Cyclic Allenes or Diradicals in the Cyclization Reactions of Dienynes Generated by Photolysis of Alkynylcyclohexadienones

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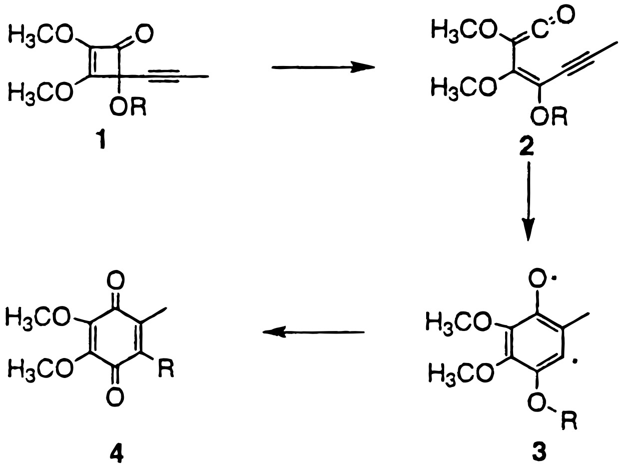
Reported here are some rearrangements involving the electrocyclic ring closure of dieneynes **7**. Such ring closures are envisaged to possibly give strained substituted cyclic allenes **8** which could also behave as diradicals **8a**. The results show that compounds such as **5** rearrange to cyclohexadienones **9a**, **9b**, or **11** through these kind of intermediates. Theoretical calculations performed on simple models similar to the intermediates suggest that the nature of these intermediates correspond to that of cyclic allenes.

Introduction

Over the past few years, Moore[1] and Liebeskind[2] have shown the utility of cyclobutendiones for the regiocontrolled synthesis of highly substituted quinones, hydroquinones, and catechols. A specific example is the conversion of 4-alkynylcyclobutenones **1** to 1,4-benzoquinones **4** (Scheme 1) through a sequence of reactions that involve tandem electrocyclic rearrangements. The relief of ring strain on **1** triggers an initial electrocyclic ring opening of this molecule to the alkynylethenylketene **2** which gives diradicals **3** upon electrocyclic ring closure. The intermediacy of diradical **3** has been suggested[3] and observed to give quinones **4** via migration of the R-substituent (R = hydrogen, trimethylsilyl, allyl).

We report here some exploratory chemistry initially designed as an extension of the above-noted benzoquinone synthesis. It was envisaged that photolysis of **5** (a six-electron system) would also generate conjugated ketenes such as **6** which could behave in analogy to **2**, resulting in the formation of rearranged products after an electrocyclic ring closure and migration of the trimethylsilyl group (Scheme 2).

Scheme 1



Results and Discussion

Photolysis of **5** (a compound readily available by the addition of lithium phenylacetylide to 4,5-dimethoxy-1,2-benzoquinone[4] in anhydrous THF at 78 °C) gave a complex mixture of products. However, when water or methanol was added to the THF solution, the respective cyclohexadienones **9a** and **9b** were realized (Scheme 2). The structures of these compounds were determined on the basis of their spectral data. For compound **9b** for example, its IR spectrum shows two strong carbonyl absorptions at 1750 and 1702 cm^{-1} corresponding to the carbonyl ester and the unsaturated carbonyl group on the ring. The ^{1}H NMR spectrum of **9b** shows two sets of aromatic protons at 7.27 and 6.87 integrating for three and two hydrogens, respectively; a singlet at 5.50, integrating for one hydrogen, corresponding to the vinyl proton; singlets at 3.89, 3.61, and 3.20, each integrating for three hydrogens corresponding to the methyl ester group, the methoxy group attached to the double bond, and the methoxy group attached to the quaternary carbon, respectively; two doublets centered at 3.19 (J = 6.5 Hz) corresponding to the two methylene protons on the molecule and a singlet at 0.15 corresponding to the methyl protons of the trimethylsilyl group. The ^{13}C NMR shows signals for all carbons in the molecule. Finally, the mass spectrum of **9b** shows a molecular ion peak at 374 (EI), corresponding to the molecular weight of **9b**. This transformation of **5** to **9a** or **9b** is envisaged to proceed via the photoinduced stereospecific ring opening

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(1) (a) Moore, H. W.; Yerxa, B. R. *Adv. Strain. Org. Chem.* **1995**, *4*, 81. (b) Moore, H. W.; Yerxa, B. R. *Chemtracts* **1992**, *5*, 273. (c) Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821.

(2) (a) Sun, L.; Liebeskind, L. S. *Tetrahedron Lett.* **1997**, *38*, 3663. (b) Sun, L.; Liebeskind L. S. *J. Org. Chem.* **1995**, *60*, 8194. (c) Gurski, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 6101. (d) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053.

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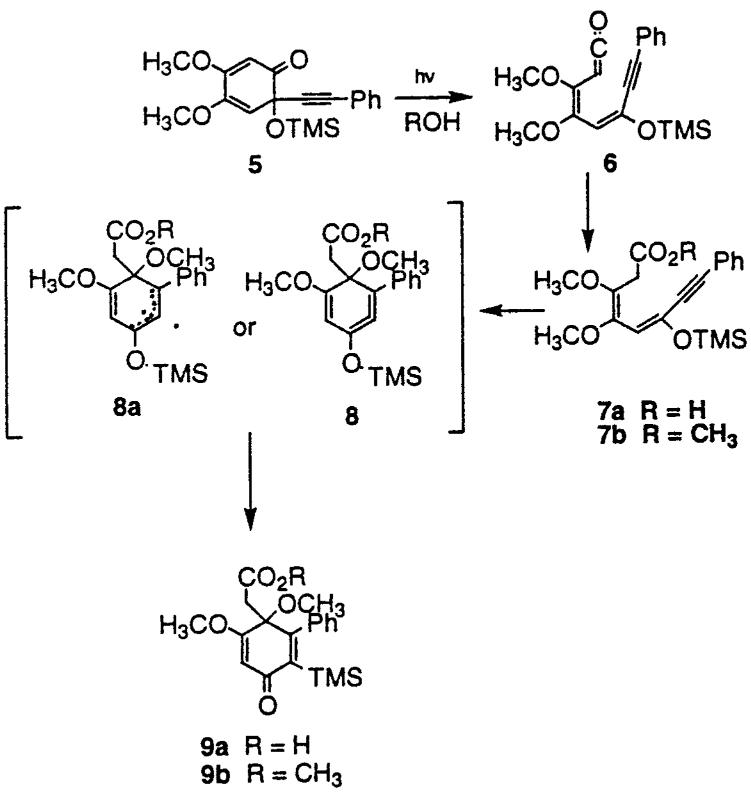
(4) (a) Wriede, U.; Fernández, M.; West, K. F.; Harcourt, D.; Moore, H. W. *J. Org. Chem.* **1987**, *52*, 4485. (b) Moore, H. W.; West, K. F.; Wriede, U.; Chow, K.; Fernández, M.; Nguyen, N. V. *J. Org. Chem.* **1987**, *52*, 2537. (c) Moore, H. W.; West, K. F. *J. Org. Chem.* **1982**, *47*, 3591.

10.1021/jo000333e CCC: $19.00

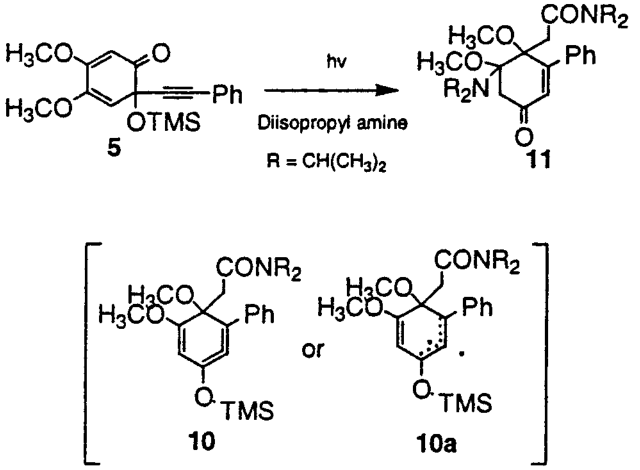
Scheme 2



of **5** to the ketene **6**. In analogy to the thermolysis of the cyclobutenone **1** (four-electron system), photolysis of **5** (six-electron system) is expected to give **6** via outward rotation of the electron-donating trimethylsilyloxy group;[5] under the protic conditions of the photolysis, the ketene is intercepted to give the dienyne **7** which could then ring close the cyclic allene **8** or the diradical species **8a**. Allenes incorporated in carbocyclic frameworks of nine or more carbon atoms are not so unusual since they are relatively unstrained.[6] However, if the ring size is decreased as in the case of a 1,2-cyclohexadiene system such as **8**, the linear allene geometry would be severely twisted and bent. To offset the increased strain, the allene moiety could prefer a bent planar structure with electrons distributed in the form of diradical **8a**. An analogy for these type of intermediates stems from the work of Paquette and collaborators[7] who reported a direct conversion of diisopropyl squarate to unsaturated diquinanes through two consecutive conrotatory processes that generate a highly strained eight-membered ring cyclic allene which is immediately protonated to relieve ring strain. The cyclic allene **8** or its diradical form **8a** gives then **9** via migration of the trimethylsilyl group from oxygen to carbon.

A variant of the above rearrangement was observed when **5** was subjected to photolysis in THF/NH[CH-(CH$_3$)$_2$]$_2$. Under these conditions the intermediate **8** or **8a** apparently suffers hydrogen atom abstraction before silyl migration. Desilylation and Michael addition of the amine to the corresponding dienone then gives the observed product **9** in 53% isolated yield (Scheme 3). This structure is consistent with the spectral data obtained for this compound.

Scheme 3



It is clear from the above examples that appropriately substituted dienynes having the proper stereochemistry may readily ring close to strained cyclic allenes or diradicals and that enones will be ultimately formed in the final step. We were interested in determining the nature of the intermediate formed during the electrocyclization **7** and to find some evidence that allows the differentiation of these intermediates as cyclic allenes or diradicals. To probe the nature of the intermediate, we carried out theoretical calculations on simpler models that resemble the structure of intermediates **8** and **10**.

Theoretical Calculations. Strained cyclic allenes have been viewed with considerable interest with regard

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[5] Houk, K. N.; Spellmeyer, D. C.; Jefford, C. W.; Rinbault, C. G.; Wang, Y.; Miller, R. D. *J. Org. Chem.* **1988**, *53*, 3, 2125 and references therein.

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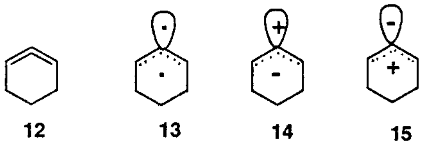
[7] (a) Paquette, L. A.; Kuo, L. H.; Doyon, J. *J. Am. Chem. Soc.* **1997**, *119*, 3038. (b) Morwick, T.; Doyon, J.; Paquette, L. A. *Tetrahedron Lett.* **1995**, *36*, 2369.

Scheme 4



to their bonding and reactivity.[8] Since allenes incorporated into rings with less than nine members cannot obtain their normal linear geometry, it has been suggested that they could exist as dipolar or diradical species.[6] In this regard, the generalized cyclic allene **12** can be viewed in the less-strained diradical form **13** or the dipolar forms **14** and **15** (Scheme 4). Opinions on the preferred structure of singlet 1,2-cyclohexadienes are mixed. Bottini and co-workers[9] have suggested a bent twisted allene which isomerizes rapidly to the diradical **13** which is the active species in [2 + 2] and [4 + 2] cycloadditions. They also suggest that species **14** is also responsible for some of the chemistry of this diene. In contrast, Moore and Ward[10] and also Greenberg and Liebman[11] prefer **15** for the structure of 1,2-cyclohexadienes, a contention supported by some INDO-MO calculations.[12]

Johnson and co-workers[13] have reported ab initio MCSCF calculations on 1,2-cyclohexadienes which support the contention that its equilibrium geometry is strongly bent and chiral (C_2 symmetry) but can easily racemize through a species best described as a diradical. Additionally, they found that structures **14** and **15** correspond to excited electronic states of structures **12** and **13**.

To prove if the intermediate described by structures **8** or **10** is a cyclic allene or if it is a diradical, we built two models to theoretically study their electronic structure and their geometrical stability, including finding the transition states linking them to final products (**18** and **21**).

The first model **16** (model A, Scheme 5) is a much simplified version of the molecules represented by structures **8** or **8a** where the fragments not directly related to the **7**−**9** transformation have been replaced by hydrogens.

The second and larger model **19** (model B, Scheme 6) differs from the first in that a phenyl ring was added. This model was built because the presence of the phenyl ring on the *meta*-position to the OH group might produce some stabilization of the proposed diradical structure:

Scheme 5

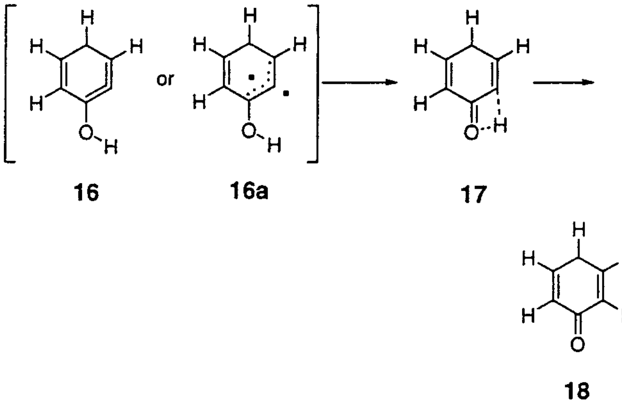


Table 1. Relative Energies in kcal/mol of the Fully Optimized Geometries for the Molecular Models A and B

molecule	HF/6-31G**	MP2(FC)/6-31G**
	Model A	
16	0	0
17	7.1	6.7
18	−64.8	−54.9
	Model B	
19	0	0
20	16.1	13.8
21	−53.5	−48.4

All the optimized parameters of these structures are available at the HF and MP2 level from the authors upon request.[14]

We performed Hartree−Fock Self-Consistent Field (HF) and single reference frozen core second-order Möller−Plesset (MP2) full geometry optimizations using the standard 6-31G** basis of the Gaussian-94 program on all the structures presented in the two previous schemes.

The most important result of these calculations is that for both models **16** or **19**, the strained cyclic allene structure corresponds to the electronic structure predicted theoretically for the molecule rather than the diradical intermediates **16a** and **19a**. The existence of diradical character would be shown by the presence of two degenerate or nearly degenerate, singly occupied open shells. On the other hand, no low-lying unoccupied orbitals were found for the optimized **16** and **19** molecules, and the HOMO−LUMO energy gap for molecule **16** is 9 eV. This result is in agreement with the previous MCSCF study.[10] For both models, the HF wave functions were good approximations, and they were successfully used as references to obtain the MP2 corrections for all six structures.

Relative energies are presented for both models in Table 1. As expected, we found that for both models the transition states **17** and **20** lie higher in energy than the corresponding products **18** and **21**. At the HF level the energy differences between **16**−**18** and **19**−**21** are 64.8 and 53.5 kcal/mol, respectively, for models **A** and **B**, while the inclusion of the correlation effects at the MP2 level reduces these values to 54.9 and 48.4 kcal/mol.

The transition states for both reactions (**17** and **20**) were found to be quite close in energy to the intermediates **16** and **19**. Again at the HF level, they lie only 7.1 and 16.1 kcal/mol above their respective intermediates' energy. At the MP2 level the picture is almost identical. It can be seen that the presence of the phenyl ring in model B increases the barrier height with respect to the

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(8) (a) Harusawa, S.; Moriyama, H.; Kase, N.; Ohishi, H.; Yoneda, R.; Kurihara, T. *Tetrahedron* **1995**, *51*, 6475. (b) Harusawa, S.; Moriyama, H.; Ohishi, H.; Yoneda, R.; Kurihara, T. *Heterocycles* **1994**, *36*, 1975. (c) Lin, J.; Pang, Y.; Young Jr., V. G.; Barton, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3794. (d) Tolbert, L. M.; Islam, M. N.; Johnson, R. P.; Loiselle, P. M.; Shakespere, W. C. *Ibid.* **1990**, *112*, 6416. (e) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J. P.; Mooring, A. M.; West, P. R. *Ibid.* **1987**, *109*, 2456. (f) Balci, M.; Harmandar, M. *Tetrahedron Lett.* **1984**, *25*, 237. (g) Balci, M.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 7607. (h) Loozen, H. J.; Castenmiller, W. A.; Buter, E. J.; Buck, H. M. *J. Org. Chem.* **1986**, *41*, 2965.

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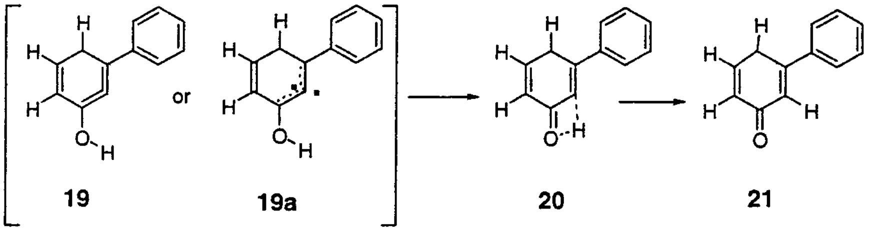
Scheme 6



same barrier in model A, thus stabilizing intermediate **19** with respect to **16**. These energy barriers are large enough to warrant the observation of the intermediates by trapping them at low temperature. Although one quantum effect we did not take into account in the present study is the inclusion of the zero-point energy (ZPE) corrections, these will be small and will not modify the stability of the intermediates.

Structures. For the intermediates **16** and **19**, C−C distances for the three linked carbon atoms (a,b,c) in the allene moiety are typical for double-bonds. Although one would expect the abc angles to be somewhat smaller than the 180° found for linear allenes, the abc angles are only slightly different than those found in benzene. For example, the abc bend angle is approximately equal to 110°, much closer to an sp^2 hybridization than the corresponding linear sp hybridization for the central carbon atom. The other bend angles in the ring are accordingly larger than the 120° expected for a regular hexagon. The fact that there is only a relatively small structural change in the ring for the cyclohexatriene to ciclohexadienone transformation is reflected in the similar stability of these structures.

Structure **19** is a symmetric C_{2v} molecule and, as expected from Hammonds postulate, the transition state resembles more reactant **19** than product **21**.

Conclusions. The photolysis of 4,5-dimethoxy-2-(phenylethynyl)-2-(trimethylsilyloxy)-3,5-cyclohexadienone **5** induces the rearrangement of this compound to enones **9a**, **9b**, and **11** in reasonable yields through a sequence of steps that involve the electrocyclic ring opening of **5**. This process generates ketenes **6a** and **6b** which are immediately captured by nucleophilic species present in the reaction media to give dienynes **7**. We have demonstrated using HF and MP2 ab initio calculations that the electrocyclization of **7** can generate intermediates that can be best described as the cyclic allenes **8** or **10.** The results shown here are also consistent with earlier literature reports in which the cyclic allene 1,2-cyclohexadiene is favored over the diradical or dipolar forms. It is also of interest to note this preference for the cyclic allene form in our study since our molecules contain an additional double bond in the ring system. We are now extending our calculations and analysis to similar examples reported in the literature that involve the generation and electrocyclization of conjugated alkynyl ketenes that can also give rise to the formation of cyclic allenes or the corresponding diradical forms.

Experimental Section

General Procedure. Melting points are uncorrected. ^{1}H and ^{13}C spectra were recorded at 200 MHz. IR spectra were recorded using FTIR apparatus. Mass spectra were obtained by EI or CI methods. All reactions were followed by TLC using E. Merck silica gel 60 F-254. Flash column chromatography was performed with E. Merck silica gel (230−400 mesh). All reactions were carried out in flame-dried glassware under a positive pressure of dry argon. Tetrahydrofuran (THF) was distilled from sodium (benzophenone indicator).

4,5-Dimethoxy-2-(phenylethynyl)-2-(trimethylsilyloxy)-3,5-cyclohexadienone (5). To a solution of 0.33 g (3.2 mmol) of phenylacetylene in 35 mL of dry THF, under argon, at −78 °C, was injected 1.6 mL (3.2 mmol) of *n*-butyllithium (2.0 M in hexanes). The mixture was stirred at this temperature for 25 min and then transferred dropwise, via cannula, to a suspension of 0.50 g (2.9 mmol) of 4,5-dimethoxy-3,5-cyclohexadiene-1,2-dione in 200 mL of dry THF also under argon at −78 °C. When the addition was complete, the mixture was stirred for an additional 1 h. The reaction was then quenched with 0.75 mL of trimethylsilyl chloride and allowed to warm to room temperature. The solvent was evaporated and the residue, dissolved in dichloromethane, passed through a flash column (silica gel, hexanes/ethyl acetate 4:1). Removal of the solvent afforded a yellow oil which crystallized upon addition of diisopropyl ether to give 0.95 g (94%) of product as white crystals: mp 108 °C; ^{1}H NMR 7.25 (m, 5H), 5.44 (s, 1H), 5.41 (s, 1H), 3.84 (s,3H), 3.75 (s, 3H), 0.28 (s, 9H). IR 2980(w), 1682(s), 1600(s), 1500(w), 1460(m), 1250(s), 1080 (s). Anal. Calcd for $C_{19}H_{22}O_4Si$: C, 66.64; H, 6.47. Found: C, 66,66; H, 6.37.

4,5-Dimethoxy-3-phenyl-4-(2-ethanoic)-2-(trimethylsilyl)-2,5-cyclohexadienone (9a). Photolysis using a 450 W medium-pressure Hanovia mercury lamp and a Pyrex filter was conducted on 0.40 g (1.17 mmol) of 4,5-dimethoxy-2-(phenylethynyl)-2-(trimethylsilyloxy)-3,5-cyclohexadienone **5** in 500 mL of wet THF, at −78 °C and under argon for 2 h. After warming the solution to room temperature, the solvent was evaporated and the solid obtained recrystallized from diisopropyl ether to give 0.16 g (40%) of the product as white crystals: mp 151−152 °C; ^{1}H NMR 7.4−7.2 (m, 3H), 6.92 (m, 2H), 5.73 (s,3H), 3.91 (s, 3H), 3.17 (s, 3H), 3.17(s, 3H, 2.77 (d, 1H, $J = 13.5$ Hz), 2.35 (d, 1H, $J = 15.5$ Hz), 0.083 (s, 9H); IR 3000 (br), 1735 (s), 1662 (s), 1600 (s), 1358 (s), 1240 (s), 1200 (s), 1100 (s). Anal. Calcd for $C_{19}H_{22}O_5Si$: C, 63.66; H, 6.18. Found: C, 63.47; H, 6.09.

4,5-Dimethoxy-3-phenyl-4-(2-methylenecarbomethoxy)-2-(trimethylsilyl)-2,5-cyclohexadienone (9b). Photolysis using a 450 W medium-pressure Hanovia mercury lamp and a Pyrex filter was conducted on 0.35 g (1.02 mmol) of **5** in 500 mL of a 1:1 mixture of THF/methanol. The solution was irradiated under an argon atmosphere at −78 °C for 1.5 h. The mixture was allowed to warm to room temperature and the solvent removed. Preparative thin-layer chromatography (silica gel, hexanes/ethyl acetate 1:1) gave an oil which upon addition of diisopropyl ether afforded 0.18 g (48%) of the product as white crystals: mp 96−97 °C (dec); ^{1}H NMR 7.27 (m, 3H), 6.87 (t, 2H, $J = 7.63$ Hz), 5.5 (s, 1H), 3.89 (s,3H), 3.61 (s, 3H), 3.20 (s, 3H), 3.19 (q, 2H, $J = 6.51$ Hz), 0.15 (s, 9H); ^{13}CNMR 194.35, 189.35, 179.38, 179.20, 169.30, 169.25, 151.11, 143.63, 127.79, 126.48, 125.88, 109.86, 58.61, 58.58, 52.00, 51.33, 42.58. IR 1750 (s), 1702 (s), 1638 (s), 1355 (s),

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(14) Gaussian 94, Revision C.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

1178 (s), 1105 (s). MS 374 (EI) 375 (CI). Exact mass calcd for $C_{20}H_{26}O_5Si$: 374.15493. Found: 374.15480.

4,5-Dimethoxy-3-phenyl-4-(2-diisopropylacetamido)-5-(isopropylamino)-2-cyclohexenone (11). Photolysis using a 450 W medium-pressure Hanovia mercury lamp and a Pyrex filter was conducted on 0.40 g (1.17 mmol) of **5** in 500 mL of dry THF containing 25 mL of freshly distilled diisopropylamine, at −78 °C, under argon for 1.5 h. The mixture was allowed to warm to room temperature and the solvent removed in vacuo. The product was isolated via preparative thin-layer chromatography (silica gel, hexanes/ethyl acetate 1:1) to afford, after evaporation of the solvent 0.29 g (53%) of a yellow oil: ^{1}H NMR 7.45−7.25 (m, 5H), 5.02 (s, 1H), 4.08 (m, 2H), 3.87 (s, 3H), 3.62 (s, 3H), 3.12 (s, 2H), 3.06 (s, 2H), 3.06 (s, 2H), 1.23 (s, 6H), 1.21 (s, 6H), 1.15 (s, 6H); ^{13}C NMR 193.07, 169.20, 165.75, 140.15, 139.86, 125.23, 129.58, 128.60, 128.54, 127.38, 127.32, 95.65, 68.34, 58.17, 46.07, 41.87, 41.50, 41.47, 38.41, 24.23, 22.90, 22.56. IR 3000 (s), 1740 (s), 1670 (s), 1580 (s), 1250 (s). Exact mass calcd for $C_{28}H_{44}O_4N_2$:472.33008. Found: 472. 33019.

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