Teflon needle valve) containing a weighed amount of NBS and benzoyl peroxide (2 mol %) and 5–7 mL of CCl_4 added. The mixture was degassed four to five times by the freeze–pump–thaw technique and placed in a controlled-temperature bath. When the reaction was completed (1–2 h), a weighed quantity (0.100–0.200 mmol) of one or two appropriate internal standards for NMR analysis (benzyl chloride, benzyl bromide, 1,1,2,2-tetrachloroethane, or hexamethyldisiloxane) was added. A 0.25-mL sample of the liquid portion of the reaction mixture was then transferred to an NMR tube containing 0.25 mL of $CDCl_3$. ^1H NMR analysis of the solution was performed as soon as possible (generally, in less than 10 min) so as to avoid significant degradation of the α-brominated products. For the competitive bromination of 9-cyclopropylanthracene versus cumene, excess 9-cyclopropylanthracene and its corresponding α-brominated product were analyzed by ^1H NMR, while unreacted cumene was analyzed by GLC. The internal standard used for GC analysis was chlorobenzene, added to the mixture along with the NMR internal standard (benzyl chloride) after the completion of the reaction. At the reaction temperature of 12.0 °C, the reaction mixture was irradiated with a 400-W medium-pressure mercury arc lamp (at a distance of 2 ft and through two layers of Pyrex) for 20–30 min. During this time, about 50–75% of the initial amount of NBS was consumed. Longer irradiation times led to decomposition of the primary reaction products.

Quantitation by GLC. After reaction, unconsumed alkyl aromatics were analyzed vs an appropriate internal standard. Analyses were performed in triplicate.

Quantitation by ^1H NMR Analysis. At least four integrations were carried out on selected proton absorptions of α-brominated products, excess competitors, and internal standards. Integral amplitudes were maximized to obtain the highest possible accuracy. The average deviation of individual integrations from the mean was generally on the order of 1%. The average chemical shift values (δ in parts per million downfield from TMS) are as follows: benzyl chloride, 4.6 (s, 2 H, CH_2Cl); benzyl bromide, 4.4 (s, 2 H, CH_2Br); 1,1,2,2-tetrachloroethane, 5.9 (s, 2 H, $\{CHCl_2\}_2$); hexamethyldisiloxane, 0.07 (s, 18 H, $(CH_3)_3 \times 2$); toluene, 2.4 (s, 3 H, CH_3); 9-methylanthracene, 3.1 (s, 3 H, CH_3); 9-ethylanthracene, 1.4 (t, 3 H, $J = 7.6$ Hz, CH_3), 3.6 (q, 2 H, $J = 7.6$ Hz, CH_2); 9-isopropylanthracene, 1.8 (d, 6 H, $J = 7.4$ Hz, 2 CH_3), 4.6 (h, 1 H, $J = 7.4$ Hz, CH); 9-cyclopropylanthracene, 0.8 (m, 2 H, *cis*-cyclopropylmethylene), 1.5 m, 2 H, *trans*-cyclopropylmethylene), 2.5 (m, 1 H, cyclopropylmethine); 9-(α-bromomethyl)anthracene, 5.5 (s, 2 H, CH_2Br); 9-(α-bromoethyl)anthracene, 2.3 (d, 3 H, $J = 7.3$ Hz, CH_3), 6.7 (q, 1 H, $J = 7.3$ Hz, CHBr); 9-vinylanthracene, 5.6 and 5.9 (dd, 2 H, $J = 2.0$ Hz and $J = 15.6$ Hz, *cis*- and *trans*-olefinic protons of CH_2), 7.4 (dd, 1 H, CH); 9-(α-bromocyclopropyl)anthracene, 1.5 (m, 2 H, *cis*-cyclopropyl H's), 2.1 (m, 2 H, *trans*-cyclopropyl H's). All absorptions used in the computations of relative reactivities were clean and well resolved.

Acknowledgment. We gratefully acknowledge the Thomas F. Jeffress and Kate Miller Jeffress Memorial Trust Fund and Department of Chemistry at Virginia Tech for financial support. M.R.H.b.M.H. acknowledges fellowship support from the Department of Chemistry, Universiti Sains Malaysia, Penang, Malaysia.

Supplementary Material Available: Detailed experimental data for the studies of the relative reactivity of 9-alkylanthracenes toward bromine atom (initial and final concentrations of reactants and products) and an Arrhenius plot of the data in Table I (5 pages). Ordering information is given on any current masthead page.

Experimental and Theoretical Study of the Reactivity of Primary and Secondary Enaminones toward Diphenylketene. A Comparison of AM1 and HAM/3 Semiempirical Methods

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Diazodiphenylethanone (**1**) reacts with acyclic enamino ketones **2** and enamino esters **3** to form products of electrophilic attack of diphenylketene at C_α (**5**) and nitrogen (**6** and **7**). The relative reactivity of the different enaminones was shown to be consistent with HOMO energies determined by the HAM/3 semiempirical method. However, this approach could not completely explain the reactivity of the cyclic enamino ketones **4**, which, by HAM/3, show a high-energy second HOMO corresponding to the nonbonded pair of electrons on oxygen.

Introduction

Our interest in understanding the reactivity of enaminones has led us to attempt to correlate experimental results with theoretical studies in the case of the reactions of primary and secondary enaminones with diphenylketene. According to perturbation theory, the major contributions to bond making when two reagents approach each other involve opposite charge attractions at the reaction sites and the interactions between the filled orbitals of one reagent and the unfilled orbitals of the other, with HOMO's and LUMO's corresponding to the most important interactions because of the proximity of their energy levels. When the HOMO/LUMO interaction is the major factor governing differential reactivity, the reaction is said to be frontier-orbital controlled.[1] Thus, a molecular orbital method which calculates reliable energy levels of frontier orbitals as well as electron density at each atom is needed in reactivity studies.

The semiempirical molecular orbital method called HAM/3 (hydrogenic atoms in molecules, version 3) was parameterized to calculate mainly ionization potentials, excitation energies, and electron affinities.[2–4] The quality of this method has been tested. Average absolute deviation in ionization potentials for molecules are in the range 0.3–0.4 eV.[5] The method has been successfully used to analyze photoelectron spectra of molecules.[6–9] The ac-

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(1) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976.

(2) (a) Asbrink, L.; Fridh, C.; Lindholm, E. *Chem. Phys. Lett.* **1977**, *52*, 63. (b) *Ibid.* **1977**, *52*, 69. (c) *Ibid.* **1977**, *52*, 72.

(3) Asbrink, L.; Fridh, C.; Lindholm, E.; de Bruijn, S. *Chem. Phys. Lett.* **1979**, *66*, 411.

(4) Lindholm, E.; Asbrink, L. *Molecular Orbitals and Their Energies, Studies by the Semiempirical HAM Method, Lecture Notes in Chemistry*; Springer-Verlag: Berlin, 1985; Vol. 38.

(5) Chong, D. P. *Theor. Chim. Acta* **1979**, *51*, 55.

(6) (a) Bieri, C.; Asbrink, L. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 149. (b) Asbrink, L.; Von Niessen, W.; Bieri, G. *Ibid.* **1980**, *21*, 93. (c) Bieri, G.; Asbrink, L.; Von Niessen, W. *Ibid.* **1982**, *27*, 129.

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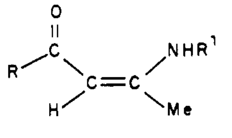
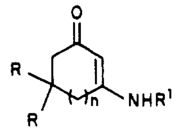
curacy of HAM/3 is generally as good as or better than the application of Koopman's theorem with ab initio (MZ and DZ) calculations in predicting ionization potentials.[10] Since HAM/3 calculates ionization potentials as the negative of occupied molecular orbital energies, occupied molecular orbitals thus calculated can be reliable.

In comparison to ionization potentials, both theoretical and experimental studies of electron affinities are limited because of difficulties involved in dealing with these quantities. Electron affinities are related to unoccupied molecular orbitals. Electron affinities calculated by HAM/3 for over 70 molecules of small and medium size agree fairly well with oberved ones.[4] Since HAM/3 can calculate reliable HOMO's and fairly reliable LUMO's, it is of interest to investigate its aplicability in studying chemical reactivities and reaction mechanisms by the frontier-orbital method.

Other semiempirical methods such as AM1,[11] MNDO,[12] MINDO/3,[13] and SINDO1[14] have been widely used to study chemical reactivities and reaction mechanisms. All of these methods study the change of the total energy or of the heat of formation during the reaction. AM1 seems to be one of the most reliable semiempirical methods known today for calculation of geometric structures, heats of formation, dipole moments, and some other properties of molecules. However neither AM1 nor the other semiempirical methods can calculate reliable electron affinities (unoccupied orbitals). Furthermore, the quality of occupied molecular orbitals calculated by these methods are only partly known. For instance, the average absolute error of calculated (AM1) first ionization potentials of 51 compounds is 0.36 eV.[11] The first ionization potential is one of the reference functions chosen for parameterization of AM1.[11,12] Reliability of calculating ionization potentials from second HOMO, third HOMO, fourth HOMO, etc. with AM1 is not known. It is desirable to know if HOMO's/LUMO's calculated with AM1 can be used profitably in the frontier-orbital method. A comparison between HAM/3 and AM1 will be of interest. In this work HAM/3 and AM1 calculations are compared with respect to the reactivity problem at hand which involves reactions of diphenylketene, generated from diazodiphenylethanone (1) under neutral thermal conditions,[15] with acyclic (2, 3) and cyclic (4) enaminones.



2 R = Me 3 R = OEt

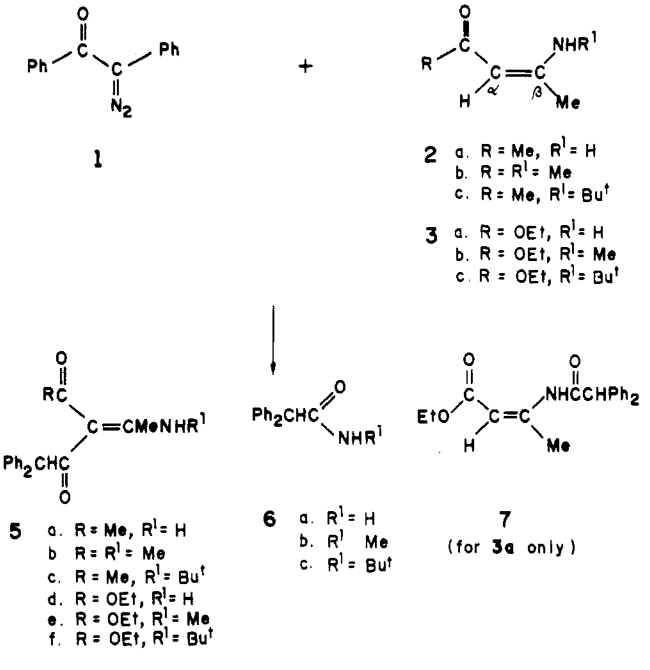


4

Results and Dicussion

Acyclic Enaminones. The reactions of diazodiphenylethanone (1) with the acyclic enamino ketones 2 and enamino esters 3 were carried out in methylene chloride[16] at room temperature and stopped 2 days after the disappearance of the characteristic absorption of the diazo bond at 2080 cm^{-1} in the IR spectrum. The reaction with enamino ketone 2a led to the formation of two colorless solid products. The mass spectra of the major product shows a molecular ion at m/z 293 and fragment ions at m/z 167, 166, 165, and 152, which correspond to the Ph$_2$CH$^+$ ion, confirming that the Wolff rearrangement did occur. The absence of the C$_\alpha$-H vinylic proton signal in the ^{1}H NMR spectrum shows that the reaction occurs at the nucleophilic C$_\alpha$ carbon position, giving product **5a**. The signal at 5.45 ppm corresponds to the Ph$_2$C*H* proton. This spectrum also shows an intramolecular chelated proton at 11.10 ppm. The other compound was identified as diphenylacetamide **6a**, and its formation probably involves initial attack of diphenylketene at the nucleophilic nitrogen. In the reactions of enamino ketones **2b** and **2c**, analogous products were obtained, i.e. **5b,c** and **6b**.

In the reactions of the enamino ester **3a**, three compounds were obtained, two of which are analogous to the products obtained in the reactions with enamino ketones, i.e., products **5d** and amide **6a**. The mass spectrum of the other compound has a molecular ion at m/z 323, showing that it is isomeric with product **5d**. The presence in the mass spectrum of the fragments corresponding to the Ph$_2$CH$^+$ ion and the presence in the ^{1}H NMR spectrum of two signals at 4.95 and 5.0 ppm corresponding to Ph$_2$CH and the vinylic proton allow us to identify this product as compound **7**, which results from the reaction of diphenylketene at the nucleophilic nitrogen. The presence of an intramolecular NH chelated proton is clearly observed in the ^{1}H NMR spectrum at 11.85 ppm. In the reactions with enamino esters **3b** and **3c**, analogous products **5e,f** and **6b,c** were obtained.



1

2 a. R = Me, R^1 = H
b. R = R^1 = Me
c. R = Me, R^1 = Bu^t

3 a. R = OEt, R^1 = H
b. R = OEt, R^1 = Me
c. R = OEt, R^1 = Bu^t

5 a. R = Me, R^1 = H
b. R = R^1 = Me
c. R = Me, R^1 = Bu^t
d. R = OEt, R^1 = H
e. R = OEt, R^1 = Me
f. R = OEt, R^1 = Bu^t

6 a. R^1 = H
b. R^1 Me
c. R^1 = Bu^t

7 (for **3a** only)

A product like **7** was obtained only for **3a**. This fact might be explained by the extra stability of compound **7** given by the intramolecular hydrogen bonding which is not possible for products like **7** formed from secondary enaminones. Given the nonaqueous nature of the reaction

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(7) Asbrink, L.; Fridh, C.; Lindholm, E. *Tetrahedron Lett.* **1977**, 4627.

(8) Asbrink, L.; Fridh, C.; Lindholm, E. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *16*, 65.

(9) Takahata, Y. *J. Mol. Struct.* (*THEOCHEM*) **1984**, *108*, 269.

(10) Takahata, Y. *Int. J. Quantum Chem.* **1986**, *30*, 453.

(11) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(12) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(13) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(14) Jug, K.; Nanda, D. N. *Theor. Chim. Acta* **1980**, *57*, 107.

(15) For reviews of Wolff rearrangement, see: (a) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971; p 475. (b) Moss, A.; Jones, M., Jr. *Carbenes*; Wiley: New York, 1973; Vol. 1, p 117. (c) Meier, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.

(16) Methylene chloride must be free of ethanol in order to avoid formation of ethyl diphenylacetate, a side product of reaction of diphenylketene.

Table I. Yields for the Reactions of Diazodiphenylethanone (1) with Enaminones 2 and 3

starting enaminone	products, % yield			total yield, %	proportion 5:(6 + 7)
	5	6	7		
2a	**5a**, 40	**6a**, 10	-	50	1:0.25
2b	**5b**, 66	**6b**, 7	-	73	1:0.11
2c	**5c**, 88	**6c**, -	-	88	1:0
3a	**5d**, 42	**6a**, 23	16	81	1:0.98
3b	**5e**, 56	**6b**, 33	-	89	1:0.59
3c	**5f**, 63	**6c**, 28	-	91	1:0.44

and the workup medium, hydrolysis of products analogous to **7** does not seem to be the route to the formation of the amides **6**. The presence of the ^{1}H NMR signals for the amides in the crude reaction mixtures shows that these products are already formed before separation. To test the intermediacy of **7** in forming **6**, this product was refluxed for several days in methylene chloride. This led to its recovery with no formation of **6a**. All attempts to isolate other products which might help explain the formation of amides **6** were unsuccessful.

Yields of all products are given in Table I. In all cases, competitive formation of decomposition products of **1** occurs. It was observed that for both enaminones **2** and **3**, the total yield of products and the relative yield of the products of reaction at the C_α carbon (proportion **5**:(**6** + **7**)) increase in going from R^1 = H to Me to Bu^t while the yields of decomposition products of diazo ketone **1** decreases, suggesting that the order of reactivity for **2** and **3** is **a** < **b** < **c**. For a given substitution on nitrogen, the total yield of products is greater for the enamino esters, suggesting greater reactivity of **3** toward diphenylketene. This was confirmed by a competitive study whereby equimolar quantities of **1**, **2b**, and **3b** were reacted. Integration of the Ph_2CH proton in the ^{1}H NMR spectrum of the crude product shows formation of approximately twice as much **5e** as **5b**. When compared to **2**, the enamino esters **3** show more tendency to form products of reaction on nitrogen.

Classical arguments can explain the increase of reaction at the C_α carbon in the order **2** (and **3**) **a** < **b** < **c**. Thus, the increase in size of the nitrogen substituent may slow down reaction at nitrogen because of steric hindrance. A more subtle effect of size involves steric interaction between the nitrogen substituent and the C_β-Me group which can cause the amino group to bend toward the carbonyl. This results in strengthening of the hydrogen bonding which can promote differences in electron distributions, perhaps causing higher electron density on the C_α carbon, which would favor reaction at this nucleophilic site. In fact, a downfield shift of the chelated NH proton in the ^{1}H NMR spectra which is an indication of increased strength of the hydrogen bonding is noted when going from **2** (and **3**) **a** to **b** to **c** with enamino esters at higher field. Also, in geometrical optimizations of these compounds using AM1, an increase in the N-C_β-Me angle and a decrease of intramolecular hydrogen bonding length were obtained in the same order.[17] The greater tendency for enamino esters **3** to react on nitrogen when compared to enamino ketones **2** can be explained by the weaker electron-withdrawing effect of the ester group compared to the acetyl group.

To explain the order of reactivity observed, molecular orbital calculations using both AM1 and HAM/3 semiempirical methods were undertaken in order to evaluate frontier orbital contributions. These calculations do not take solvent effects into account. However, the assumption we make is that, since the same solvent is used in all reactions, it does not influence differential reactivity because its effect is cancelled. Since HAM/3 does not allow for geometric optimization, the structures used in the HAM/3 calculations were those obtained by AM1 optimizations,[17] i.e., the *Z,s-Z* form and bond angles and bond lengths which lead to a minimum energy. In fact, it was seen that the relative energy levels of HOMO's and LUMO's obtained by HAM/3 do not vary significantly when either standard bond angles and bond lengths[18] or optimized values were used. As is necessary in HAM/3 computations, the HOMO and LUMO energies (i.e. ionization potentials and electron affinities, respectively) were calculated separately.

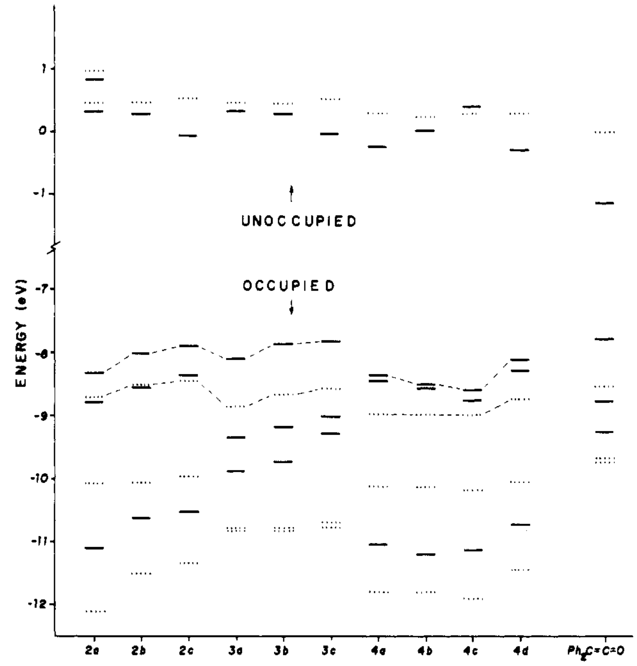

Figure 1. Energy levels of the three highest occupied molecular orbitals and LUMO for the enaminones **2**, **3**, **4**, and diphenylketene calculated by HAM/3 (—) and AM1 (···).

Table II. LUMO and HOMO Energies of the Enaminones 2, 3, 4 and of Diphenylketene Calculated by HAM/3 and AM1

	energies, eV			
	HAM/3		AM1	
	LUMO	HOMO	LUMO	HOMO
2a	0.328	-8.324	0.466	-8.717
2b	0.270	-8.020	0.466	-8.545
2c	-0.143	-7.902	0.525	-8.458
3a	0.307	-8.113	0.452	-8.864
3b	0.280	-7.863	0.435	-8.679
3c	-0.041	-7.824	0.516	-8.597
4a	-0.248	-8.372	0.257	-8.985
4b	0.023	-8.520	0.223	-9.028
4c	0.397	-8.656	0.276	-9.002
4d	-0.296	-8.131	0.284	-8.761
Ph_2CCO	-1.172	-7.790	-0.011	-8.551

As can be seen in Figure 1 and in Table II the difference in energy between the HOMO of the enaminones and the LUMO of diphenylketene is generally smaller than the reverse HOMO/LUMO combination, and these are therefore the orbitals which will be considered. These are also the orbitals expected to interact if one considers the electrophilic nature of diphenylketene. The analysis of

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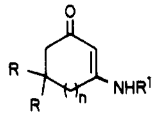
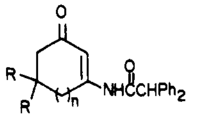
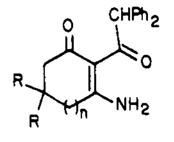
(17) Eberlin, M. N.; Takahata, Y.; Kascheres, C. *J. Mol. Struct. (THEOCHEM)*, in press.

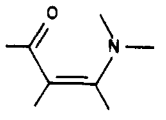
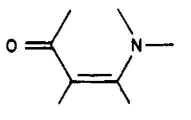
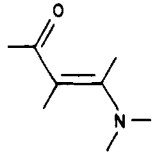
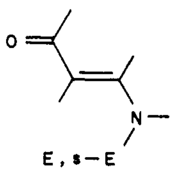
(18) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; MacGraw: New York, 1970.

Table III. Products and Yields of the Reaction of Diazo Ketone 1 with Cyclic Enaminones 4

starting enaminone	products (% yields)[a]		
 4	 8	 9	% yield of enaminone 4 recovered
4a: R = Me; R^1 = H; *n* = 1	**8a**, 91 (73)	**9a**, 8 (6)	**4a**, 20
4b: R = H; R^1 = H; *n* = 1	**8b**, 96 (53)	**9b**, -	**4b**, 45
4c: R = H, R^1 = H; *n* = 0	**8c**, 68 (54)	**9c**, -	**4c**, 20
4d: R = Me; R^1 = Me; *n* = 1	**8d**, -	**9d**, -	**4d**, 90

[a] The yield in parenthesis does not take into account recovered enaminone.

Table IV. HOMO and Second HOMO Energy Levels (in eV) of 2a in Four Forms

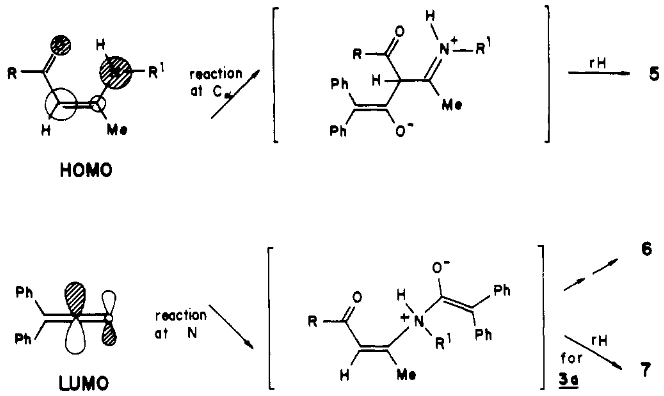
	 Z,s-Z	 Z,s-E	 E,s-Z	 E,s-E
HOMO	-8.355	-8.376	-8.554	-8.317
second HOMO	-9.603	-8.804	-9.495	-8.817
ΔE, eV	1.248	0.428	0.941	0.500

HOMO energies of these enaminones obtained by the HAM/3 method (Figure 1, Table II) shows that for equal substitution on nitrogen the HOMO energy of enamino esters **3** is greater than for enamino ketones **2** and within each series the HOMO energy follows the order **a** < **b** < **c**. If one considers that by frontier-orbital theory a higher energy HOMO implies greater reactivity of the enaminone as a nucleophile, we can see an excellent agreement between HAM/3 HOMO energies and the reactivity observed. On the other hand, the analysis of HOMO energies obtained by AM1 (Figure 1, Table II) shows only a partial agreement. The HOMO energies increase in the order **a** < **b** < **c** within each series, but the HOMO energy of **2** is greater than **3** for equal substitution on nitrogen.

The HOMO of the enaminones corresponds to a π molecular orbital. With respect to site selectivity, the two largest coefficients obtained by both methods are on nitrogen and the C_α carbon for all the molecules treated. [It should be noted that, although the HOMO and LUMO energies obtained by HAM/3 may be more accurate, this does not necessarily mean that the electronic distributions in these orbitals is more correct.] The absolute magnitude of the two coefficients is somewhat greater at C_α.[19] Therefore, for the enaminones **2** and **3**, the products formed are consistent with a HOMO-controlled process in which initial attack occurs at these centers as shown in Scheme I.

Cyclic Enaminones. The acyclic enaminones **2** and **3** are known to exist principally in the *Z,s-Z* form. The reactions of diphenylketene with the cyclic enamino ketones **4a–d** were also carried out (in refluxing methylene chloride for 24 h) to see the effect of fixing the enaminone in the *E,s-E* form. In the reaction of **4a**, the formation of two colorless solid products was observed. The mass spectra of these compounds give the same molecular ion at *m/z* 333 and the fragments corresponding to the Ph_2CH^+ ion, showing that they are isomers resulting from the reaction of diphenylketene at different nucleophilic positions of the enaminone system. The presence in the ^1H NMR spectrum of the vinylic proton at 5.02 ppm for the major product and the absence of this signal in the other allowed us to identify these compounds as **8a** and **9a**, resulting from the electrophilic attack of the diphenylketene on nitrogen and at the C_α carbon positions, respectively. The presence of two NH signals in the ^1H NMR spectrum of compound **9**, one at a much lower field (5.8 and 11.0 ppm), clearly shows an intramolecular hydrogen bonded configuration for this compound.

Scheme I



In the reactions with enamino ketones **4b** and **4c** the only products obtained correspond to reaction on nitrogen (**8b** and **8c**, respectively). The secondary cyclic enamino ketone **4d** was practivally all recovered when it was submitted to reaction, and only products of diazoketone decomposition were observed. The yields are given in Table III.

In contrast to the acyclic enaminones studied, these results show that primary cyclic enamino ketones have a greater preference for reaction at nitrogen and that the secondary cyclic enamino ketone **4d** is unreactive. This same trend was noted in reactions of these enaminones with the $Cu^{II}(acac)_2$ benzoylphenyl carbenoid intermediate.[20] For these fixed *E,s-E* enaminones, intramolecular hydrogen bonding is not possible, which can decrease

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(19) Tables of coefficients and charges are available from the authors.

(20) Eberlin, M. N.; Kascheres, C. *J. Org. Chem.* **1988**, *53*, 2084.

Table V. Physical Data Obtained for the Products in the Reactions of Diazodiphenylethanone 1 with Enaminones 2, 3, and 4

product	elution solvent[a]	mp, °C (lit.)	formula	anal. data (%)[b]			^{1}H NMR data[c] (δ, CDCl$_3$, J in Hz)	IR data (KBr), ν_{max}, cm^{-1}	MS data, m/e (relative intensity)
				C	H	N			
5a	CH$_2$Cl$_2$/hexane, 4:1	146–7	$C_{19}H_{19}NO_2$	77.7 (77.8	6.6 6.5	4.6 4.8)	1.83 (3 H, s), 2.02 (3 H, s), 5.42 (1 H, s), 7.1–7.45 (10 H, m), 10.8 (1 H, br)	3270, 3120, 1670, 1590, 1470, 1270, 730, 705	293 (M$^+$, <1), 167 (17), 166 (12), 165 (20), 152 (8), 126 (75), 84 (100)
5b	CH$_2$Cl$_2$/hexane, 1:1	120–1	$C_{20}H_{21}NO_2$	78.0 (78.2	7.0 6.9	4.3 4.6)	1.85 (3 H, s), 2.03 (3 H, s), 2.92 (3 H, d, J = 7), 5.42 (1 H, s), 7.1–7.45 (10 H, m), 12.2 (1 H, br)	1660, 1600, 1580, 1270, 740, 710	307 (M$^+$, 1), 167 (7), 166 (4), 165 (7), 152 (2), 140 (100), 98 (55), 56 (23)
5c	CH$_2$Cl$_2$/hexane, 1:1	145–7	$C_{23}H_{27}NO_2$	78.9 (79.1	7.9 7.8	3.8 4.0)	1.42 (9 H, s), 1.92 (3 H, s), 2.02 (3 H, s), 5.35 (1 H, s), 7.1–7.45 (10 H, m), 12.6 (1 H, br)	1660, 1600, 1570, 1195, 715	349 (M$^+$ <1), 182 (98), 167 (3), 166 (2), 165 (4), 152 (1), 126 (100), 84 (32), 57 (12)
5d	CH$_2$Cl$_2$/hexane, 4:1	116–7	$C_{20}H_{21}NO_3$	74.4 (74.3	6.5 6.6	4.0 4.3)	1.13 (3 H, t, J = 7), 2.05 (3 H, s), 4.08 (2 H, q, J = 7), 5.7 (1 H, br), 5.85 (1 H, s), 7.27 (10 H, s), 11.0 (1 H, br)	3370, 1690, 1590, 1455, 1280, 1105, 750, 710	323 (M$^+$, 5), 167 (9), 166 (5), 165 (10), 156 (100), 152 (4), 128 (30)
5e	CH$_2$Cl$_2$/hexane, 2:3	oil	$C_{21}H_{23}NO_3$	74.6 (74.8	6.7 6.9	3.9 4.2)	1.13 (3 H, t, J = 7), 2.08 (3 H, s), 2.92 (3 H, d, J = 5), 4.07 (2 H, q, J = 7), 5.75 (1 H, s), 7.27 (10 H, s), 12.4 (1 H, br)	1700, 1595, 1315, 1230, 1150, 1085, 705[h]	337 (M$^+$, <1), 170 (100), 167 (11), 166 (7), 165 (10), 152 (3), 142 (30), 56 (48)
5f	CH$_2$Cl$_2$/hexane, 1:4	78–80	$C_{24}H_{29}NO_3$	75.8 (76.0	7.7 7.7	3.4 3.7)	1.12 (3 H, t, J = 7), 1.38 (9 H, s), 2.15 (3 H, s), 4.08 (2 H, q, J = 7), 5.62 (1 H, s), 7.22 (10 H, s), 12.6 (1 H, br)	1705, 1595, 1195, 1170, 1080, 705	379 (M$^+$, <1), 212 (96), 167 (18), 166 (7), 165 (10), 156 (100), 152 (4), 128 (44), 57 (38)
6a	MeOH/CH$_2$Cl$_2$, 3:100	168–9 (166–7)[d]							
6b	CH$_2$Cl$_2$/hexane, 4:1	167–8 (166.6)[e]							
6c	CH$_2$Cl$_2$/hexane, 1:1	207–8 (201–2)[f]							
7	CH$_2$Cl$_2$/hexane, 3:7	oil	$C_{20}H_{21}NO_3$	74.5 (74.3	6.7 6.6	4.1 4.3)	1.25 (3 H, t, J = 8), 2.43 (3 H, s), 4.13 (2 H, q, J = 8), 4.93 (1 H, s), 5.00 (1 H, s), 7.42 (10 H, s), 11.6 (1 H, br)	1720, 1670, 1635, 1494, 1260, 1140, 705[h]	323 (M$^+$, 4), 168 (12), 167 (51), 166 (19), 165 (33), 156 (100), 152 (14), 128 (50), 110 (40)
8a	MeOH/CH$_2$Cl$_2$,[g] 3:100 R_f = 0.43	205–6	$C_{22}H_{23}NO_2$	79.1 (79.3	7.0 7.0	3.9 4.2)	1.05 (6 H, s), 2.20 (2 H, s), 2.37 (2 H, s), 5.02 (1 H, s), 6.52 (1 H, s), 7.1 (1 H, br), 7.29 (10 H, s)	3280, 3200, 3105, 3010, 2950, 1720, 1620, 1530, 1215, 1165, 1125, 750, 705	333 (M$^+$, 18), 305 (11), 249 (8), 194 (24), 168 (39), 167 (100), 166 (24), 165 (25), 152 (13)
8c	MeOH/CH$_2$Cl$_2$, 1:100	216–7	$C_{20}H_{19}NO_2$	78.5 (78.7	6.4 6.3	4.3 4.6)	1.7–2.7 (6 H, m), 5.07 (1 H, s), 5.85 (1 H, br), 6.57 (1 H, s), 7.30 (10 H, s)	3280, 1705, 1620, 1510, 1220, 1185, 1135, 745, 705	305 (M$^+$, 13), 277 (19), 249 (6), 194 (18), 168 (34), 167 (100), 166 (15), 165 (21), 152 (11)
8d	MeOH/CH$_2$Cl$_2$, 2:100	216–7	$C_{19}H_{17}NO_2$	78.5 (78.3	6.1 5.9	4.9 4.8)	2.2–2.8 (4 H, m), 5.04 (1 H, s), 6.34 (1 H, s), 7.27 (10 H, s), 7.6 (1 H, br)	3240, 3180, 3080, 3000, 1710, 1665, 1605, 1520, 1180, 1140, 750, 705	291 (M$^+$, 18), 194 (8), 168 (23), 167 (100), 166 (15), 165 (33), 152 (16)
9a	MeOH/CH$_2$Cl$_2$,[g] 3:100 R_f = 0.57	191–3	$C_{22}H_{23}NO_2$	79.0 (79.3	6.8 7.0	4.0 4.2)	0.98 (6 H, s), 2.25 (2 H, s), 2.38 (2 H, s), 5.8 (1 H, br), 6.80 (1 H, s), 7.25 (10 H, s), 11.0 (1 H, br)	1630, 1580, 1490, 1190, 745, 705	333 (M$^+$, 19), 167 (16), 166 (100), 165 (6), 83 (27), 55 (4), 42 (7)

[a] The decomposition products of diazo ketone 1 were eluted with CH$_2$Cl$_2$/hexane, 1:5. [b] Found and (required). [c] Standard Me$_4$Si. [d] Sohár, P. Puskás, J. *Acta Chim. Acad. Sci. Hung.* **1968**, *58*, 295. [e] Plato, C. *Anal. Chem.* **1972**, *44*, 1531. [f] Ritter, J. J.; Murphy, F. X. *J. Am. Chem. Soc.* **1952**, *74*, 763. [g] Preparative TLC (SiO$_2$).

conjugation when compared to acyclic *Z,s-Z* enaminones. This would increase the electron density on nitrogen and thus favor reaction at this site. On the other hand, attack at the C_α carbon position might be slowed down because of the development of substantial 1,3-diaxial interaction in the transition state, which we expect to be important for the volumous diphenylketene. Further information has been obtained using AM1 geometric optimization,[17] which shows that while *Z,s-Z* acyclic enaminones have a planar nitrogen, it is not planar in cyclic enamino ketones, which is an indication of the decrease in conjugation. In agreement with this suposition, shorter bond lengths for C=O and C=C bonds and longer bond lengths for OC–C and C–N bonds were obtained.

The HOMO energies obtained by HAM/3 and AM1 (Figure 1, Table II) do not show as much agreement with the reactivity observed as did the acyclic enaminones. An interesting result of the HAM/3 calculations for the cyclic enaminones is the high energy of the second HOMO which corresponds to a nonbonded electron pair on oxygen. Thus, this orbital would also have to be considered in any analysis of reactivity. In fact, this might explain the greater tendency for cyclic *E,s-E* enamino ketones to give high yields of O-alkylated salts upon alkylation when compared to acyclic enaminones[21] and to give O-acylated products[22] or C_α-acyl derivatives via unstable O-acylated intermediate salts[23] upon acylation. Calculations on compound **2a** using standard geometric models[18] and fixed in the four possible geometric forms show that the high energy of the second HOMO (Table IV) is a function of the *s-E* conformation. Thus to explain the reaction of the cyclic enaminones **4**, the possibility of prior reaction of the diphenylketene on oxygen to form an unstable intermediate that then reacts further with another molecule of enaminone cannot be dismissed. However at some point during the reaction a greater preference for reaction at nitrogen would have to be explained.

Conclusion

In conclusion, we can see that molecular orbital considerations clarify the reactivity of this system, especially when HAM/3 is used for calculating frontier-orbital energies. Although this method, which has been developed for first row elements, is readily available,[24] it has not been explored by organic chemists. Considering the importance of frontier orbitals in understanding reactivity, we should see more use of HAM/3 in the future.

Experimental Section

The ^{1}H NMR spectra were recorded with a Varian T-60 or Bruker AW-80 spectrometer using tetramethylsilane as internal reference. IR spectra were recorded on a Perkin-Elmer 399B spectrometer. Electron-impact mass spectra were obtained with a Varian MAT 311A mass spectrometer at 70 eV. Melting points were obtained on a Reichert apparatus and are uncorrected.

Enaminones **2**, **3**, and **4**[21] and diazo ketone **1**[25] were prepared according to reported methods.

Reactions of Diazodiphenylethanone (1) with Enaminones 2 and 3. A solution of **1** (222 mg, 1.00 mmol) and the enaminone (1.00 mmol) in ethanol-free methylene chloride (5 mL) was left at room temperature (22–23 °C) in the absence of light for 7 days. After evaporation of the solvent, the products were separated by column chromatography with neutral aluminum oxide using mixtures of hexane, methylene chloride, and methanol as eluents. Solid products were recrystallized with methylene chloride–hexane.

Reactions of 1 with Enaminones 4. A solution of **1** (222 mg, 1.00 mmol) and the enaminone **4** (1.00 mmol) in ethanol-free methylene chloride [50 mL (200 mL for **4c**)] was left at reflux for 1 day. The products were separated and purified by the same procedure as for enaminones **2** and **3**.

For elution solvents, yields and physical data of the products see Table V.

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Olefin Epoxidation Using Elemental Fluorine

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F_2 reacts with water and CH_3CN, apparently to produce the relatively stable complex HOF·CH_3CN. This is probably the best known oxygen-transfer reagent and can epoxidize olefins quickly and efficiently. Various types of alkenes including aliphatic, benzylic, enones, dienones, maleates, and fumarates have been examined, and all react with the reagent to produce the corresponding mono- or diepoxides in good to excellent yields. This epoxidation is fully stereospecific, and the configuration of the starting olefin is fully retained in the resulting oxirane. In cases where exceptionally stable oxocarbocations can be formed as in 1,1-diphenylethene, the reaction produces vicinal glycols in good yields. Since the origin of the epoxides' oxygen is in the water, this method is very suitable for introducing the isotopes ^{17}O and ^{18}O into various molecules.

Although F_2 has been known for more than a century, it was widely assumed to be unsuitable for organic synthesis. Most of the usual organic substrates were considered to be too fragile and vulnerable for this powerful and corrosive element. Only a few sporadic attempts to use it were thus recorded, most of them with highly stable polyhalogenated compounds.[1]

About 10 years ago we started to demonstrate systematically that, properly handled, fluorine can be a very helpful fluorinating agent, which not only does not destroy

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(1) See for example: Miller, W. T.; Staffer, J. O.; Fuller, J.; Currie, A. C. *J. Am. Chem. Soc.* **1964**, *86*, 51. But see however, also: Merritt, R. F.; Stevens, T. E. *J. Am. Chem. Soc.* **1966**, *88*, 1822.

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