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.

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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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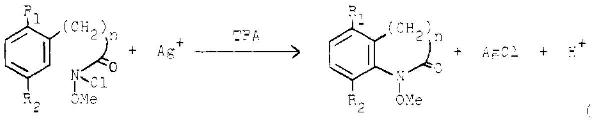
Several naturally occurring 1-methoxy-2-oxindoles and indoles have been isolated from plants.[1] Although several synthetic methods of 1-methoxyindoles have been known,[2] those of 1-methoxy-2-oxindoles are scarcely known, and the controlled reduction of 2-nitrophenylacetic acid derivatives by zinc[3] 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)

1–5 **6–12**

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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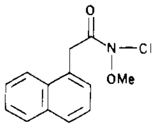
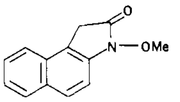
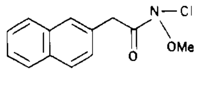
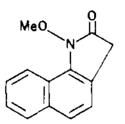
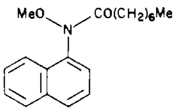
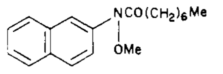
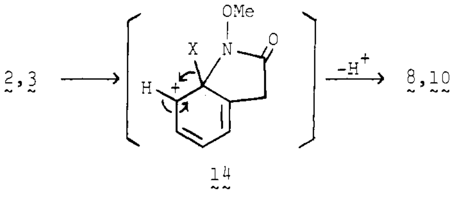
Table I. Electrophilic Aromatic Substitution by *N*-Chloro-*N*-methoxyamides

entry[a]	starting compd	product	yield, %
1	**1**	**6**	87.5
2	**4**	**11**	87
3	**5**	**12**	60
4[b]			68
5[b]			69
6	PhCON(Cl)OMe + benzene[c]	PhN(OMe)COPh	70.8
7	Me(CH$_2$)$_6$CON(Cl)-OMe + benzene[c] **13**	PhN(OMe)CO(CH$_2$)$_6$Me	93
8[b]	**13** + naphthalene[d]	 	80.1 10.9

[a] All the experiments were performed by using Ag_2CO_3 and TFA. [b] TFA-$MeNO_2$ (1:1, v/v) was used as solvent. All products were hydrogenated to the corresponding amides, which were identified by the comparison of their melting points with the literature values. [c] 10 mol equiv. [d] 5 mol equiv.

Scheme I



available and relatively stable.[4] (2) The experimental conditions are very simple; under the best conditions, the reaction is carried out at ambient temperature with a short reaction time in the presence of the transition-metal salts (Ag^+, Zn^{2+}, Pd^{2+}, Fe^{2+}, etc.). The electrophilic aromatic chlorination mainly occurred in the absence of metal salts. Addition of 2 equiv of the metal salt to a substrate are usually used to prevent the side reaction. Species of the counteranions of the metal salts are not strictly limited, and in the case of silver salt, anions (CO_3^{2-}, SO_4^{2-}, BF_4^-, OAc^-, $OCOCF_3^-$, and $OSO_2CF_3^-$) are effective. Acidic media are essential to the reaction and TFA, formic acid, and acetic acid are used as reaction media, in which TFA usually gives best results. Displacement of protic acids with Lewis acids does not bring good results. (3) Intramolecular as well as intermolecular reactions work well, and the yields based on *N*-chloro-*N*-methoxyamides are high.

In the case of 2-chloro and 2-bromo compounds **2** and **3**, the main products were **7** (71%) and **9** (51%); however, an unexpected mode of cyclization occurred to some extent to give 7-halogeno-1-methoxy-2-oxindoles[5] (**8**, 8.8%, **10**, 12.5%) which could be rationalized by way of an ipso intermediate (**14**) (Scheme I).

Concerning the possible reaction mechanisms, it is assumed that the reactions are initiated by acid-catalyzed heterolysis of the nitrogen-chlorine bond promoted with metal ions. A nitrenium ion thus generated is stabilized by acid[6] and by the capto-dative (push-pull) effect of the electron-withdrawing carbonyl and electron-donating methoxyl groups, as is stated in the case of the stabilization of aminyl free radicals,[7] and is long-lived enough to react with an aromatic ring. In brief, the carbonyl and the methoxyl groups, acid, and metal ions, all of them, play important roles for the generation and stabilization of a nitrenium ion. This conclusion has been drawn from the following facts: (1) *N*-Chloro-*N*-methyl- and *N*-chloro-*N*-acetoxyphenylacetamides failed to cyclize. (2) Various hydroxy(2-phenylethyl)amines such as *O*-tosyl, *O*-(2-mesitylsulfonyl), *N*,*O*-diacyl, and *N*-chloro-*O*-acyl compounds failed to cyclize in acidic conditions. (3) Radical mechanisms are not supported because oxygen atmosphere or an addition of a radical scavenger *N*,*N*-diphenylpicrylhydrazil[8] did not affect the aromatic methoxyamidation reaction at all.

Registry No. 1, 91523-28-3; **2**, 91523-29-4; **3**, 91523-30-7; **4**, 91523-31-8; **5**, 91523-32-9; **6**, 65816-14-0; **7**, 91523-33-0; **8**, 91523-34-1; **9**, 91523-35-2; **10**, 91523-36-3; **11**, 91523-37-4; **12**, 91523-38-5; Ag_2CO_3, 534-16-7; Ag_2SO_4, 10294-26-5; $AgBF_4$, 14104-20-2; AgOAc, 563-63-3; $AgOC(O)CF_3$, 2966-50-9; $AgOSO_2CF_3$, 2923-28-6; Zn, 7440-66-6; Pd, 7439-92-1; Fe, 7439-89-6.

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(4) *N*-Methoxyamides are chlorinated by *tert*-butyl hypochlorite in CH_2Cl_2 with cooling to give *N*-chloro-*N*-methoxyamides in quantitative yield.

(5) Identification of **8** and **10** was performed by the comparison of the ^1H NMR spectrum with those of other regioisomers (**9** and 5- and 6-bromo-1-methoxy-2-oxindoles).

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A Zinc-Alkyl Caged Cobalt(III) Derivative

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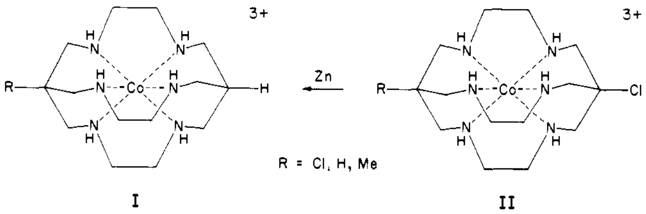
During the syntheses of the proton-capped cage complexes (I) by reduction of the chloro-capped species (II) with zinc dust in



water,[1] species were isolated which analyzed for $CoC_{14}H_{31}N_6$-$ZnCl_4 \cdot 2H_2O$ (from II, R = Cl) and $CoC_{15}H_{33}N_6ZnCl_4 \cdot 2H_2O$ (from II, R = Me). The UV-visible spectra were similar to those of I, and the ^1H NMR spectra exhibited a complex group of resonances centered at ca. 3 ppm (ref TPS, TPS = 2,4,6-triisopropylbenzenesulfonate) characteristic of other unsymmetrically capped (hexaazabicyclo[6.6.6]icosane)cobalt(III) complexes.[2] The ^{13}C NMR spectra were also consistent with intact cage complexes, incorporating two resonances at −29.5 and −30.9 ppm (product from II, R = Cl) and −24.8 and −30.4 ppm vs. dioxane

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