtained: mp 155–156 °C; ^{1}H NMR (CCl_4) δ 1.18 (s, 3 H, Me), 1.56 (s, 2 H), 1.72 (s, 4 H), 2.18 (s, 6 H); mass spectrum (75 eV), *m/e* (relative intensity) 172 (5.2, M^+), 170 (13, M^+), 135 (11.5), 93 (100). Anal. ($C_{10}H_{15}Cl$) C, H, Cl.

2-Chloroadamantane. 2-Adamantanol (25 g) (Aldrich) was treated with PCl_5 (50 g) in 300 mL of diethyl ether under reflux for 30 min. The resulting crude product was recrystallized in methanol, and yielded 21 g (75%) of pure 2-chloroadamantane, mp 190–191 °C (lit.[43] mp 186–188 °C, 190–191.8 °C).

Experimental Procedure Used in Organolithium Synthesis. In Pentane. Pentane (25 mL) and finely cut lithium wire with 2% sodium (280 mmol) were added under an argon stream to a three-necked Morton flask containing 15 g of coarsely crushed glass and equipped with a carbon dioxide ice condensor and a Hershberg stirrer. The solution was vigorously stirred for 20 min under pentane reflux. Then, while continuing vigorous stirring under a slight argon stream, 20 mmol of halogenated derivative (RCl) in 75 mL of pentane was slowly added. The presence of crushed glass, together with vigorous stirring, allowed the metal surface to be scoured while generating lithium sand, and, later, enabled removal of the lithium chloride adsorbed at the metal surface. After the disappearance of the RCl, a sample was subjected to deuterolysis and analyzed by GLC and mass spectrometry to determine the organolithium concentration.

(43) (a) Hoek, W.; Strating, J.; Wynberg, H. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1045. (b) Kovacic, P.; Chen Chang, J. H. *J. Org. Chem.* **1971**, *36*, 3138.

In Ether. A 125-mL, three-necked Morton flask equipped with a Hershberg stirrer and containing 15 g of coarsely crushed glass was cooled to −50 °C under a heavy argon stream. Once cooled to this temperature, the argon stream was diminished and 0.024 mol of lithium powder and 10 mL of anhydrous diethyl ether were introduced into this flask. After 10 min of vigorous stirring, 0.004 mol of halide (RBr) dissolved in 10 mL of dry ether were added dropwise for 30 min, during which vigorous stirring was continued. Fifteen minutes after this addition, a deuterolysis sample was removed and analyzed by GLC and mass spectrometry to determine the yield of lithium compound.

Acknowledgment. We express our gratitude to S. Briand for her invaluable collaboration.

Registry No. I (Y = H), 281-23-2; Ia, 3732-30-7; Ib, 935-56-8; Ic, 768-90-1; II (Y = OH), 30545-19-8; II (Y = H), 2292-79-7; IIa, 69261-61-6; IIb, 32401-16-4; IIc, 30545-17-6; III (Y = OH), 22635-86-5; IIIa, 69261-60-5; IIIb, 22650-12-0; IIIc, 31297-35-5; IV (Y = OH), 1905-16-4; IVa, 86550-17-6; IVb, 66117-95-1; IVc, 61898-33-7; V (Y = OH), 13987-76-3; Va, 86550-18-7; Vb, 17768-27-3; Vc, 53398-55-3; VI (Y = OH), 700-57-2; VIa, 38256-03-0; VIb, 7346-41-0; VIc, 7314-85-4; VII (Y = H), 281-46-9; VII (Y = 3-homoadamantyl), 32621-99-1; VIIa, 86550-19-8; VIIb, 27011-47-8; VIIc, 14504-84-8; VIII (Y = OH), 14504-80-4; VIIIa, 59239-90-6; VIIIb, 793-40-8; VIIIc, 15364-55-3; PCl_5, 10026-13-8; Et_2O, 60-29-7; thionyl bromide, 507-16-4; thionyl chloride, 7719-09-7; 9-bromoanthracene, 1564-64-3; anthranilic acid, 118-92-3; 9-chloroanthracene, 716-53-0; pentane, 109-66-0.

Photochemical Additions of Alkenes to Phthalimides. Mechanistic Investigations on the Stereochemistry of Alkene Additions and the Effect of Aryl Substituents on the Regiochemistry of Alkene Additions

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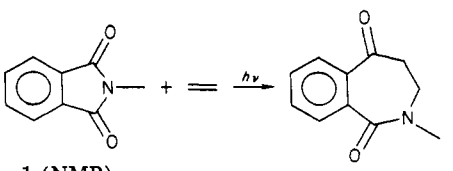
The mechanism of the photochemical addition of alkenes to phthalimides was investigated by determining the stereochemistry of the addition and the effect of aryl substituents on the regiochemistry. Intra- and intermolecular examples were examined. The stereochemistry of the addition of *cis*- and *trans*-2-butene to *N*-methylphthalimide to give 2,3,4-trimethyl-2-benzazepine-1,5-dione was studied. It was found that both alkenes added stereospecifically, each giving the corresponding *cis*- or *trans*-2,3,4-trimethyl-2-benzazepine-1,5-dione with >95% stereospecificity. The mechanistic implication of this result is either that the photochemical addition is a concerted (2 + 2) addition or that any intermediate biradical closes faster than rotation around the C–C bond which would result in loss of stereochemistry. A second approach to this problem employed the directive effects of aryl substituents. The proposed biradical intermediate is similar in structure to the phthalimide radical anion. The directive effects of aryl substituents have been experimentally determined in this system and are consistent with theoretical predictions. Theoretical predictions for aryl-substituent directive effects in the alternative concerted (2 + 2) process are opposite to those for the biradical case, which predicts that donors will direct meta and acceptors para. Irradiation of 4-methoxy- and 4-carbomethoxy-*N*-methylphthalimide in the presence of 1-hexene afforded the benzazepinedione addition products that resulted from addition to the para and meta C(O)–N bonds, respectively. These results are entirely consistent with a concerted process.

Over a period of years several groups have been working on the photochemistry of the phthalimide system. These molecules have exhibited diverse photochemical behavior,[1] including electron-transfer reactions,[2] photoreduction reactions,[3] Paterno–Büchi reactions,[4] and the addition of alkenes to form benzazepinediones (eq 1, NMP = *N*-methylphthalimide), which we reported in 1977.[5] The



1 (NMP) 2 (1)

(1) Mazzocchi, P. H. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 421.

(2) (a) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *Tetrahedron Lett.* **1978**, 4361. (b) Maruyama, K.; Kubo, Y. *Chem. Lett.* **1978**, 851. (c) Maruyama, K.; Kubo, Y.; Machida, M.; Oda, K.; Kanaoka, Y.; Fukuyama, K. *J. Org. Chem.* **1978**, *43*, 2303. (d) Maruyama, K.; Kubo, Y. *J. Am. Chem. Soc.* **1978**, *100*, 7772. (e) Machida, M.; Oda, K.; Maruyama, K.; Kubo, Y.; Kanaoka, Y. *Heterocycles* **1980**, *14*, 779. (f) Hayashi, H.; Nagakura, S.; Kubo, Y.; Maruyama, K. *Chem. Phys. Lett.* **1980**, *72*, 291. (g) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1981**, *46*, 3612.

(3) Kanaoka, Y.; Hatanaka, Y. *Chem. Pharm. Bull.* **1974**, *22*, 2205.

(4) Mazzocchi, P. H.; Minamikawa, S.; Bowen, M. *Heterocycles* **1978**, *9*, 1713. Machida, M.; Takechi, H.; Kanaoka, Y. *Tetrahedron Lett.* **1982**, *23*, 4981. Mazzocchi, P. H.; Klingler, L.; Edwards, M.; Wilson, P.; Shook, D. *Ibid.*, in press.

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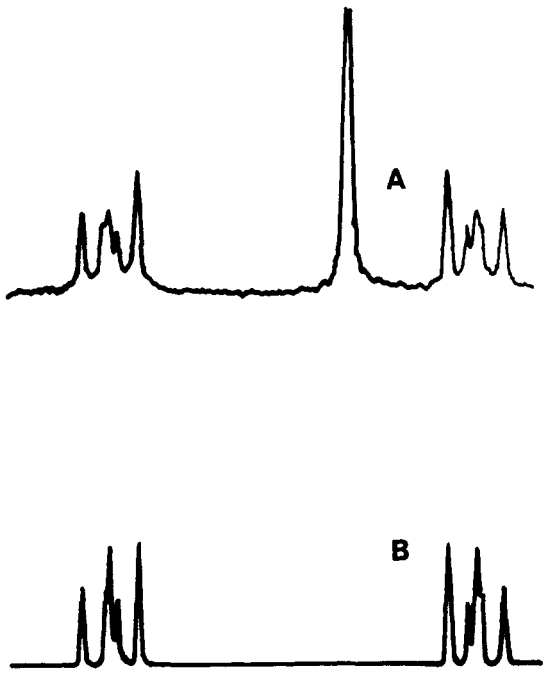
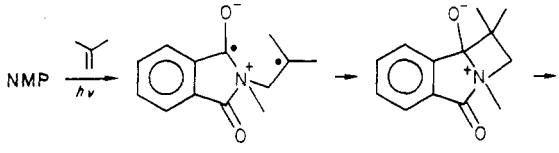


Figure 1. Authentic (A) and computer-simulated (B) A_2B_2 portions of the ^1H NMR spectrum of **13**.

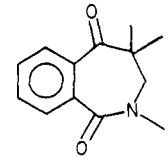
novelty of this latter reaction led us to examine its mechanism, and in this paper we report the detailed results of these investigations. We have previously reported on the extensive scope of this reaction, which includes addition with alkenes, dienes, vinyl ethers, vinyl esters, and an allene.[5f]

Mechanistic Possibilities

We considered two mechanistic possibilities seriously: (1) addition to afford zwitterionic biradical **3**, which would



3 **4**



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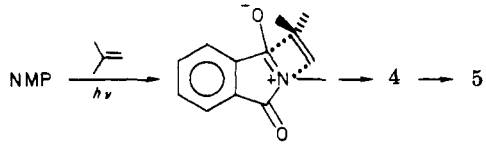
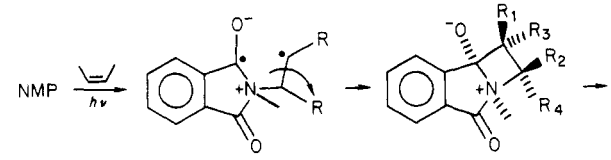


6

close to **4** and subsequently reopen to **5**, and (2) a concerted addition, possibly through an oriented exciplex **6** to give intermediate **4** directly. These alternatives were attractive because they nicely explain the observed regiochemistry of the addition, the former on the basis of radical stability and the latter on the basis of FMO considerations. Our experiments were designed to differentiate these possibilities.

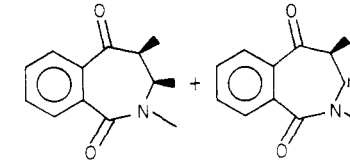
Stereochemistry of the Addition

Our first approach[5d] was to look at the stereochemistry of the addition process. It is clear that in the extreme case where the lifetime of biradicals such as **7** is long with respect to molecular rotations, the *Z* and *E* stereochemistry on the unreacted alkene will be lost in these biradicals, giving rise to four possible intermediates (**8**) and a mixture



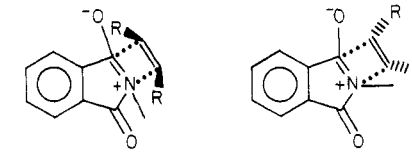
7

8a, R_1, R_2 = Me; R_3, R_4 = H
b, R_1, R_2 = H; R_3, R_4 = Me
c, R_1, R_4 = H; R_2, R_3 = Me
d, R_1, R_4 = Me; R_2, R_3 = H



9 **10**

of cis and trans products **9** and **10**. On the other hand, a suitably substituted alkene could react via a pair of nonequivalent exciplexes or transition states such as **11** and **12**, which would collapse to zwitterionic intermediates **8a**



11 **12**

and **8b**, respectively. Contrary to the situation with the other two alternatives, the formation of **8a** and **8b** and the opening to **9** will take place without loss of stereochemistry.

On the basis of this reasoning, studies were undertaken with *cis*- and *trans*-2-butene and NMP. Preparative-scale photolysis using *cis*-2-butene followed by preparative TLC workup gave a mixture of *cis*- and *trans*-3,4-dihydro-2,3,4-trimethyl-2-benzazepine-1,5-dione in 39% yield. Careful analysis of the NMR spectrum of this mixture showed H_b as a pair of multiplets, each of which consisted of a doublet of quartets at δ 4.46 and 3.96 with *J*'s = 2.3, 7, and 9.9, 7 Hz, respectively. This portion of the NMR spectrum is shown in Figure 1.

Confirmation of this assignment was obtained by means of a deuterium exchange experiment using NaOD, which resulted in the exchange of the proton α to the carbonyl group, H_a. The NMR spectrum of the mixture of **9** and **10** with H_a exchanged showed no resonances at δ 2.5–2.9 for H_a, and H_b now appeared as quartets (J = 7 Hz) at δ 4.46 and 3.96.

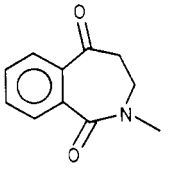
Initial attempts to look at reactions of NMP with pure *cis*- and *trans*-2-butene led to product mixtures: NMP with *cis*-2-butene gave approximately a 2:1 excess of product with the δ 3.96 multiplet whereas *trans*-2-butene gave approximately a 2:1 excess of product with the δ 4.46 multiplet. Prolonged workup led to further changes in the composition of the product mixture, and analysis of the

(5) (a) Mazzocchi, P. H.; Bowen, M. J.; Narain, N. K. *J. Am. Chem. Soc.* **1977**, *99*, 7063. (b) Mazzocchi, P. H.; Minamikawa, S.; Bowen, M. *J. Org. Chem.* **1978**, *43*, 3079. (c) Maruyama, K.; Kubo, Y. *Chem. Lett.* **1978**, *769*. (d) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *J. Org. Chem.* **1979**, *44*, 1186. (e) Mazzocchi, P. H.; Khachik, F.; Wilson, P.; Highet, R. *J. Am. Chem. Soc.* **1981**, *103*, 6498. (f) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P.; Bowen, M.; Narian, N. *J. Org. Chem.* **1981**, *46*, 4846.

cis-2-butene during the course of the reaction showed that slow cis–trans isomerization was occurring. It was clear that these stereochemical experiments would have to be conducted under conditions that would preclude starting material (2-butene) and product isomerization, and we would need to unequivocally determine the stereochemistry of the product.

Although **9** and **10** were unknown at the time, the N-demethylated analogues were known. On the basis of equilibration experiments, the most stable isomer had quite reasonably been assigned the trans configuration and the least stable isomer the cis.[6] Surprisingly these compounds had H_a–H_b coupling constants of J = 2.3 Hz and J = 10.1 Hz, respectively. Acid-catalyzed isomerization of **9** and **10** in separate experiments afforded an equilibrated mixture with a **9**:**10** ratio of 1.

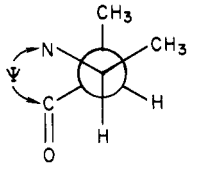
In view of our equilibration data and the rather exceptional coupling constant relationship, we decided to further investigate the stereochemistry of this system. Clearly, a 9.9-Hz coupling constant for **9** is only consistent with a H_a–C–C–H_b dihedral angle of 0° in this system. Since this can only be true if the ring is essentially planar, we chose to work on the parent **13**, reasoning that ring planarity would be most likely there and least likely when two *cis*-methyl groups are present.



13

Buys and Lambert[7] have developed an equation that has been shown to give accurate assessments of the angle Φ for rings (eq 2) where $R = J_{trans}/J_{cis}$.

$$\cos \Psi = \left[\frac{3}{2 + 4R}\right]^{1/2} \qquad (2)$$



We obtained the required coupling constants by computer simulation of the A_2B_2 portion of the NMR spectrum of **13**, which gave values of J_{gem} = −20 Hz, J = 6.8 Hz, J = 4.2 Hz, with the identification of the cis and trans couplings unknown. The experimental and simulated spectra are shown in Figure 2. Application of eq 2 can be made in two ways. If we assume $J_{cis} > J_{trans}$, this equation gives a value of Φ = 35°, whereas the assumption $J_{trans} > J_{cis}$ gives Φ = 54°. It is clear that neither alternative predicts a planar ring, forcing us to conclude that our material with the J = 9.9 Hz coupling constant (and the N-demethylated analogue with J = 10.1 Hz) is the trans isomer and that the cis has J = 2.3 Hz.

We avoided 2-butene isomerization and product epimerization by two simple expedients. Reactions were carried to <10% conversion in the presence of a 50 molar excess of either *cis*- or *trans*-2-butene, assuring that little cis → trans isomerization of starting material had occurred. Careful solvent evaporation at low temperature and examination of the 220-MHz NMR spectrum of the crude reaction mixture allowed us to estimate the amounts of cis

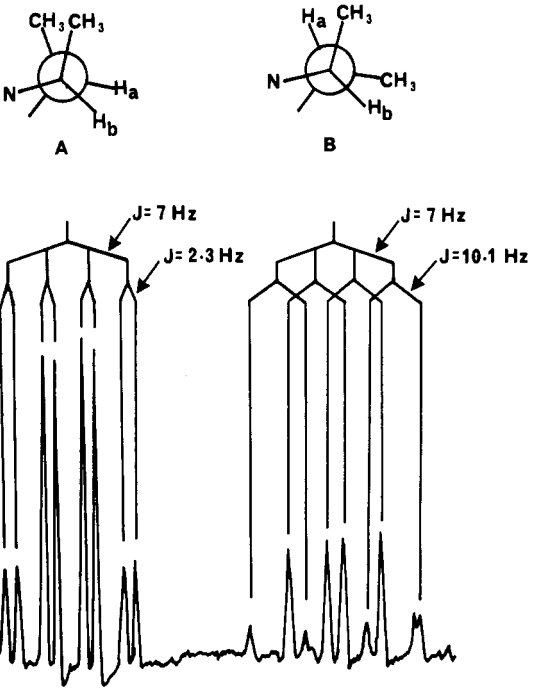


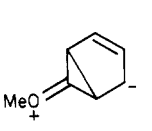
Figure 2. Portion of the 100-MHz ^1H NMR spectrum of a mixture of **9** and **10** showing the resonance from proton H_b in **9** (A) and **10** (B).

product from *trans*-2-butene and vice versa. We observed no cis product from *trans*-2-butene and no trans product from *cis*-2-butene, although we are limited by our analytical technique to a 95% certainty in the latter case.

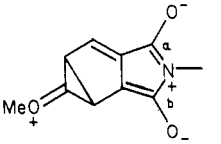
Our conclusion is that this reaction is stereospecific in addition to being regiospecific, and we therefore favor alternative **2**, the concerted process. However, these data do not rule out alternative **1** where closure of the biradical intermediate is faster than bond rotation with concomitant loss of stereochemistry. We chose to investigate the mechanism of the reaction in more detail by examining the effect of aryl substituents[5e] on the regiochemistry of the reaction.

Aryl Substituent Effects

Our rationale for these experiments stems from predictions of the directive effects of aryl substituents on the various reaction mechanism. For example, the product distribution in the concerted process (case 2) should be a function of the C–N double-bond character or excitation localization, and this in turn should depend on the aromatic substituent in the aryl-substituted imide. It has previously been shown in electrophilic aromatic photosubstitution reactions that donors direct the incoming electrophile to the meta position. Zimmerman[8] has suggested **14** as a reasonable model for the excited state of a



14

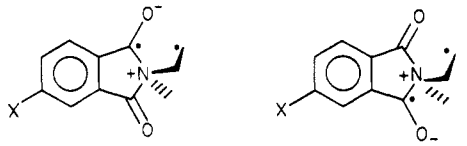


15

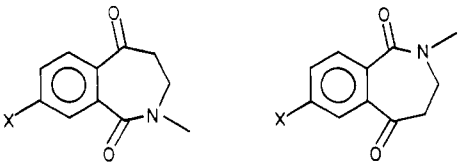
donor-substituted benzene ring. Incorporation of this model into the phthalimide system as in **15**, and assuming that concerted (2 + 2) addition will most likely take place at the site of maximum C–N double-bond character, we

(6) Howard, K. A.; Koch, T. H. *J. Am. Chem. Soc.* **1975**, *97*, 7288.
(7) Buys, H. R. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1003. Lambert, J. B.; Koeng, F. R. *Org. Magn. Reson.* **1971**, *3*, 389. Lambert, J. B. *Acc. Chem. Res.* **1971**, *4*, 87; *J. Am. Chem. Soc.* **1967**, *89*, 1836.
(8) Zimmermann, H. E.; Sandel, U. R. *J. Am. Chem. Soc.* **1963**, *85*, 915. Havinga, E.; Cornelisse, J. *Pure Appl. Chem.* **1976**, *47*, 1.

predict that reaction will preferentially occur at bond a with donor substituents and bond b with acceptors. The important point here is that donor and acceptor substituents should have opposite effects. The stepwise alternative involves addition to give a dipolar biradical reasonably described by canonical forms A and B, which can



A B



16 17

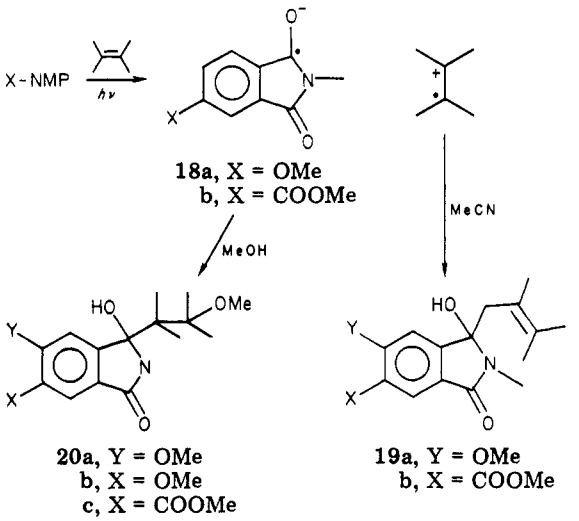
be viewed as either a radical or radical-anion intermediate with respect to the aryl substituents. Since virtually all substituents stabilize radicals, we would expect that if radical stability determined product regiochemistry, the same result would be obtained from all the substituted imides, i.e., canonical form A would be most stable and closure to **16** would result.

Consideration of this intermediate as a radical anion results in a quite different prediction. Acceptor groups should stabilize canonical form A and donor groups canonical form B, resulting in preferential closure to products **16** and **17**, respectively. This prediction is in accord with electrochemical studies[9,10] which show that para substitution by donor groups disfavors reduction of carbonyl groups whereas acceptor substituents favor this reaction. It is noteworthy that this regiochemical prediction is contrary to that proposed for a concerted reaction.

More convincing than this prediction is experimental evidence we have obtained on the directive effects of substituents on phthalimide radical anions in two reactions.[11,12] Photochemical electron transfer from 2,3-dimethyl-2-butene to NMP gives the radical-anion radical-cation pair which can either be trapped with methanol to give **20**[11] or undergo proton transfer and radical-pair coupling to give **19**.[12] Of particular interest in these two studies are the product distributions when X is a strong donor (OMe) and strong acceptor (CO_2Me).

In the trapping reaction, when X = OMe we obtain a 66:34 mixture of **20a** to **20b**, whereas only one product, **20c**, is obtained when $X = CO_2Me$. In the case of the photoreduction product **19**, the situation is even more dramatic in that each substituted phthalimide results in a single photoproduct; **18a** affords **19a** and **18b** gives **19b**. It is noteworthy that these results are in accord with our predictions for reaction via a radical anion.

We have carried out two experiments to investigate the regiochemistry of the (2 + 2) addition reaction with aryl-substituted phthalimides. The first of these involves the addition of 1-hexene to a series of 4-substituted

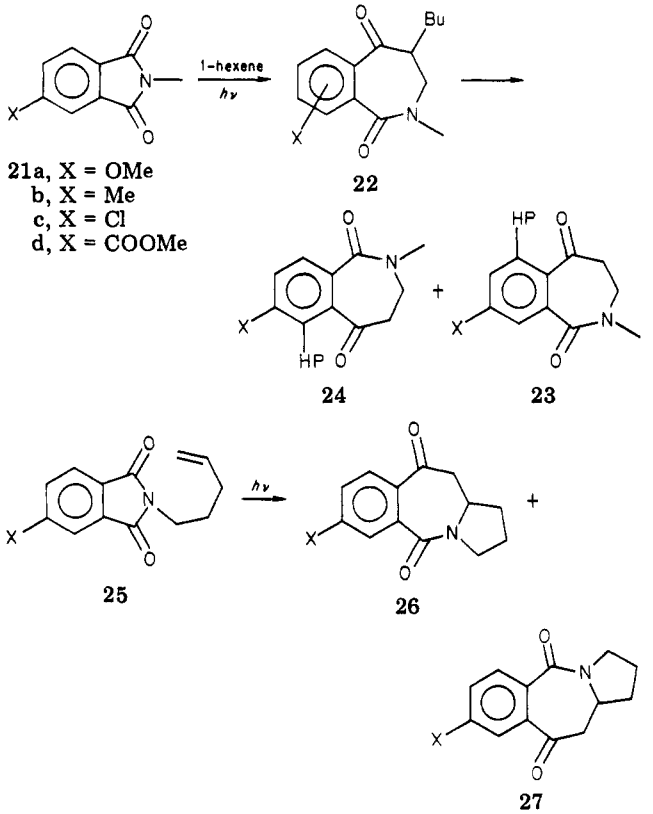


18a, X = OMe
b, X = COOMe

20a, Y = OMe
b, X = OMe
c, X = COOMe

19a, Y = OMe
b, X = COOMe

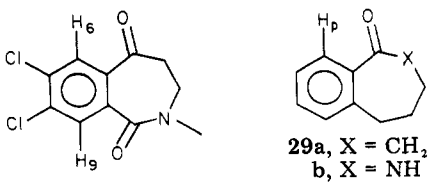
phthalimides **21** in which the initially formed adduct **22**



21a, X = OMe
b, X = Me
c, X = Cl
d, X = COOMe

22 **24** **23** **25** **26** **27**

undergoes an efficient type-II process to afford the dealkylated analogues **23** and **24**. In a complementary experiment we examined the regiochemistry of the intramolecular cyclization of a series of *N*-pentenylphthalimides (**25**) substituted on the aromatic ring. Determination of the product regiochemistry was accomplished by examination of the ^1H NMR spectra. The spectrum of **28** shows H_6 and H_9 as a pair of singlets at δ 8.01 and 7.76, presumably because there is differential deshielding by the lactam and ketone carbonyl groups on these peri hydrogens. Our preliminary assignment of H_6 to the most



28 **29a**, X = CH_2
b, X = NH

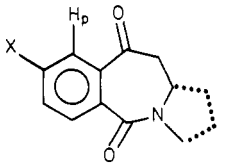
(9) Zuman, P. "Substituent Effects in Polarography"; Plenum Press: New York, 1967; pp 43–129.
(10) Bartel, E. T.; Grabowski, Z. R. *Pr. Conf. Polarogr.* **1956**, *323*. Holleck, L.; Marsen, H. *Z. Electrochem.* **1953**, *57*, 944.
(11) Mazzocchi, P. H.; Khachik, F. *Tetrahedron Lett.* **1978**, 4361.
(12) Mazzocchi, P. H.; Khachik, F. *Tetrahedron Lett.*, in press.

Table I. Product Distributions (%) from Photolysis of 21 with Hexene and from Photolysis of 25

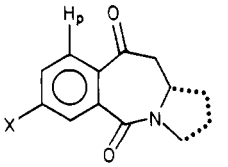
	% distribution from 21			
compd	a, X = OMe	b, X = CH_3	c, X = Cl	d, X = CO_2Me
23	100	57	52	27
24	0	43	48	73
% yield	32	32	45	46
	% distribution from 25			
compd	a, X = OMe	b, X = CH_3	c, X = Cl	d, X = CO_2Me
26	85	53	38	22
27	15	47	62	78
% yield	80	69	71	27

downfield shifted proton was corroborated by examination of the ^1H NMR spectra of **29a** and **29b**. In **29a** the peri hydrogen appears as a doublet of doublets at δ 7.72, whereas this proton is part of the aromatic multiplet at δ 6.96–7.36 in **29b**.

Our assignment of product regiochemistry follows from examination of the coupling pattern of the most downfield shifted proton (H_p in **30** and **31**). For example, in **23c** H_p



30



31

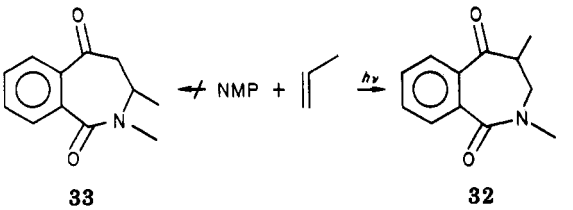
appears as a doublet (J = 8 Hz) at δ 7.88, whereas Hp appears as a doublet (J = 2 Hz) at δ 7.88 in **24c**. Clearly, in the first case H_p has a proton in the ortho position while there is a proton in the meta position to H_p in the second case. Similar analyses were used in all bicyclic and tricyclic cases. The product distribution is shown in Table I.

The experimental results are in accord with our predictions for a concerted reaction. Theoretical considerations aside, these results are contrary to our experimental findings under conditions where we know that we have generated a phthalimide radical anion; i.e., these intra- and intermolecular additions must proceed by a different mechanism. We feel that these results strongly favor a concerted (2 + 2) addition that may proceed through collapse of a preliminary oriented exciplex.

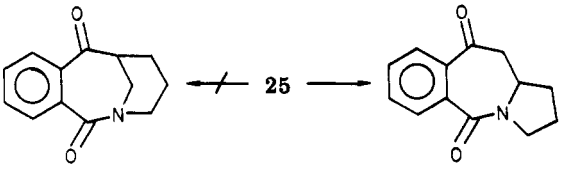
Orientation of Intramolecular Addition

The intramolecular cyclization of *N*-pentenylphthalimide first reported by Maruyama and Kubo is intriguing because it takes place with the "wrong" regiochemistry. For example, in bimolecular cases the sense of the addition is such that the least substituted carbon in the alkene becomes bonded to the nitrogen and the most substituted to the carbonyl carbon. We observe **32** but not **33**. However, in the intramolecular cases we always observe additions in the opposite sense; i.e., we obtain **34** but not **35**. We believe that this difference in regiochemistry in the intramolecular case is probably steric in origin and and involves the difference in steric demands involved in the formation of the intermediates (**36** and **37**, respectively) or exciplexes leading to **34** and **35**.

Since there appears to be a significant electronic driving force for the regiochemical orientation in the bimolecular case, there arises the question of the "cost" involved in the intramolecular reaction proceeding with the incorrect regiochemistry. Although we have no conclusive data on this



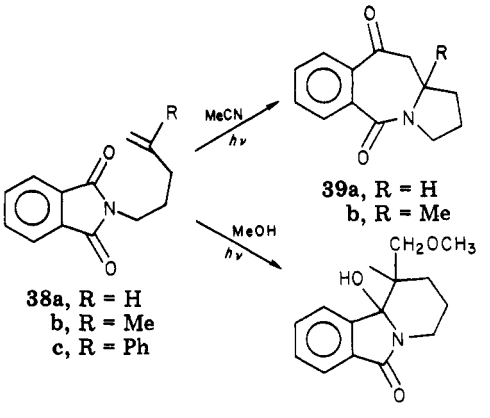
33 **32**



35 **34**

36 **37**

point, we do have two interesting experiments that are relevant. The *N*-(4-methyl-4-pentenyl)- and *N*-(4-phenyl-4-pentenyl)phthalimides (**38b** and **38c**) are intramolecular analogues of the 2-methylpropene + NMP and α-methylstyrene + NMP systems, both of which react to give the corresponding benzazepinediones.



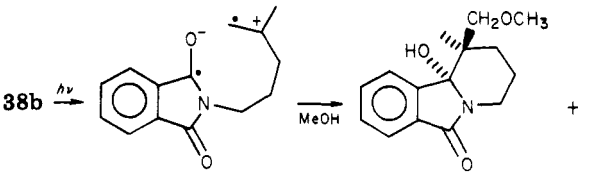
38a, R = H
b, R = Me
c, R = Ph

39a, R = H
b, R = Me

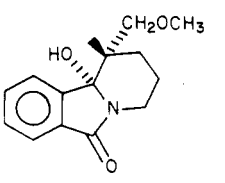
40

The reactivity in the pentenyl system decreased in the order **38a** > **38b** > **38c**; i.e., in comparative studies **38a** gave **39a** in 90% yield after 1 h of irradiation (50% conversion) whereas **38b** gave **39b** in 63% yield after 4 h (50% conversion) and prolonged irradiation of **38c** afforded no product.

Change of solvent to methanol with **38b** results in the complete disappearance of benzazepinedione product (**39b**) and the appearance of trapped product **40** as a pair of



40a



40b

Table II. Selected Quantum Yields for Addition in Inter- and Intramolecular Cases

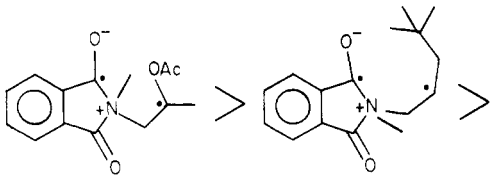
substrate	Φ addition
NMP + isopropenyl acetate	0.070[a]
NMP + 4,4-dimethylpentene	0.044[a]
38a	0.149[b]
38b	0.022[b]
38b (CH_3OH)[c]	0.26[b,c]

[a] Solutions were 0.04 M in NMP and 2.0 M in alkene. All irradiations were conducted at 297 nm. [b] Solutions were 0.1 M in imide. [c] Quantum yield for trapped product 40.

diastereoisomers in 67% yield after 1.5 h (75% conversion). By comparison in the intermolecular case, 2-methylpropene gives a 51% yield of benzazepinedione in addition to trapped product when the reaction is carried out in methanol.

It is clear that electron transfer competes with addition in both intermolecular and intramolecular cases. When diffusion in the intermolecular case is neglected, the intrinsic rates of electron transfer should be essentially identical in both cases, forcing us to conclude that in the intramolecular addition process the rate of (2 + 2) addition has decreased as a result of the "wrong" regiochemical orientation.

Zimmerman[13] has used radical stability arguments to rationalize reactivity differences in reactions that are known to be concerted. In the present case the quantum yield comparison between the mono- and disubstituted alkenes in the bimolecular case is instructive. Using radical stability reasoning, we expect isopropenyl acetate to be



41 42

43 44

more reactive than 4,4-dimethylpentene, and this is reflected in the quantum yields in Table II. The same result is obtained if the phthalimide in its ene form is considered as an α,β-unsaturated ketone and one analyzes the situation as a photoaddition of an "X-substituted olefin to a *Z*-substituted olefin".

In the intramolecular case, **38a** shows a dramatic increase in quantum yield when compared to the bimolecular case even though the "biradical" involved is primary.

We presume this is a proximity effect due to the intramolecular nature of the reaction. The decrease in quantum yield observed with **38b** cannot be due to radical stabilization effects since this biradical intermediate is also primary. Although the generation of a quaternary carbon may be part of the reason for this reactivity decrease, an additional possibility is that the polarization of the alkene favors the regiochemistry opposite to that dictated by steric factors and actually observed. This effect should increase as the polarization of the alkene increases. The trend observed in Table II suggests that this may be the case although we have insufficient data unequivocally to establish this point.

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Experimental Section

Melting points were measured on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Dr. Franz Kasler of the University of Maryland. IR spectra were recorded on a Perkin-Elmer 281 spectrophotometer. NMR spectra were recorded on a Varian XL-100, EM-360, or an HA-220 spectrometer. Analytical GLC determinations were performed on an HP 5830-a gas chromatograph equipped with an HP 18850-A integrating printer/plotter. Analytical HPLC determinations were performed on a Varian Model 5000 liquid chromatograph interfaced to the HP 18850-A printer/plotter. UV determinations were made on a Hitachi 100-80A spectrophotometer.

Photolyses: General Procedure. Photolyses were carried out in either quartz test tubes or large photochemical reactors by using a 450-W Hanovia medium-pressure Hg arc lamp and a water-cooled quartz immersion well. The reactions were cooled by immersion in an ice or an ice/salt (−20 °c) bath to minimize the loss of low-boiling or gaseous alkenes. The reactions were interrupted at 1.5-h intervals so that ice and salt could be added to the cold bath.

Photolysis of NMP and *cis*-2-Butene: 3,4-Dihydro-2,3,4-trimethyl-2-benzazepine-1,5-dione. *cis*-2-Butene (5.4 mL, 0.06 mol) was condensed into a quartz test tube at −20 °C, 0.2 g (0.0012 mol) of NMP and 30 mL of precooled CH_3CN were quickly added, and the tube was capped with a serum stopper. The sample was irradiated for 3 h at −20 °C.

Solvent was removed in vacuo, and the products were separated by preparative TLC on silica (3:1 ether/hexanes), affording 0.075 g of recovered NMP along with 0.066 g (39%) of a mixture of cis and trans benzazepine-1,5-dione (oil): IR ($CDCl_3$) 1680, 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.88–7.38 (m, 4 H), cis isomer [4.46 (dq, 1 H, J = 2.3, 7 Hz), 3.13 (s, 3 H), 2.69 (dq, 1 H, J = 2.3, 7 Hz), 1.36 (d, 3 H, J = 7 Hz), 1.33 (d, 3 H, J = 7 Hz)], trans isomer [3.96 (dq, 1 H, J = 9.9, 7 Hz), 3.56 (s, 3 H), 2.78 (dq, 1 H, J = 9.9, 7 Hz), 1.29 (d, 3 H, J = 7 Hz), 1.75 (d, 3 H, J = 7 Hz)]; MS, m/e (high resolution) 217.1094 (M^+ theory requires 217.1103).

Photolyses of NMP with *cis*-2-Butene and *trans*-2-Butene. A solution containing 100 mg of NMP, 2 mL (0.02 mol) of *trans*-2-butene, and 15 mL of CH_3CN was irradiated for 1 h and the solvent carefully removed in vacuo. The crude mixture was dissolved in 0.5 mL of $CDCl_3$, and a 220-MHz ^1H NMR spectrum was measured between 1000 and 700 Hz (4.55–3.18 ppm). Only a partially resolved doublet of quartets was observed at 872 Hz.

The solvent was carefully removed from two samples that were identical except that they contained *cis*-2-butene. The 220-MHz ^1H NMR spectra measured between 1000 and 700 Hz showed 984 Hz (dq, J = 2.3, 7 Hz). No signal at 872 Hz was observable.

Spectral Simulation of the A_2B_2 Portion of the ^1H NMR Spectrum of 3,4-Dihydro-2-methyl-2-benzazepine-1,5-dione (13). The SPINS NMR simulation program was employed on a Varian 620/i computer to simulate the A_2B_2 portion of the 100-MHz ^1H NMR spectrum of the parent benzazepinedione. Chemical shifts were obtained from a ^1H NMR spectrum of an authentic sample. As a starting point, the coupling constants J_{AB} were obtained from the ^1H NMR spectrum of a mixture of *cis*- and *trans*-2,3,3-trimethylbenzazepinediones. Several iterations involving changes in J_{AA} and J_{AB} were required to obtain a match. The following data were obtained: $F(A)$ = 369.2 (Hz), $F(A')$ = 369.2, $F(B)$ = 298.0, $F(B')$ = 298.0, $J_{AA'}$ = −20 Hz, J_{AB} = 4.2 Hz, $J_{AB'}$ = 6.8 Hz, $J_{A'B}$ = 6.8 Hz, $J_{A'B'}$ = 4.2 Hz, $J_{BB'}$ = −20 Hz.

Photolysis of NMP and 4,4-Dimethylpentene. NMP (200 mg, 0.0012 mol) and 6 mL (0.06 mol) of 4,4-dimethylpentene were irradiated for 3 h at 0 °C in acetonitrile. Solvent was removed, and the products were separated by preparative TLC on silica (20% hexanes in ether). NMP (90 mg) was recovered along with 59 mg (33%) of 4-(2,2-dimethylpropyl)-3,4-dihydro-2-methyl-2-benzazepine-1,5-dione (oil): IR ($CDCl_3$) 2960, 1685, 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.9 (m, 1 H), 7.7–7.4 (m, 3 H), 3.56 (t, 2 H), 3.24 (s, 3 H), 3.0 (m, 1 H), 1.7 (dd, 1 H, from partially resolved ABX),

1.29 (d, 1 H, from partially resolved ABX), 1.02 (s, 9 H); MS, m/e (high resolution) 259.1561 (M^+ theory requires 259.1572).

2,3,4,5-Tetrahydro-2-benzazepin-1-one (Homodihydrocarbostyril, 29b). This compound was prepared by the Beckmann rearrangement of 1-tetralone oxime[15] (4 g, 0.025 mol) in polyphosphoric acid (120 g). Recrystallization from ethanol gave 3.53 g (80%) of 2,3,4,5-tetrahydro-2-benzazepin-1-one: mp 142.5–143 °C; NMR ($CDCl_3$) δ 8.7 (br s, 1 H), 7.36–6.96 (m, 4 H), 2.8 (t, 2 H, J = 7 Hz), 2.5–2.1 (m, 4 H).

Benzosuberone (29a) was purchased from Aldrich: NMR ($CDCl_3$) δ 7.72 (d, 1 H, J = 7 Hz), 7.47–7.12 (m, 3 H), 2.97–2.7 (m, 4 H), 1.84 (m, 4 H).

4,5-Dichloro-*N*-methylphthalimide. 4,5-Dichlorophthalic acid (85 g, 0.362 mol) was added to 175 mL (1.85 mol) of acetic anhydride and the solution refluxed (165 °C) for 5 h. The acetic anhydride was removed in vacuo and the crude 4,5-dichlorophthalic anhydride was washed with ethanol and collected by vacuum filtration; 75.3 g (96%); mp 129–130 °C.

The 4,5-dichlorophthalic anhydride was added to 200 mL of aqueous methyl amine (40%). Water and methyl amine were removed in vacuo; 50 mL of H_2O was added to the flask, and 6 N HCl was added slowly until the solution was mildly acidic. Water was removed in vacuo, and the solid precipitate was collected and washed with H_2O.

The dry, solid 4,5-dichlorophthalic acid monomethylamide was placed in a flask without further purification and heated to 160 °C for 6 h. The 4,5-dichloro-*N*-methylphthalimide formed during the dehydration sublimed; therefore, the reaction was terminated when the reaction flask was virtually empty, and the product was coating a cold finger. No further purification was necessary: 61.2 g (76.5% from the anhydride); mp 174–174.5 °C; IR (KBr) 3090, 1695 cm^{-1}; NMR ($CDCl_3$) δ 7.8 (s, 2 H), 3.15 (s, 3 H). Anal. Calcd for $C_9H_5Cl_2NO_2$: C, 46.99; H, 2.19; N, 6.09. Found: C, 47.00; H, 2.06; N, 5.93.

Photolysis of 4,5-Dichloro-*N*-methylphthalimide and 1-Hexene in CH_3CN. 4,5-Dichloro-*N*-methylphthalimide (0.350 g, 0.0015 mol) and 5.1 g (0.06 mol) of 1-hexene were irradiated in 30 mL of CH_3CN for 3 h at 0 °C. The solvent was removed, and the crude mixture was separated by preparative TLC on silica (3:1, ether/hexanes). 4,5-Dichloro-*N*-methylphthalimide (150 mg) was recovered along with 55 mg (25%) of 7,8-dichloro-3,4-dihydro-2-methyl-2-benzazepine-1,5-dione (28): mp 170 °C; IR ($CDCl_3$) 1690, 1645 cm^{-1}; NMR ($CDCl_3$) δ 8.01 (s, 1 H), 7.76 (s, 1 H), 3.68 (m, 2 H), 3.23 (s, 3 H), 3.0 (m, 2 H). Anal. Calcd for $C_{11}H_9Cl_2NO_2$: C, 51.19; H, 3.52; N, 5.43. Found: C, 51.09; H, 3.52; N, 5.15.

Preparation of Ethyl 4-Methylpentenoate. NaH (4.6 g, 10.1 mol, 50% in oil) was placed in a dry 250-mL, three-necked flask; mineral oil was removed by washing with pentane, 50 mL of dry Me_2SO was added immediately, and the solution was heated to 75 °C for 1 h.

The methylsulfinyl carbanion solution was cooled to 18 °C and 35.7 g (0.1 mol) of dry methyltriphenylphosphonium bromide in 100 mL of dry Me_2SO was added dropwise. After addition was complete, the solution was allowed to come to room temperature (30 min), 11 mL (0.08 g) of ethyl levulinate in 10 mL of dry Me_2SO was added dropwise to the Wittig reagent, and the reaction was allowed to stir at room temperature for 6 h.

After quenching with 500 mL of cold water, the product was extracted with four 150-mL portions of pentane, the combined pentane extracts were washed with two 200-mL portions of H_2O and dried over $MgSO_4$, and the crude product was distilled to give 6.82 g (60%) ethyl 4-methyl-4-pentenoate: bp[16] 85 °C (20 mm); NMR ($CDCl_3$) δ 4.72 (s, 2 H), 4.15 (q, 2 H, J = 7 Hz), 2.4 (s, 4 H), 1.75 (s, 3 H), 1.25 (t, 3 H, J = 7 Hz).

Preparation of 4-Methyl-4-penten-1-ol. Ethyl 4-methyl-4-pentenoate (6.8 g, 0.048 mol) in 50 mL of dry ether was added slowly to a slurry of 5.4 g (0.14 mol) of $LiAlH_4$ in 800 mL of ether and the reaction heated at reflux overnight. Quenching of excess hydride was accomplished by successive addition of 5.4 mL of H_2O, 5.4 mL of 15% NaOH, and 16.2 mL of H_2O.[17] After addition was complete, the solution was allowed to stir for 1 h. The solution was filtered and the precipitate washed with an additional 100 mL of ether. The combined filtrates were dried over $MgSO_4$ and filtered, and the ether was removed in vacuo to give 3.6 g of crude product. The product was distilled to give 3.4 g (71%) of 4-methyl-4-penten-1-ol: bp[18] 65–68 °C (20 mm); NMR ($CDCl_3$) δ 4.74 (s, 2 H), 3.65 (t, 2 H, J = 7 Hz), 2.3 (s, 1H), 2.2–1.6 (m, 4 H), 1.76 (s, 3 H); IR ($CDCl_3$) 3610, 3440, 3080, 2940, 1650 cm^{-1}.

Preparation of 5-Bromo-2-methyl-1-pentene. To a solution of 3.3 g (0.028 mol) of 4-methyl-4-penten-1-ol in 75 mL of dry pyridine was added 16.0 g (0.084 mols) of dry *p*-toluenesulfonyl chloride, and the solution was cooled in the freezer for 16 h. The solution was acidified with 10% HCl and extracted with three 75-mL portions of ether. The ether extracts were washed with 10% HCl, 5% $NaHCO_3$, and water and dried over $MgSO_4$, and the ether was removed in vacuo to give 6.48 g (91%) of crude tosylate; NMR ($CDCl_3$) δ 7.8 (d, 2 H, J = 8 Hz), 7.3 (d, J = 8 Hz), 4.65 g (m, 2 H), 4.05 (t, 2 H, J = 7 Hz), 2.48 (s, 3 H), 2.2–1.7 (m, 4 H), 1.65 (s, 3 H). The crude tosylate was used without further purification.

The tosylate (6.48 g, 0.025 mol) was dissolved in 10 mL of acetone, 4.32 g (0.05 mol) of dry LiBr in 50 mL of dry acetone was added, and the solution was refluxed at 75 °C overnight. The solution was poured into 200 mL of cold water and extracted with three 75-mL portions of ether. The combined ether extract was washed with water and dried over $MgSO_4$, and the ether was removed by distillation at atmospheric pressure. Distillation of the residue gave 3.1 g of product: bp 46–48 °C (20 mm); NMR ($CDCl_3$) δ 4.72 (s, 2 H), 3.38 (t, 2 H, J = 7 Hz), 2.2–1.8 (m, 4 H), 1.68 (s, 3 H).

Preparation of 2-(4-Methyl-4-pentenyl)phthalimide (38b). Potassium phthalimide (5.5 g, 0.030 mol) was placed in a dry 250-mL, three-necked flask under nitrogen (100 mL). Dry DMF was added via an addition funnel, and the solution was heated to 50 °C; 3.1 g (0.018 mol) of 5-bromo-2-methyl-1-pentene in 10 mL of dry DMF were added dropwise to the solution. The reaction was heated to 150 °C for 12 h. Care was taken to shield the reaction from direct light due to the photosensitivity of the bromopentene. Upon cooling, excess potassium phthalimide was quenched by pouring the solution into a 1-L separatory funnel containing 500 mL of water. The product was extracted with three 80-mL portions of CH_2Cl_2. The combined extract was washed with four 100-mL portions of H_2O to remove all DMF and dried over $MgSO_4$. CH_2Cl_2 was removed in vacuo, and the crude product was distilled by bulb-to-bulb distillation to give 3.87 g (94%) of **38b**, clear liquid: bp 178 °C (1 mm); NMR ($CDCl_3$) δ 7.92–7.62 (m, 4 H), 4.72 (d, 2 H, J = 2 Hz), 3.68 (t, 2 H, J = 7 Hz), 2.2–1.6 (m, 4 H), 1.72 (s, 3 H); IR ($CDCl_3$) 1765, 1700 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59, N, 6.11. Found: C, 73.37; H, 6.66; N, 6.09.

4-Methyl-*N*-(4-pentenyl)phthalimide (25b). General Procedure. A solution of 10 g (0.055 mol) of 4-methylphthalic acid in 150 mL of acetic anhydride was stirred at reflux for 24 h. Solvent was removed in vacuo to afford the crude anhydride. One hundred milliliters of xylenes was added followed by 6.61 g (0.110 mol) of urea, and the mixture was stirred at reflux for 20 h. Solvent was removed in vacuo and the residual solid washed with water to remove unreacted urea. Recrystallization from methylene chloride gave 8.4 g (0.052 mol) of 4-methylphthalimide. A 1-g (6.2 mmol) sample of 4-methylphthalimide was reacted with 1 equiv of NaH in 50 mL of dry DMF under nitrogen for 1 h at 70 °C, then 0.92 g (6.2 mmol) of 5-bromo-1-pentene was added, and the mixture was stirred overnight at 70 °C. The reaction was diluted with 2 × 100 mL of methylene chloride. The extract was washed with 100 mL of 2 N NaOH and 4 × 100 mL of water, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo to afford 1.3 g (93%) of crude product. Distillation under reduced pressure gave pure material which solidified on cooling: mp 38–40 °C; IR ($CHCl_3$) 1770 cm^{-1}; NMR ($CDCl_3$) δ 7.6 (m, 3 H), 5.8 (m, 1 H), 5.0 (m, 2 H), 3.6 (t, 2 H), 1.9 (m, 4 H). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.33; H, 6.59; N, 6.11. Found: C, 73.56; H, 6.80; N, 6.03.

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4-Chloro-*N*-(4-pentenyl)phthalimide (25c). This compound was prepared by the general procedure from 4-chlorophthalic acid in 87% overall yield. Pure material showed the following: mp 47–49 °C; IR ($CHCl_3$) 1770, 1710 cm^{-1}; NMR ($CDCl_3$) δ 7.7 (m, 3 H), 5.8 (m, 1 H), 5.0 (m, 2 H), 3.7 (t, 2 H), 2.0 (m, 4 H). Anal. Calcd for $C_{13}H_{12}NO_2Cl$: C, 62.32; H, 4.83; N, 5.59. Found: C, 62.37; H, 5.02; N, 5.43.

4-Methoxy-*N*-(4-pentenyl)phthalimide (25a). A solution of 4-hydroxyphthalic acid (5 g, 0.027 mol), 50 mL of methanol, and a catalytic amount of sulfuric acid was stirred at reflux overnight. Solvent was removed in vacuo to afford the crude diester (4.7 g, 0.022 mol). The diester was dissolved in 170 mL of acetone and reacted with K_2CO_3 (16.5 g, 120 mmol) at 50 °C for 1 h. Methyl iodide (6.8 g, 0.048 mol) was added, and the mixture was stirred at reflux overnight. K_2CO_3 was removed by filtration and solvent removed in vacuo to afford 4-methoxydimethylphthalate (3.6 g, 0.016 mol). Forty milliliters of acetone and 15 mL of 11 N NaOH were added, and the solution was stirred overnight at 25 °C, acidified, and the solvents removed in vacuo. The crude 4-methoxyphthalic acid was extracted into acetone. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. Recrystallization from water afforded 2.8 g (0.014 mol) of pure product. 4-Methoxy-*N*-(4-pentenyl)-phthalimide was prepared from 4-methoxyphthalic acid by the general procedure for 4-methyl-*N*-(4-pentenyl)phthalimide in 63% overall yield. Pure product showed the following: mp 40–41 °C; IR ($CHCl_3$) 1760, 1710 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (m, 3 H), 5.7 (m, 1 H), 5.0 (m, 2 H), 3.9 (s, 3 H), 3.6 (t, 2 H), 1.9 (m, 4 H). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.62; H, 6.40; N, 6.00.

4-Carbomethoxy-*N*-(4-pentenyl)phthalimide (25d). 4-Carbomethoxyphthalic anhydride was prepared in quantitative yield from 4-(chlorocarbonyl)phthalic anhydride by the method of Puskas and Fields[20] and was found to have properties identical with those reported. 4-Carbomethoxy-*N*-(4-pentenyl)phthalimide was prepared from the anhydride by the general procedure in 96% overall yield. Pure product showed the following: mp 36–38 °C; IR ($CHCl_3$) 1780, 1720 cm^{-1}; NMR ($CDCl_3$) δ 8.1 (m, 3 H), 5.7 (m, 1 H), 5.0 (m, 2 H), 4.0 (s, 3 H), 3.7 (t, 2 H), 1.9 (m, 4 H). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.20; H, 5.60; N, 5.20.

Photolysis of 4-Methyl-*N*-(4-pentenyl)phthalimide: General Procedure. 4-Methyl-*N*-(4-pentenyl)phthalimide (0.2 g, 8.7×10^{-4} mol) was dissolved in 50 mL of acetonitrile in a quartz tube and was irradiated through a Pyrex filter for 4 h. Acetonitrile was removed in vacuo and the starting material removed by preparative TLC on silica gel (90% ether; 10% hexanes). The mixture of isomers, isolated in 69% yield, contained 53% **26b** and 47% **27b**, which were separated via preparative HPLC (70:30 ether/hexanes). Pure **26b**: mp 113–115 °C; IR (CH_2Cl_2) 1680, 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.7 (m, 4 H), 4.3 (m, 1 H), 3.8 (t, 2 H), 3.0 (dd, 2 H), 2.5 (s, 3 H), 2.1 (m, 4 H). Pure **27b**: mp 108–110 °C; IR (CH_2Cl_2) 1680, 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.6 (m, 4 H), 4.2 (m, 1 H), 3.8 (t, 2 H), 2.9 (dd, 2 H), 2.5 (s, 3 H), 2.1 (m, 4 H). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.33; H, 6.59; N, 6.11. Found for isomer mixture: C, 73.26; H, 6.86; N, 6.24.

Photolysis of 4-chloro-*N*-(4-pentenyl)phthalimide was carried out according to the general procedure for photolysis of 4-methyl-*N*-(4-pentenyl)phthalimide. The mixture of isomers was isolated in 71% yield, contained 38% **26c** and 62% **27c**, and was separated via medium-pressure liquid chromatography. Pure **26c**: mp 110–112 °C; IR (CH_2Cl_2) 1690, 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.8 (m, 4 H), 4.3 (m, 1 H), 3.8 (t, 2 H), 3.0 (dd, 2 H), 2.0 (m, 4 H). Pure **27c**: mp 128–130 °C; IR (CH_2Cl_2) 1690, 1640 cm^{-1}; NMR ($CDCl_3$) δ 7.8 (m, 4 H), 4.3 (m, 1 H), 3.8 (t, 2 H), 3.0 (dd, 2 H), 2.1 (m, 4 H). Anal. Calcd for $C_{13}H_{12}NO_2Cl$: C, 62.32; H, 4.83; N, 5.59. Found for isomer mixture: C, 62.03; H, 4.71; N, 5.79.

Photolysis of 4-methoxy-*N*-(4-pentenyl)phthalimide was carried out according to the general procedure for photolysis of 4-methyl-*N*-(4-pentenyl)phthalimide. The mixture of isomers was isolated in 80% yield, contained 85% **26a** and 15% **27a**, and was separated via preparative HPLC. Pure **26a**: mp 123–125 °C; IR (CH_2Cl_2) 1690, 1630 cm^{-1}; NMR ($CDCl_3$) δ 7.6 (m, 4 H), 4.2 (m, 1 H), 3.9 (s, 3 H), 3.8 (t, 2 H), 2.9 (dd, 2 H), 2.0 (m, 4 H). Pure **27a**: mp 103–104 °C; IR (CH_2Cl_2) 1675, 1635 cm^{-1}; NMR ($CDCl_3$) δ 7.4 (m, 4 H), 4.2 (m, 1 H), 3.8 (s, 3 H), 3.7 (t, 2 H), 2.8 (m, 2 H), 1.9 (m, 4 H). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found for isomer mixture: C, 68.28; H, 6.23; N, 5.94.

Photolysis of 4-carbomethoxy-*N*-(4-pentenyl)phthalimide was carried out according to the general procedure. The mixture of isomers was isolated in 27% yield and contained 22% **26d** and 78% **27d**, which could not be completely separated via chromatography. A mixture of primarily **26d** was isolated as an oil and showed the following: IR ($CDCl_3$) 1730, 1690, 1635 cm^{-1}; NMR ($CDCl_3$) δ 8.2 (m, 4 H), 4.2 (m, 1 H), 4.0 (s, 3 H), 3.8 (t, 2 H), 3.0 (m, 2 H), 2.1 (m, 4 H). A mixture of primarily **27d** was isolated as an oil: IR ($CDCl_3$) 1730, 1690, 1630 cm^{-1}; NMR ($CDCl_3$) δ 8.2 (m, 4 H), 4.2 (m, 1 H), 4.0 (s, 3 H), 3.8 (t, 2 H), 3.0 (dd, 2 H), 2.1 (m, 4 H). Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found for isomer mixture: C, 66.10; H, 5.80; N, 5.17.

Photolysis of *N*-(4-Methyl-4-pentenyl)phthalimide in Acetonitrile. *N*-(4-Methyl-4-pentenyl)phthalimide was irradiated according to the general procedure. Starting material (94 mg) was recovered along with 64.5 mg (63%) of **39b**: mp 97–98 °C; NMR ($CDCl_3$) δ 8.18–7.96 (m, 2 H), 7.74–7.52 (m, 2 H), 3.87 (m, 2 H), 3.24 (d, 1 H, AB, J = 18 Hz), 3.0 (d, 1 H, AB, J = 18 Hz), 2.1–1.9 (m, 4 H), 1.21 (s, 3 H); IR ($CDCl_3$) 3060, 2980, 2880, 1680, 1615, 1440 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 72.98; H, 6.80; N, 6.29.

Photolysis of *N*-(4-Methyl-4-pentenyl)phthalimide in Methanol. *N*-(4-Methyl-4-pentenyl)phthalimide was irradiated according to the general procedure in methanol. Preparative TLC gave 50 mg of recovered starting material along with 130 mg (76%) of a mixture of two solvent-incorporated adducts. Further purification by HPLC on silica (75% ether in Skelly F) gave 62 mg of **40b**: mp 145–146 °C; IR ($CDCl_3$) 3380, 2940, 1690, 1100 cm^{-1}; NMR ($CDCl_3$) δ 7.84 (m, 1 H), 7.56 (m, 3 H), 5.52 (s, 1 H), 4.3 (m, 1 H), 3.92 (d, 1 H, J = 10 Hz), 3.58 (s, 3 H), 3.38 (d, 1 H, J = 10 Hz), 3.2 (m, 1 H), 1.7–1.2 (m, 4 H), 0.44 (s, 3 H). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.92; H, 7.33; N, 5.36. Found: C, 68.64; H, 7.40; N, 5.29.

The other diastereomer **40a** was also obtained: 54 mg; mp 159–161 °C; IR ($CDCl_3$) 3570, 3300, 2950, 1675 cm^{-1}; NMR ($CDCl_3$) δ 7.74–7.4 (m, 4 H), 4.1 (d, 1 H, J = 12 Hz), 3.16 (m, 1 H), 2.97 (s, 3 H), 2.87 (d, 1 H, J = 9 Hz), 2.4 (d, 1 H, J = 9 Hz), 1.8–1.5 (m, 5 H), 1.39 (s, 3 H).

Photolysis of 4-Methyl-*N*-methylphthalimide (21b) and 1-Hexene: General Procedure. A solution of 2.00 g (0.011 mol) of **21b** in 70 mL of 1-hexene and 350 mL of acetonitrile was irradiated for 6 h with a Hanovia medium-pressure mercury lamp through quartz. Silica gel chromatography using 10% CH_2Cl_2 in ethyl ether gave a mixture of **24b** and **23b** in the ratio 43:57; 0.44 g, 32%. Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.94; H, 6.40; N, 6.90. Found: C, 70.98; H, 6.58; N, 6.73.

Preparative HPLC (12% CH_2Cl_2 in ethyl ether) on silica gel followed by recrystallization from ethyl ether/hexane gave the individual pure isomers. Compound **24b**: mp 65–67 °C; NMR ($CDCl_3$) δ 2.44 (s, 3 H), 2.95 (m, 2 H), 3.23 (s, 3 H), 3.68 (m, 2 H), 7.35 (dd, 1 H, J = 8.0 Hz, J = 2.0 Hz), 7.58 (d, 1 H, J = 8.0 Hz), 7.70 (d, 1 H, J = 2.0 Hz); IR ($CDCl_3$) 1640, 1685 cm^{-1}. Compound **23b**: mp 84–86 °C; NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.96 (m, 2 H), 3.22 (s, 3 H), 3.68 (m, 2 H), 7.44 (m, 2 H), 7.80 (d, 1 H, J = 8.0 Hz); IR ($CDCl_3$) 1640, 1685 cm^{-1}.

Photolysis of 4-Chloro-*N*-methylphthalimide (21c) and 1-Hexene. Irradiation of 0.20 g (0.001 mol) of **21c** in 15 mL of 1-hexene and 25 mL of acetonitrile gave, after workup, 0.095 g (45%) of a mixture of **24c** and **23c** in a 48:52 ratio. Further HPLC purification gave **24c**: mp 80–82 °C; NMR ($CDCl_3$) δ 2.97 (m, 2 H), 3.23 (s, 3 H), 3.69 (m, 2 H), 7.51 (dd, 1 H, J = 8.0 Hz, J = 2.0 Hz), 7.64 (d, 1 H, J = 8.0 Hz), 7.88 (d, 1 H, J = 2.0 Hz); IR ($CDCl_3$) 1635, 1700 cm^{-1}. Anal. Calcd for $C_{11}H_{10}NO_2Cl$: C, 59.06; H, 4.47; N, 6.26; Cl, 15.88. Found: C, 58.81; H, 4.77; N, 5.91; Cl, 15.60. Compound **23c**: mp 106–108 °C; NMR ($CDCl_3$) δ 2.98 (m, 2 H), 3.23 (s, 3 H), 3.70 (m, 2 H), 7.59 (dd, 1 H, J = 8.0 Hz, J = 2.0 Hz), 7.63 (d, 1 H, J = 2.0 Hz), 7.88 (d, 1 H, J = 8.0 Hz); IR ($CDCl_3$) 1630, 1680 cm^{-1}.

Photolysis of 4-Methoxy-*N*-methylphthalimide (21a) and 1-Hexene. Photolysis of **21a** by the general procedure and workup gave a single product characterized as **23a** in 32% yield: mp 95–96

(20) Puskas, I.; Fields, E. K. *Ind. Eng. Chem., Prod. Res. Dev.* **1970**, *9*, 407.

°C; NMR ($CDCl_3$) δ 2.96 (m, 2 H), 3.22 (s, 3 H), 3.68 (m, 2 H), 3.88 (s, 3 H), 7.10 (d, 1 H, J = 2.0 Hz), 7.15 (dd, 1 H, J = 10 Hz, J = 2.0 Hz), 7.86 (d, 1 H, J = 10.0 Hz); IR ($CDCl_3$) 1630, 1680 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.94; N, 6.39. Found: C, 65.74; H, 6.09; N, 6.49.

Photolysis of 4-Carbomethoxy-*N*-methylphthalimide (21d) and 1-Hexene. Photolysis by the general procedure gave a pair of products characterized as **23d** and **24d** in a 27:73 ratio in 46% yield. Pure compound **24d**: mp 118–119 °C NMR ($CDCl_3$) δ 3.01 (m, 2 H), 3.25 (s, 3 H), 3.71 (m, 2 H), 3.96 (s, 3 H), 7.70 (d, 1 H, J = 8.0 Hz), 8.21 (dd, 1 H, J = 8.0 Hz, J = 2.0 Hz), 8.55 (d, 1 H, J = 2.0 Hz); IR ($CDCl_3$) 1635, 1690, 1720 cm^{-1}.

Compound **23d**: mp 86–87 °C; NMR ($CDCl_3$) δ 3.00 (m, 2 H), 3.25 (s, 3 H), 3.71 (m, 2 H), 3.96 (s, 3 H), 8.27 (dd, 1 H, J = 8.0 Hz, J = 2.0 Hz), 8.31 (d, 1 H, J = 2.0 Hz), 8.47 (d, 1 H, J = 8.0 Hz). For the mixture: Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.16; H, 5.26; N, 5.67. Found: C, 62.75; H, 5.29; N, 5.57.

Quantum Yield Determinations. Quantum yields were determined by using a blackbox apparatus and a 200-W superpressure Hg lamp in a Bausch and Lomb high-intensity grating monochromator. Light was monitored by a digital electronic actinometer which was calibrated by ferrioxalate actinometry between runs. Samples were submitted to three freeze–pump–thaw cycles before irradiation at 297 nm. Analysis was by HPLC and results are presented in Table I.

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Registry No. **9**, 69656-56-0; **10**, 69656-55-9; **13**, 64837-64-5; **21a**, 63196-45-2; **21b**, 29103-90-0; **21c**, 63197-17-1; **21d**, 79431-06-4; **23a**, 79431-11-1; **23b**, 79431-12-2; **23c**, 79431-07-5; **23d**, 79431-09-7; **24b**, 79431-13-3; **24c**, 79431-08-6; **24d**, 79431-10-0; **25a**, 86611-64-5; **25b**, 86611-65-6; **25c**, 86611-66-7; **25d**, 86611-67-8; **26a**, 86611-68-9; **26b**, 86611-69-0; **26c**, 86611-70-3; **26d**, 86611-71-4; **27a**, 86611-72-5; **27b**, 86611-73-6; **27c**, 86611-74-7; **27d**, 86611-75-8; **28**, 86632-09-9; **29a**, 826-73-3; **29b**, 6729-50-6; **38b**, 86611-76-9; **39b**, 86611-77-0; **40a**, 86611-78-1; **40b**, 86611-79-2; *N*-methylphthalimide, 550-44-7; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 4-(2,2-dimethylpropyl)-3,4-dihydro-2-methyl-2-benzapine-1,5-dione, 86611-80-5; 4,4-dimethylpentene, 762-62-9; 4,5-dichloro-*N*-methylphthalimide, 86611-81-6; 4,5-dichlorophthalic acid, 56962-08-4; 4,5-dichlorophthalic anhydride, 942-06-3; methylamine, 74-89-5; 4,5-dichlorophthalic acid monomethylamide, 86611-82-7; 1-hexene, 592-41-6; methyltriphenylphosphonium bromide, 1779-49-3; ethyl levulinate, 539-88-8; ethyl 4-methyl-4-pentenoate, 4911-54-0; 4-methyl-4-penten-1-ol, 22508-64-1; 4-methyl-4-penten-1-ol tosylate, 25163-50-2; 5-bromo-2-methyl-1-pentene, 41182-50-7; potassium phthalimide, 1074-82-4; 4-methylphthalic acid, 4316-23-8; 4-methylphthalimide, 40314-06-5; 5-bromo-1-pentene, 1119-51-3; 4-hydroxyphthalic acid, 610-35-5; dimethyl 4-hydroyphthalate, 22479-95-4; dimetyl 4-methoxyphthalate, 22895-19-8; 4-methoxyphthalic acid, 1885-13-8; 4-carbomethoxyphthalic anhydride, 28281-76-7.

Substituent Effects on the Formation of Aminocarboxy-Type Capto-Dative Free Radicals

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The interplay of steric effects and inductive, electronic effects on the formation of aminocarboxy-type, capto-dative free radicals from their dimers is described. Irradiation of 5,5-bis(acetoxymethyl)-5,6-dihydro-3-methyl-1,4-oxazin-2-one (**7**), 5,5-bis[(caproyloxy)methyl]-5,6-dihydro-3-methyl-1,4-oxazin-2-one (**8**), 5,5-bis(acetoxymethyl)-5,6-dihydro-3-ethyl-1,4-oxazin-2-one (**9**), and 3-(acetoxymethyl)-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (**10**) in 2-propanol solvent yielded photoreductive dimers bi[5,5-bis(acetoxymethyl)-3-methyl-2-oxomorpholin-3-yl] (**3**), bi[5,5-bis[(caproyloxy)methyl]-3-methyl-2-oxomorpholin-3-yl] (**4**), bi[5,5-bis(acetoxymethyl)-3-ethyl-2-oxomorpholin-3-yl] (**5**), and bi[3-(acetoxymethyl)-5,5-dimethyl-2-oxomorpholin-3-yl] (**6**). Upon dissolution in chloroform solvent **3**, **5**, and **6** underwent bond homolysis at the 3–3′ bond to give the respective oxomorpholin-3-yl radicals characterized by EPR spectroscopy. The rate constants and activation parameters for bond homolysis were determined by using *N*-methylisatin and diphenylpicrylhydrazyl as radical trapping agents and ranged from 21 to 30 kcal/mol. The variation in $\Delta H^{\ddagger}$ was assigned to inductive, electronic effects and steric effects based upon EPR hyperfine splitting constants.

Radicals stabilized by the synergistic effect of electron-donating and -withdrawing groups have been named capto-dative by Viehe and co-workers[1] and merostabilized by Katritzky and co-workers[2] and have been discussed in terms of a push–pull effect by Balaban and co-workers.[3] Important examples in carbon chemistry include the aminocarboxy-,[4] aminocyano-,[5] and thiocyano-substituted[6,7] methyl radicals as well as cyano-[8,9] and carboxy-substituted pyridinyls.[10,11]

As emphasized in general by Griller and Ingold, radical persistence is a function of steric interactions and electronic delocalization.[12] For capto-dative radicals electronic

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