the theoretical calculations of the electronic absorption spectra for group 3A metalloporphyrins.[13] In addition, this formulation is consistent with the ESR data of 3 which indicate that the initial reduction site occurs at the ligand and specifically at the tungsten atom. This formulation is also consistent with a shift of the potential for π radical formation to more negative values and would also suggest the formation of a transient $[(P)In^I(M^0(CO)_3Cp)]^{2-}$ species after the second reduction and before cleavage of the metal–metal bond. Unfortunately, this dianion has not been isolated but is postulated to be a transient species by cyclic voltammetry,

Acknowledgment. The support of the National Science Foundation (Grant CHE 8215507) is gratefully acknowledged. We also thank Jean-Luc Cornillon for help in obtaining the ESR spectra of reduced $(TPP)InClO_4$,

Registry No. 1, 91312-86-6; **2**, 91312-84-4; **3**, 91312-85-5.

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[13] Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter I, and references therein.

Steric Compression Control of Photochemical Reactions in the Solid State

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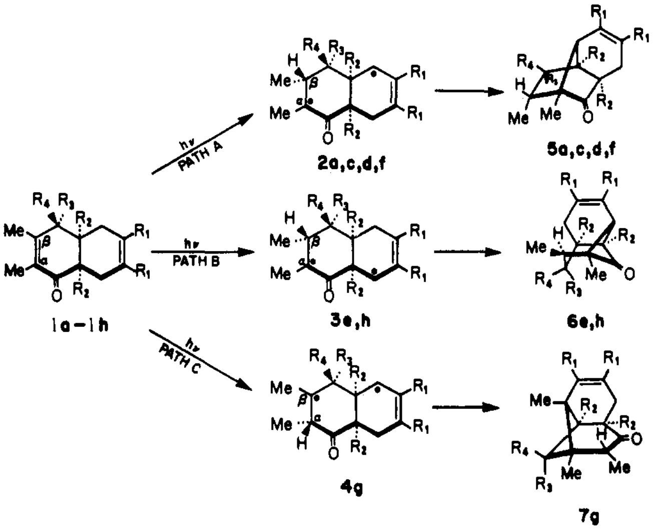
There is considerable current interest concerning the question of what factors govern the α vs. β regioselectivity of hydrogen atom abstraction by the carbon–carbon double bonds of photoexcited α,β-unsaturated ketones.[1] Recent work from our laboratory[2] has shown that enones of general structure **1**, when irradiated in the crystalline phase, undergo one of two possible photorearrangements (path A or path B, Scheme I), both of which are initiated by intramolecular allylic hydrogen atom transfer to the β-carbon atom of the enone moiety.[3] In one instance, however, that of enone **1g**, irradiation in the solid state led exclusively to the product resulting from initial hydrogen atom abstraction by the α-carbon atom of the enone chromophore (path C).[4]

In this communication we demonstrate with the aid of X-ray crystallography that in all likelihood, this change in reactivity is caused by specific crystal lattice packing effects near the reaction site that are unique to enone **1g**. We suggest the term "steric compression control" for this effect and show that it can also be applied to bimolecular reactions (e.g., [2 + 2] photocycloadditions) in the solid state.

One possible explanation for the anomalous behavior of compound **1g** is that the allylic hydrogen atom being abstracted in this case is much closer to the enone α-carbon atom than to the β-carbon. That this is not so is evident from the carbon–hydrogen distances summarized in Table I. These values, which are taken from the X-ray work,[5] show no trend between ground-state abstraction distance and preferred reactivity.

Scheme I, Reactants and Products in Solid-State Photorearrangements[a]



[a] Refer to Table I for list of substituents.

A second possible explanation is that the acetate group (R_4) of enone **1g** favors the formation of biradical **4** (path C) through interaction with the radical center produced on the adjacent β-carbon atom.[6] This is rendered unlikely by the observation that enone **1h** (R_3 = OAc) as well as enone **1i** ($R_1 = CH_3$, $R_2 = R_3$ = H, and R_4 = OAc)[7] behave normally, i.e., react via initial β-carbon abstraction, when photolyzed in the solid state. Using similar logic, other explanations that utilize the difference between acetate and hydroxyl (e.g., hydrogen bonding capability) can be discounted.

A clue to the explanation we favor came from an inspection of the crystal packing diagrams for enones **1a**–**1h**. It appeared that the change in hybridization of C_α or C_β from sp^2 to sp^3, which necessarily accompanies hydrogen transfer to these atoms, would force the methyl groups at these centers into close contacts with certain hydrogen atoms on neighboring molecules and thus sterically impede the reaction. The only exceptions to this were the C_α methyl group of compound **1g** and the C_β methyl group of enone **1d** whose pyramidalizations appeared to be totally unimpeded. This formed the basis of our working hypothesis, namely, that *it is the void space surrounding the methyl group at the α-carbon atom of enone **1g** that allows reaction and pyramidalization at this center in contrast to the steric compression which would attend reaction and pyramidalization at the β-carbon atom.*

This hypothesis was tested by simulating pyramidalization at C_α and C_β by computer and determining the new intermolecular hydrogen–hydrogen contacts which develop. With the X-ray crystal structure derived coordinates of enones **1a**–**1h** as a starting point, the methyl groups attached to C_α and C_β were rotated downward by intervals of 11°, 22°, 33°, 44°, and 55° (fully pyramidalized) keeping all other coordinates unchanged (Figure 1). The results supported the hypothesis: Pyramidalization at

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[1] (a) Byrne, B.; Wilson, C. A., II; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1550–1560. (b) Schuster, D. I. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 199–204. (c) Chan, C. B.; Schuster, D. I. *J. Am. Chem. Soc.* **1982**, *104*, 2928–2929.

[2] Appel, W. K.; Jiang, Z. Q.; Scheffer, J. R.; Walsh, L. *J. Am. Chem. Soc.* **1983**, *105*, 5354–5363.

[3] Preferential hydrogen abstraction by the β-carbon atom of α,β-unsaturated ketones is normally observed in solution as well.[1] For enones **1a**–**h**, however, irradiation in solution leads exclusively to intramolecular [2 + 2] photocycloaddition.[2] The reasons for these solution-phase/solid-state reactivity differences have been discussed.[2]

[4] The photochemistry of enones **1g** and **1h** has not been reported previously. The synthesis of these compounds as well as the characterization of their solid-state photoproducts **7g** and **6h**, respectively, will be detailed in a subsequent full paper. All four compounds gave satisfactory elemental analyses and exhibited spectra completely in accord with their assigned structures.

[5] Compounds **1a** and **1b**: Greenhough, T. J.; Trotter, J. *Acta Crystallogr. Sect. B*, **1980**, *B36*, 1831–1835. Compound **1c**: Secco, A. S.; Trotter, J. *Ibid.* **1982**, *B38*, 2190–2196. Compound **1d**: Greenhough, T. J.; Trotter, J. *Ibid.* **1980**, *B36*, 2843–2846. Compound **1e**: Greenhough, T. J.; Trotter, J. *Ibid.* **1980**, *B36*, 1835–1839. Compound **1f**: Secco, A. S.; Trotter, J. *Ibid.* **1982**, *B38*, 1233–1237. Compounds **1g** and **1h**: Ariel, S.; Trotter, J. *Ibid.*, submitted for publication.

[6] For a discussion of the interaction of acyloxy groups with adjacent radical centers (1,3-dioxolan-2-yl radical formation), see: Beckwith, A. L. J.; Ingold, K. U. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 242–244. See also: Barclay, L. R. C.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 1793–1796.

[7] The crystal structure of enone **1i** has not been determined. Photolysis of **1i** in the solid state gives **5i**. Scheffer, J. R.; Walsh, L., unpublished results.

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Table I. Reactants, Hydrogen Abstraction Distances, and Steric Compressions in Solid-State Photorearrangements.

							steric compression accompanying pyramidalization[a]	
enone	R_1	R_2	R_3	R_4	$H\cdots C_\alpha$, Å	$H\cdots C_\beta$, Å	C_α	C_β
1a	CH_3	CH_3	H	OH	2.78	2.75	yes	yes
1b	CH_3	CH_3	OH	H	2.88[b]	2.92[b]	yes	yes
1c	CH_3	CH_3	OH	CH_3	2.86	2.81	yes	yes
1d	H	CH_3	H	OH	2.82	2.78	yes	no
1e	H	CH_3	OH	H	2.74	2.85	yes	yes
1f	H	H	H	OH	2.92	2.84	yes	yes
1g	CH_3	CH_3	H	OAc	2.74	2.70	no	yes
1h	CH_3	CH_3	OAc	H	2.79	2.84	yes	yes

[a] Yes indicates a hydrogen–hydrogen contact upon pyramidalization of ≤1.9 Å. In some cases, more than one contact is developed. No indicates no contacts ≤2.2 Å. The exact values are not given as they vary with methyl group rotation.[8] [b] Enone **1b** does not react when photolyzed in the solid state.[10]

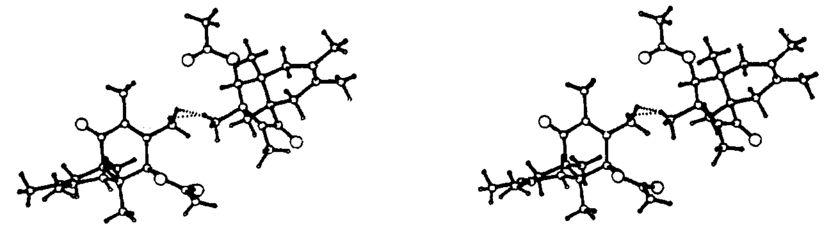


Figure 1. Stereodiagram of enone **1g** with full pyramidalization at C_β in upper right molecule. The molecule at lower left is unchanged. The steric compression accompanying pyramidalization is indicated by the dotted lines (1.71 and 1.87 Å). Pyramidalization at C_α is unimpeded.

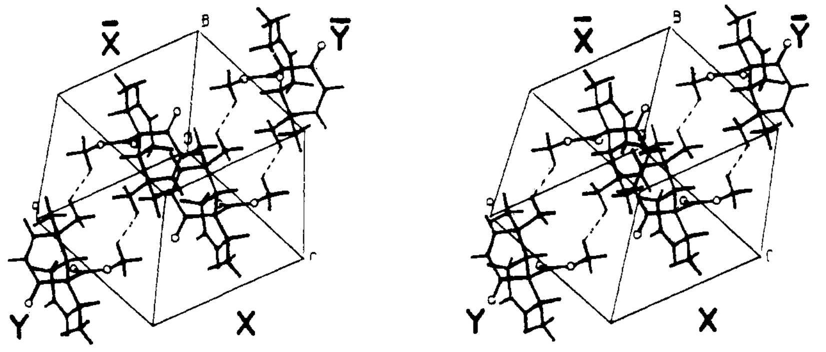
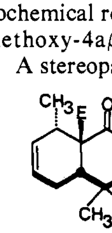


Figure 2. Stereopacking diagram of compound **8**. Molecules X and $\bar{X}$ are related through a center of symmetry. Translation of X along *a* generates Y, and translation of $\bar{X}$ along $-a$ generates $\bar{Y}$.

C_α of enone **1g** and C_β of **1d** led to no significant steric compression (hydrogen–hydrogen contacts greater than 2.2 Å), whereas pyramidalization in all other cases led to new contacts averaging 1.6 ± 0.3 Å (Table I).[8] According to the Lennard-Jones "6-12" potential function which relates interatomic distance and nonbonded repulsion energy,[9] steric compression between hydrogen atoms is negligible above 2.2 Å but rises steeply at distances of less than 2 Å. For example, a repulsion energy of 23.3 kcal/mol is calculated at an interatomic distance of 1.6 Å.

We interpret these results in terms of the relative activation energies for rate-determining hydrogen atom transfer. Steric compression accompanying reaction at both enone carbon atoms in the solid state raises both activation energies but maintains the intrinsic[3] (solution) ordering of β below α (enones **1a**, **1b**, **1c**, **1e**, **1f**, and **1h**). Compression at α accentuates this relative ordering (enone **1d**), and compression at β reverse the ordering with the result that reaction at the α-carbon atom becomes preferred (enone **1g**).[10]

The concept of steric compression control also accounts for the anomalous lack of photochemical reactivity observed for 4,4,8α-trimethyl-8aβ-carbomethoxy-4aβ,5,8,8a-tetrahydro-1(4*H*)-naphthalen-1-one (**8**),[11] A stereopacking diagram of compound **8** (Figure 2) shows that the centrosymmetrically related molecules X and $\bar{X}$ are ideally arranged to undergo [2 + 2] photodimerization. The potentially reactive enone double bonds are



8 ($E = CO_2CH_3$)

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(8) Rotation of the methyl hydrogen atoms about the enone carbon to methyl carbon bond does not alter these conclusions. Details of the steric compression calculations will be presented in the full paper. The assumption that hydrogen abstraction occurs from a planar enone excited state is consistent with recent work by: Schuster, D. I.; Greenberg, M. M.; Nunez, I. M.; Tucker, P. C. *J. Org. Chem.* **1983**, *48*, 2615–2619. See also: Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Rao, J. M.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706–2707. Excited-state twisting around the α,β-unsaturated double bond would also lead to steric compression and is therefore less likely to be important in the solid state for enones **1a** and **1h**.

(9) Warshel, A.; Lifson, S. *J. Chem. Phys.* **1970**, *53*, 582–594. Very similar results are obtained using Allinger's MM2 potential function. Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134.

(10) This interpretation also helps to explain the photochemical inertness of enone **1b**. Originally this unreactivity was ascribed solely to the unusually long hydrogen abstraction distances involved, but it now can be seen to be due in addition to the steric compression (the most severe among the eight compounds studied) which would accompany abstraction.

(11) Synthesis: Browne, E. N. C. Ph.D. Thesis, University of Alberta, Canada, 1980. Crystal Structure: Ariel, S.; Trotter, J. *Acta Crystallogr.*, in press.

parallel, directly above one another and only slightly offset along the double-bond axis (0.52 Å); the center-to-center distance is 3.79 Å.[12] Nevertheless, compound **8** is photochemically inert when irradiated in the solid state.[13] That this is not an intrinsic property of this molecule was shown by the fact that its solution-phase irradiation at the same wavelength leads to essentially quantitative yields of the cage compound resulting from intramolecular [2 + 2] cycloaddition.

Inspection of the packing diagram (Figure 2) reveals the probable reason for the remarkable lack of solid-state reactivity of enone **8**. As the potentially reactive molecules X and $\bar{X}$ start to move toward one another in the initial stages of [2 + 2] photocycloaddition, each experiences increasingly severe steric compression of two of its methyl groups (dotted lines). The key feature of this steric compression is that it is developed, not between the potential reactants X and $\bar{X}$ (after all, a certain amount of steric compression between reactants must always accompany bond formation between them), but between X and $\bar{Y}$ and $\bar{X}$ and Y. Thus molecules Y and $\bar{Y}$ act as stationary impediments to the dimerization.

These ideas were tested by computer simulation of the motion of molecules X and $\bar{X}$ toward one another along the double-bond center-to-center vector while keeping the coordinates of molecules Y and $\bar{Y}$ unchanged.[14] The results show that as the distance between the two potentially reactive double bonds is decreased from the initial value of 3.79 to 2.35 Å by moving each molecule 0.72 Å toward the other, the four hydrogen–hydrogen contacts (dotted lines) are reduced from 2.3 to 1.9 Å. These numbers are clearly indicative of steric compression inhibition of photodimerization. A hydrogen–hydrogen distance of 1.9 Å corresponds to a repulsion energy of 3.1 kcal/mol,[9] and, since there are four such interactions, a total repulsion energy of 12.4 kcal/mol is obtained for the reacting pair. This occurs at a predimerization geometry in which the 2p–2p orbital overlap is still relatively small.[15] Further movement of X and $\bar{X}$ toward each other becomes prohibitively expensive owing to the fact that the hydrogen–hydrogen repulsion energy rises very steeply below 1.9 Å.

In summary, the interactions delineated in our work provide strong support for Cohen's "reaction cavity"[16] and Gavezzotti's "volume analysis"[17] view of solid-state specificity, namely, that "a prerequisite for crystal reactivity is the availability of free space around the reaction site."[17]

Acknowledgment. We thank Professor H-J. Liu for a generous sample of compound **8** and are grateful to the National Sciences and Engineering Research Council of Canada for financial support.

Registry No. 1a, 74069-47-9; **1b**, 74069-48-0; **1c**, 78872-20-5; **1d**, 74069-55-9; **1e**, 74069-49-1; **1f**, 81768-03-8; **1g**, 91606-32-5; **1h**, 91606-33-6.

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[12] A large body of evidence now exists that verifies the original suggestion of Schmidt and Cohen that solid-state [2 + 2] photodimerization is the virtually inevitable result of a packing arrangement that orients the reacting double bonds in a parallel arrangement at center-to-center distances of 4.1 Å or less. Review: Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647–678.

[13] Photolysis of single crystals of **8** for up to 40 h at −16 to −18 °C (to prevent melting) with a Liconix helium cadmium 325-nm CW laser showed less than 1% reaction by capillary gas chromatography.

[14] With the crystal structure derived coordinates of compound **8** as a starting point, molecules X was moved toward its centrosymmetrically related neighbor $\bar{X}$ in 0.24-Å increments, keeping all other coordinates unchanged, and the new methyl–methyl contacts (dotted lines, Figure 2), were calculated. By symmetry, the contacts developed by moving X toward $\bar{X}$ are identical with those developed by moving $\bar{X}$ toward X. The results indicate that in the initial stages of the attempted dimerization, the simultaneous motion of X and $\bar{X}$ toward each other is less expensive in terms of steric compression than keeping one partner stationary while moving the other toward it. Details will be presented in the full paper.

[15] This conclusion is based on the analysis of the plots of the overlap integral S_{ij} vs. distance for 2p–σ and 2p–π bonding: Roberts, J. D. "Molecular Orbital Calculations"; W. A. Benjamin: New York, 1961; p 30. See also: Salem, L. *J. Am. Chem.Soc.* **1968**, *90*, 543–552. Using Roberts' data, we estimate that at a center-to-center separation of 2.35 Å (offset 0.33 Å), the p-orbital overlap between molecules X and $\bar{X}$ is less than 20% of maximum.

[16] Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386–393.

[17] Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220–5225.

Electrophilic Aromatic Substitution with a Nitrenium Ion Generated from *N*-Chloro-*N*-methoxyamides. Application to the Synthesis of 1-Methoxy-2-oxindoles

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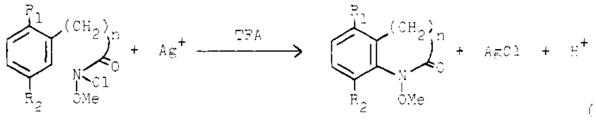
Several naturally occurring 1-methoxy-2-oxindoles and indoles have been isolated from plants.[1] Although several synthetic methods of 1-methoxyindoles have been known,[2] those of 1-methoxy-2-oxindoles are scarcely known, and the controlled reduction of 2-nitrophenylacetic acid derivatives by zinc[3] will be the sole route having general applicability if the starting compounds can be readily obtainable.

In this communication we wish to report the electrophilic aromatic substitution with a nitrenium ion generated from *N*-chloro-*N*-methoxyamides to introduce a methoxyamide group to an aromatic ring. This direct methoxyamidation by *N*-chloro-*N*-methoxyamides is reported for the first time and is of great synthetic interest because the produced *N*-acyl-*N*-methoxy aromatic amines are hitherto prepared with difficulty and are easily converted to primary amines by catalytic hydrogenation and subsequent hydrolysis. Intramolecular aromatic substitution by a methoxyamide group to a suitably situated benzene ring in the molecule gives nitrogen heterocycles having *N*-methoxy function. The overall stoichiometry is shown by eq 1.



1–**5** **6**–**12** (1)

1,**6**, n=1; $R_1=R_2=H$
2,**7**, n=1; $R_1=Cl$; $R_2=H$
8, n=1; $R_1=H$; $R_2=Cl$
3,**9**, n=1; $R_1=Br$; $R_2=H$
10, n=1; $R_1=H$; $R_2=Br$
4,**11**, n=2; $R_1=R_2=H$
5,**12**, n=3; $R_1=R_2=H$

The typical experimental procedure is as follows: A solution of silver carbonate (1.54 g, 5.58 mmol) in trifluoroacetic acid (TFA) (15 mL) was added to *N*-chloro-*N*-methoxyphenylacetamide (**1**) (557 mg, 2.79 mmol) cooled in an ice bath with stirring. The stirring was continued for 18 min to complete the cyclization, then the solvent was removed under reduced pressure at 20 °C. The residue was basified with 5% Na_2CO_3 with cooling and the aqueous solution was extracted with dichloromethane (2 × 40 mL). The combined extracts were washed with saturated brine (30 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel eluting with benzene–ethyl acetate (5:1) to give 1-methoxy-2-oxindole (**6**) (398.2 mg, 87.5%), mp 84–84.5 °C (lit.[3a] mp 84–86 °C),

Several examples are listed in Table I. The characteristic features contributing to the synthetic success of this substitution are as follows: (1) *N*-Chloro-*N*-methoxyamides are readily

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[1] Wenkert, E.; Orr, J. C.; Garratt, S.; Hansen, J. H.; Wickberg, B.; Leicht, C. L. J. Org. Chem. **1963**, *27*, 4123. Morimoto, H.; Oshio, H. *Liebigs Ann. Chem.* **1965**, *682*, 212. Nagel, D. W.; Pachler, K. G. R.; Steyn, P. S.; Vleggaar, R.; Wessels, P. L. *Tetrahedron* **1976**, *32*, 2625.

[2] Acheson, R. M. "Studies in Organic Chemistry 3"; Elsevier Scientific Publishing Co.: New York, 1979; pp 1–33. Sundberg, R. J. "The Chemistry of Indoles"; Academic Press: New York and London, 1970; pp 372–377. Somei, M.; Shoda, T. *Heterocycles* **1981**, *16*, 1523. Foucaud, A.; Razorilalana-Rabearivony, C.; Loukakou, E.; Person, H. *J. Org. Chem.* **1983**, *48*, 3639.

[3] (a) Wright, W. B., Jr.; Collins, K. H. *J. Am. Chem.* Soc. **1956**, *78*, 221. (b) Acheson, R. M.; Hunt, P. G.; Littlewood, D. M.; Murrer, B. A.; Rosenberg, H. E. *J. Chem. Soc., Perkin Trans 1* **1978**, 1117. (c) Somei, M.; Sato, H.; Kaneko, C. *Heterocycles* **1983**, *20*, 1797.

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