New Intramolecular α-Arylation Strategy of Ketones by the Reaction of Silyl Enol Ethers to Photosensitized Electron Transfer Generated Arene Radical Cations: Construction of Benzannulated and Benzospiroannulated Compounds†

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Efficient intramolecular α-arylation of ketones is achieved by the reaction of silyl enol ethers to photosensitized electron transfer (PET) generated arene radical cations. The arene radical cations are generated by one-electron transfer from the excited state of the methoxy-substituted arenes to ground-state 1,4-dicyanonaphthalene (DCN). This arylation strategy has provided the unique opportunity of constructing five- (**23**), six- (**18**), seven- (**25**) and eight-membered (**27**) benzannulated as well as benzospiroannulated (**34**) compounds. The explanation for the formation of **27** has been advanced by considering the proximity between the arene radical cation and silyl enol ether due to the self-coiling in the aqueous environment.

Introduction

α-Arylation of ketones, although infrequently used, is an important carbon−carbon bond formation strategy that could be utilized for the rapid access of an otherwise inaccessible molecule. For example, the intramolecular version of such an approach could provide a unique means of constructing aromatic annulated products.[1−4] Semmelhack[5] and Bunnett[6] have used the photo $S_{RN}1$ reaction protocol for the intramolecular arylation reaction by coupling ketone enolate anions with halo arenes; however, due to the predominance of *β*-hydrogen transfer, of the annulation yields are reduced. Moreover, experimental conditions for such cyclizations are drastic and difficult. Another intramolecular arylation approach reported by Urabe et al.[7] employed addition of arene radical, generated by the reaction of Bu_3SnH on the aromatic bromide, to the enol ether double bond; however, this strategy suffers from the usual problems of radical reactions. Other ketone arylation procedures, for example, the dichlorobis(tri-*o*-tolylphosphine)palladium(II)-catalyzed reaction of an α-stannyl ketone[8] or enol stannane[9] intermediates with an aryl bromide, electrophilic arylation of enol silanes with diazonium salts,[10] and the nickel(II)-catalyzed coupling of α-bromo enol silane with an aryl Grignard reagent,[11] are also not easily adaptable for intramolecular reactions. Furthermore, these procedures suffer from limitations such as the requirement of special reagents, a large excess of substrates, drastic reaction conditions, or multistep operations. Visualizing the interesting application of intramolecular α-arylation reaction of ketones for constructing polycyclic compounds, our attention was drawn toward the possible utilization of a direct nucleophilic reaction of an aromatic ring with highly polarized ionic structure of enol silyl ether[12] via photosensitized electron transfer (PET) generated arene radical cation intermediate. The origin of this concept may be found from our broad research interest in the area of PET reactions of synthetic relevance in general[13] and intramolecular nucleophilic additions to the PET-generated arene radical cation in particular[14] (Figure 1). We have explored the intramolecular arylation of silyl enol ethers via PET-generated arene radical cation in detail[15] and report herein the construction of five-, six-, seven- and eight-membered aromatic annulated products and spirocyclic compounds, in good yields.

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† Dedicated with respect to Dr. H. R. Sonawane on the occasion of his 65th birthday.

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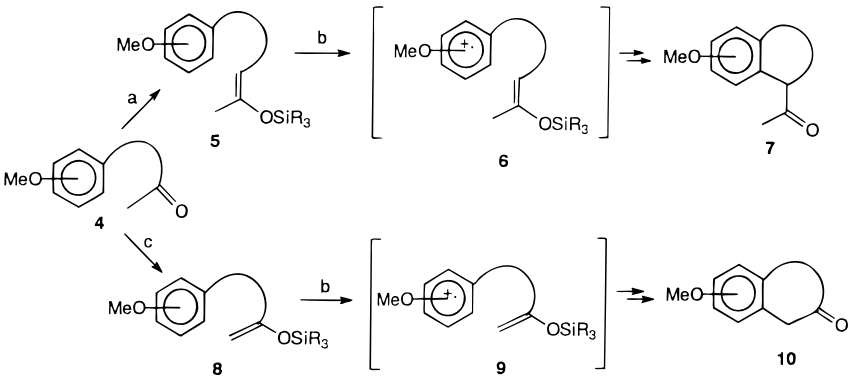
Scheme 1[a]



[a] Reagents: (a) thermodynamic enolization, (b) *hν*, DCN, PET reaction; (c) kinetic enolization.

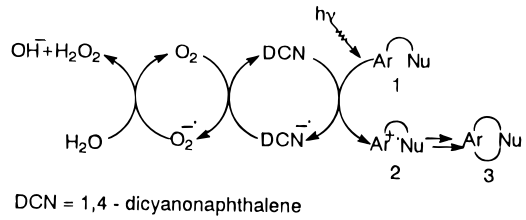


Figure 1.

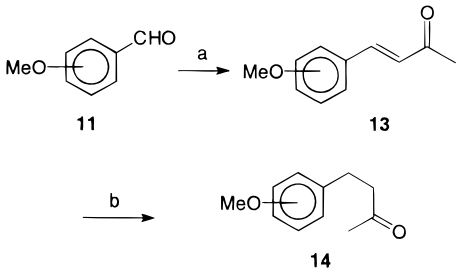
Results and Discussion

Benzannulation Reaction. It was obvious to us at the beginning of our project that two different types of silyl enol ethers could be obtained from a substrate of type **4** by following the reported procedures[16] of synthesizing either thermodynamic **5** or kinetic **8** silyl enol ethers. Therefore, the arylation of these enol silanes was expected to produce two different types of annulated compounds **7** or **10**, varying in ring sizes from the same ketone **4** as shown in Scheme 1.

Initially, substrate **14a** was selected for evaluating the intramolecular arylation reaction as per the depictions shown in Scheme 1. The methoxy substitution on the benzene ring was essential for making the arene ring capable of participating in PET processes[14] from their excited state in the presence of DCN (1,4-dicyanonaphthalene) as an electron acceptor. Compounds **14** were easily obtained in 96% yield by the catalytic hydrogenation of **13**, prepared by the reaction of methoxy-substituted benzaldehydes **11** and acetone in the presence of 10% NaOH (Scheme 2). Silyl enol ethers **15** could be prepared quantitatively (98%) by the reaction of *tert*-butyldimethylsilyl chloride (TBDMSCl) (6 mmol) on the lithium enolate of **14**, generated by the reaction of LDA (5 mmol) at −78 °C. Compounds **15** were sufficiently pure enough to proceed to the next step.

PET reaction of **15a** utilized essentially the conditions that had been successfully used in a number of earlier cyclization reactions of electron-rich arenes tethered with nucleophiles.[14] These conditions consisted of the irradiation of **15a** (2 mmol) in the presence of DCN (0.34 mmol) in CH_3CN/H_2O (4:1) solvent using Pyrex-filtered light (>280 nm, 450 W Hanovia medium-pressure lamp) without removing dissolved air from the reaction mixture.

Scheme 2[a]



14a: 4-(4-methoxy-phenyl)-butan-2-one
14b: 4-(3,4-dimethoxy-phenyl)-butan-2-one

[a] Reagents: (a) acetone (**12**), 10% aqueous NaOH, dilute HCl; (b) H_2, 10% Pd/C, EtOH.

It has been ascertained by comparative UV spectroscopy that almost all light (>99%) is absorbed by **15a** under the present photolysis reaction conditions. The irradiation was continued until most of the **15a** disappeared (4 h, monitored by TLC). Removal of the solvent at reduced pressure followed by chromatographic purification gave **17a** (72%, isolated yield) and starting ketone **14a** (~10%). DCN was recovered quantitatively (98%) at the end of the reaction. Partial reversal of **15a** to **14a** in the dark is ascertained by an adequate control experiment. Product **17a** was characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data.

Mechanistically, the formation of **18a** from **15a** could be explained by considering the steps as shown in Scheme 3. Intermediate **16a** is formed by an electron transfer from the excited singlet state of the arene moiety of **15a** to the ground state of DCN. Intramolecular nucleophilic reaction of silyl enol ether to the electron-deficient arene radical cation followed by the aromatization of **17a** leads to the formation of **18a**. Compound **18a** was characterized by detailed ^{1}H NMR, ^{13}C NMR, mass spectral, and HRMS data and further confirmed by comparing the ^{1}H NMR spectral data with the reported values.[17a] $DCN^{\bullet-}$ produced by the acceptance of an electron from the excited arene moiety reverts back to its original state via ET mediated by oxygen as shown in Figure 1. Photoreaction in an inert atmosphere leads to the fast consumption of DCN along with the formation of complicated mixture of products.

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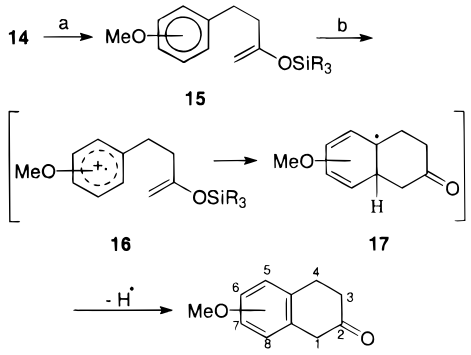
(17) Registry no. provided by the author: 4133-34-0. Aldrich FT-NMR **1**(2), 797A. (b) Registry no. provided by the author: 2472-13-1. Aldrich FT-NMR **1**(2), 797B.

Scheme 3[a]



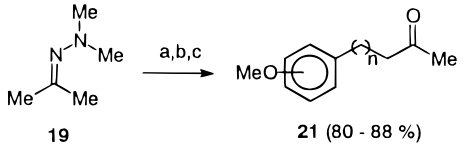
[a] Reagents: (a) LDA, TBDMSCl, THF, −78 °C; (b) *hν*, DCN, CH_3CN; H_2O (4:1), 4 h.

Similar PET activation of **15b** gave **18b** (70%). The regiochemistry of methoxy groups in **18b** is assigned on the basis of the detailed ^1H NMR spectral analysis of the aromatic protons and further confirmed by comparing it with the reported values.[17b] The observed regiospecificity of these cyclizations is in accord with the earlier calculated electron densities (Huckel or MNDO) at different carbons of the HOMO of the arene radical cation.[18] It may be worthy of note that this cyclization strategy provides a direct access to arene-substituted *β*-tetralones, which are very important precursors in the synthesis of many biologically/medicinally active compounds.[19] *β*-Tetralones are otherwise generally prepared with difficulty, via 1,2-transposition of α-tetralones.[20]

Because we hoped to maintain the versatility of this cyclization reaction irrespective of the number of methylene groups or the position of the silyl enol ether group, substrates **21** were synthesized. The preparation of **21** (80−84%) involved the alkylation of acetone hydrazone **19** (5 mmol) with the corresponding phenyl alkyl bromides **20** (5 mmol) through the steps as shown in Scheme 4. It was envisaged that the cyclization of thermodynamically prepared enol silyl ether **22** would provide indan systems **23**, while kinetically produced enol silyl ethers **24** will give benzocycloheptanone frameworks.

To evaluate the feasibility of transforming **21** into corresponding indan systems[21] (**23**), silyl enol ether **22a** was first prepared in 83% yield by heating a mixture of **21a** (5 mmol), TBDMSCl (6 mmol), and imidazole (12 mmol) in DMF (10 mL) for 48 h (Scheme 5). PET activation of **22a** by following the usual irradiation conditions, as described for **15a**, produced **23a** in 65% yield. Product **23a** was characterized by IR, ^1H NMR, and ^{13}C NMR spectral analysis. An identical reaction

Scheme 4[a]



21a: 5-(4-methoxy-phenyl)-pentan-2-one
21b: 5-(3,4-dimethoxy-phenyl)-pentan-2-one
21c: 5-(3,4,5-trimethoxy-phenyl)-pentan-2-one
21d: 6-(3,4-dimethoxy-phenyl)-hexan-2-one

[a] Reagents: (a) *n*-BuLi, THF, −78 °C; (b) $Ar(CH_2)_nBr$ (**20**); (c) $NaIO_4$, MeOH/THF, phosphate buffer.

from **22b** also produced **23b** in 70% yield, confirming the generality of the reaction. It was further envisaged that the kinetically produced silyl enol ethers **24** upon PET activation should produce corresponding benzocycloheptanones **25**. In this context, when the PET cyclizations of **24a** and **24b** were carried out by following the identical PET reaction as described earlier, which produced corresponding benzocycloheptanone derivatives **25a** (65%) and **25b** (74%), respectively. These compounds displayed characteristic ^1H NMR, ^{13}C NMR, and mass spectral data. The observed efficiency and the good cyclization yields of **25** encouraged us to include substrate **21c** also as an example in our study as the cyclization of its corresponding silyl enol ether **24c** would lead to an easy construction of **25c**, which was initially utilized by Schreiber et al.[22] and subsequently by others[23] as a precursor for the synthesis of a potent mitotic inhibitor colchicine.[24] PET activation of **24c** indeed, produced **25c** in 66% yield.

Next, we decided to explore the scope and limitations of this methodology by envisaging the construction of the benzocyclooctane moiety as it is often most difficult[25] to prepare because of entropy factors and transannular interactions. In comparison to five- and six-membered ring-forming reactions, few methods for direct formation of eight-membered rings are available.[26,27] In this context, compound **21d** was selected. This compound was obtained (82%) by following the same reaction sequences as outlined in Scheme 6. Kinetically produced silyl enol ether **26** was subjected to the usual PET reaction as described for **15a**. To our pleasant surprise, **26** underwent smooth cyclization to produce **27** in 70% yield as a solid, mp 85−86.5 °C. Small amounts (>10%) of starting ketone wrtr recovered in this case too (Scheme 6). The ease observed during this cyclization may possibly be explained by considering the proximity between the arene radical cation and enol silyl ethers in aqueous medium due to self-coiling as demonstrated by Jiang et al.[28] However, further study is in progress in this regard and would be published separately somewhere else.

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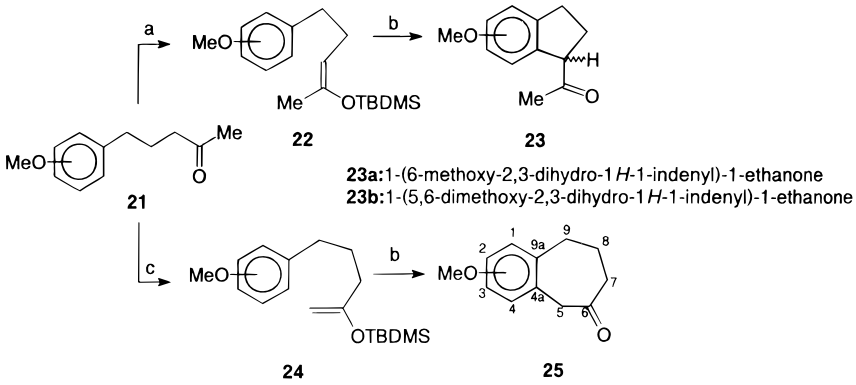
Scheme 5[a]

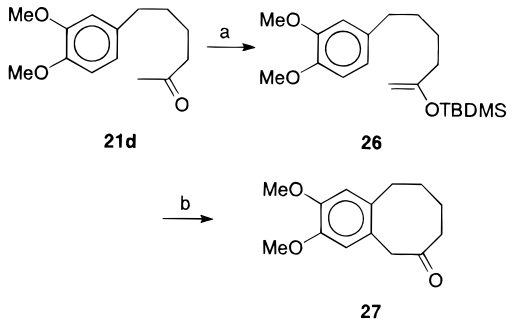


23a: 1-(6-methoxy-2,3-dihydro-1*H*-1-indenyl)-1-ethanone
23b: 1-(5,6-dimethoxy-2,3-dihydro-1*H*-1-indenyl)-1-ethanone

25a: 3-methoxy,6,7,8,9-tetrahydro-5*H*-benzo[a]cyclohepten-6-one
25b: 2,3-dimethoxy,6,7,8,9-tetrahydro-5*H*-benzo[a]cyclohepten-6-one
25c: 1,2,3-trimethoxy,6,7,8,9-tetrahydro-5*H*-benzo[a]cyclohepten-6-one

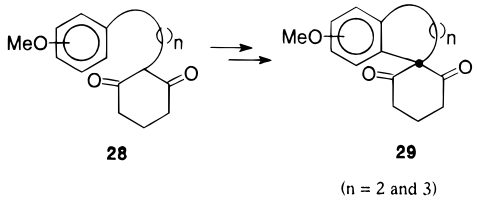
[a] Reagents: (a) ImH, TBDMSCl, DMF, reflux, 80%; (b) *hν*, DCN, CH_3CN/H_2O (4:1); (c) LDA, TBDMSCl, THF, −78 °C (93%).

Scheme 6[a]



[a] Reagents: (a) LDA, TBDMSCl, THF, −78 °C; (b) *hν*, DCN, CH_3CN.

Scheme 7

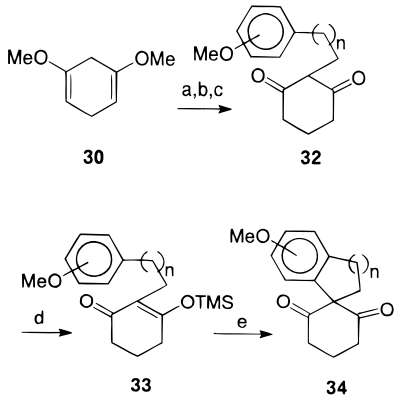


(n = 2 and 3)

Benzospiroannulation Reaction. Once it was established that intramolecular arylation of ketones can be efficiently effected by the reaction of the corresponding silyl enol ethers to PET-generated arene radical cation and five-, six-, seven-, and eight-membered benzannulated compounds could easily be constructed, our attention was focused on the possible exploitation of this strategy for the construction of benzospiroannulated molecules **29** starting from **28** (Scheme 7). The spiroannulated compounds of general structures **29** are either the part of biologically active *Cannabis spiranoids*[29] **29a** ($m = 1$) or have been utilized **29b** ($m = 2$) for the synthesis of other biologically important molecules.[30]

The known syntheses of these spirocyclics are rather cumbersome.[29−31] In this context, diones **32** were prepared (78−82%) by following the reported[32] procedure as shown in Scheme 8. Heating **32** (5 mmol) with hexamethyldisilazane (HMDS) (25 mmol) in the presence of freshly crystallized imidazole (8 mmol) produced[33] enol silanes **33a** (80%) and **33b** (76%), respectively. Usual PET activation of **33a** as well as **33b**. in an identical manner as described for **15a**, gave spirocyclic compounds **34a** (71%) and **34b** (69%), respectively (Scheme 8). These compounds were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectral data.

Scheme 8[a]



34a: 6'methoxyspiro[cyclohexane-1,1'-(2',3'-dihydro indene)-2,6-dione
34b: 6'-methoxyspiro[cyclohexane-1,1'-(3',4'-dihydro-2'H-naphthalene)]-2,6-dione

[a] Reagents: (a) *t*-BuLi, THF, −78 °C; (b) $Ar(CH_2)_nBr$ (**31**); (c) acetone, HCl, reflux; (d) HMDS, ImH, reflux; (e) *hν*, DCN, CH_3CN.

In conclusion, we have developed a new intramolecular α-arylation strategy of ketones by the reaction of silyl enol ethers with the PET-generated arene radical cations.

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This strategy has provided an easy and novel approach for constructing the five-, six-, seven-, and eight-membered benzannulated products as well as benzospiroannulated compounds.

Experimental Section

Reactions were monitored by thin-layer chromatography (TLC) or gas chromatography (GC). All yields reported refer to isolated material. Temperatures above and below ambient temperature refer to bath temperatures unless otherwise stated. Solvents and anhydrous liquid reagents were dried according to established procedures by distillation under argon atmosphere from the appropriate drying agent. Reagents were procured from Aldrich Chemical Co. and SD Fine Chemicals, India. Column chromatography was performed using silica gel (100−200 mesh, SD fine Chemicals, India) by standard chromatographic techniques. All nuclear magnetic resonance spectra were recorded on either 200 MHz FT NMR or 300 MHz NMR spectrometers using $CDCl_3$ as solvent. IR spectra were taken on an FT-IR instrument. Mass spectra were obtained at a voltage of 70 eV. Melting points (mp) were measured were uncorrected.

General Procedures for the Synthesis of Starting Ketones. Ketones **14** were prepared by the hydrogenation of **13** in 92−96% yields. A representative experimental detail for **14a** is described below.

4-(4-Methoxyphenyl)butan-2-one (14a). Compound **13a** (5 g, 28 mmol) was quantitatively hydrogenated in anhydrous ethanol using 10 mg of 10% Pd on activated carbon at rt at 60 psi of H_2 pressure. Reaction was stopped when the consumption of H_2 ceased. The catalyst was filtered off, and the solution was concentrated under reduced pressure. Flash chromatography purification over silica gel with EtOAc/petroleum ether (15:85) as eluent gave **14a** as a pale yellow oil. Yield: 4.8 g, 90%. IR (neat): 2935, 1716, 1612, 1514, 1247, 1035, 910 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.15 (d, 2H, J = 9.52 Hz), 6.85 (d, 2H, J = 9.52 Hz), 3.75 (s, 3H), 2.70−2.85 (m, 4H), 2.20 (s, 3H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 207.73, 158.30, 133.32, 129.45, 114.15, 55.25, 45.41, 30.03, 29.10. MS (*m*/*e*): 178 (M^+), 163 (5), 135 (13), 121 (100), 108 (17), 91 (25), 77 (19), 65 (13).

4-(3,4-Dimethoxyphenyl)butan-2-one (14b). Yield: 84%. IR (neat): 2937, 1716, 1591, 1456, 1236, 1028, 912 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.65−6.80 (m, 3H), 3.85 (s, 3H), 2.65−2.90 (m, 4H), 2.15 (s, 3H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 208.01, 149.15, 147.64, 133.89, 120.30, 112.09, 111.72, 56.09, 55.99, 45.47, 30.16, 29.55. MS (*m*/*e*): 208 (M^+), 193 (5), 165 (57), 151 (100), 135 (15), 119 (17), 107 (26), 91 (25), 77 (25), 65 (15).

Ketones **21** were prepared by the alkylation of acetone dimethylhydrazone **19** using the corresponding phenyl alkyl bromides **20**. A representative experimental procedure for **21a** is described below.

5-(4-Methoxyphenyl)pentan-2-one (21a). To a previously dried 250 mL round-bottom flask equipped with a magnetic stirring bar and argon gas balloon was added **19** (1.5 g, 15 mmol) in 50 mL of anhydrous THF. The flask was cooled to −78 °C, and *n*-butyllithium (2.20 M in hexane, 6.80 mL) was added (the mixture turned red). After 30 min, **20a** (3.23 g, 15 mmol) in THF (50 mL) was added. The reaction mixture was warmed to ambient temperature, quenched with 20 mL of aqueous NH_4Cl solution, and diluted with ethyl acetate (50 mL). The organic layer was washed with water (3 × 100 mL) and brine (100 mL), concentrated by rotatory evaporation, and then taken into 50 mL of MeOH. To this solution were added 5 mL of phosphate buffer (pH = 7) solution (Na_2HPO_4/NaH_2PO_4) and $NaIO_4$ (6.50 g, 31 mmol) in 10 mL of water and stirred for 30 min at rt. The reaction mixture was concentrated and then dissolved in ethyl acetate, washed with water (20 mL), dried, and concentrated. Column chromatography (eluting with (10:80) ethyl acetate/petroleum ether) gave 2.54 g (84%) of **21a** as pale yellow oil. IR (neat): 2945, 1720, 1610, 1510 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.1 (d, 2H, J = 9.8 Hz), 6.7 (d, 2H, J = 9.80 Hz), 3.75 (s, 3H), 2.55 (t, 2H, J = 7.5 Hz), 2.40 (t, 2H, J = 7.5 Hz), 2.10 (s, 3H), 1.85 (m, 2H).

5-(3,4-Dimethoxyphenyl)pentan-2-one (21b). Yield: 80%. Viscous liquid. IR (neat): 2900, 1710, 1515, 1580, 1515, 1420, 1360, 1260, 1160, 1020 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.60−6.75 (m, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 2.65 (t, 2H, J = 7.5 Hz), 2.45 (t, 2H, J = 7.5 Hz), 2.20 (s, 3H), 1.90 (m, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 208.54, 149.23, 147.63, 134.52, 120.54, 112.25, 111.78, 56.02, 42.89, 34.79, 29.95, 25.57.

5-(3,4,5-Trimethoxyphenyl)pentan-2-one (21c). Yield: 80%. Viscous liquid. IR (neat): 2945, 2262, 1700, 1612, 1510 1045, 950 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.45 (s, 2H), 3.90 (s, 6H), 3.85 (s, 3H), 2.65 (t, 2H, J = 7.42 Hz), 2.45 (t, 2H, J = 7.42 Hz), 2.20 (s, 2H), 1.85 (m, 2H).

6-(3,4-Dimethoxyphenyl)hexan-2-one (21d). Yield: 82%. Viscous liquid. IR (neat): 2920, 1710, 1590, 1500, 1440, 1420, 1355, 1260, 1160, 1030, 850, 800, 770, 740 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.75 (m, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 2.55 (t, 2H, J = 7.25 Hz), 2.45 (t, 2H, J = 7.25 Hz), 2.10 (s, 3H), 1.50 (m, 4H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 208.38, 148.58, 146.89, 134.57, 119.91, 111.60, 111.15, 55.55, 55.45, 43.06, 34.94, 30,71, 29.36, 23.07. MS (*m*/*e*): 236 (M^+), 178 (15), 163 (12), 151 (100), 137 (15), 121 (16), 107 (24), 91 (26), 77 (30).

Preparation of 32. This is illustrated by taking **32a** as an example.

2-[(4′-Methoxyphenyl)ethyl]-1,3-cyclohexanedione (31a). To a solution of *t*-BuLi (1.6 M in *n*-pentane, 9.7 mL, 1.11 equiv) at −78 °C was added 1,5-dimethoxy-1,4-cyclohexadiene[31] 1.98 g (14 mmol) dissolved in THF (80 mL). The resultant solution was stirred at −78 °C for 1 h. HMPA (1.2 equiv, freshly distilled from $LiAlH_4$) was added, and stirring was continued for an additional 10 min. Addition of 2-(4-methoxyphenyl)-ethyl bromide (3.87 g, 18 mmol, 1.31 equiv, freshly filtered through a short column of neutral alumina) dissolved in THF (10 mL) to the flask resulted in an immediate change in the color of the reaction mixture (maroon to light brown). The reaction mixture was allowed to warm to room temperature, diluted with 5 mL of brine, and then extracted three times with 50 mL portions of pentane. The combined pentane extracts were washed twice with brine and dried over $MgSO_4$. Removal of the solvent followed by concentration at reduced pressure gave a thick pale yellow oil product, which was subsequently dissolved in acetone (20 mL of spectrograde, previously purged with a stream of N_2 for 15 min). To this solution was added 1 N hydrochloric acid (4 mL) with vigorous stirring, and the contents were allowed to stir for an additional 1 h. The acetone was removed under reduced pressure, the residue was diluted with 10 mL of brine, and the mixture was extracted four times with 10 mL portions of CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$. Removal of the solvent afforded (2.82 g, 82%) of 2-[(4′-methoxyphenyl)ethyl]-1,3-cyclohexanedione as a white solid. Mp: 142−143.5 °C. IR ($CHCl_3$): 2960, 2230, 1650, 1620, 1520, 1480, 1385, 1260, 1240, 1200, 1160, 930 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.15 (d, 2H, J = 9.47 Hz), 6.85 (d, 2H, J = 9.47 Hz), 5.35 (s, 1H), 4.00 (t, 2H, J = 7.37 Hz), 3.80 (s, 3H), 3.00 (t, 2H, J = 7.37 Hz), 2.35 (m, 4H), 1.95 (m, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 199.78, 177.88, 158.60, 129.99, 129.61, 114.15, 102.98, 69.29, 55.37, 36.88, 34.24, 29.12, 21.33.

2-[3′-(Methoxyphenyl)propyl]-1,3-cyclohexanedione (31b). Yield: 78%. White solid. Mp: 154 °C. IR ($CHCl_3$): 2960, 1650, 1500, 1460, 1440, 1380, 1260, 1240, 1190, 1050, 920 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.25 (dd, J = 9.75 Hz, 1H), 6.75 (m, 3H), 5.35 (s, 1H), 3.90 (t, J = 7.31 Hz, 2H), 3.80 (s, 3H), 2.70 (t, J = 7.31 Hz, 2H), 2.40 (m, 4H), 2.00 (m, 4H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 199.35, 177.88, 159.68, 142.30, 129.24, 120.54, 114.10, 111.20, 102.49, 67.42, 54.85, 36.48, 31.88, 29.71, 29.79, 21.01. MS (*m*/*e*): 260 (M^+), 228 (3), 208 (4), 166 (26), 148 (10), 135 (9), 122 (100), 107 (14), 91 (41), 84 (25), 77 (28), 55 (56).

General Procedures for the Preparation of Enol Silyl Ethers of Ketones (24a and 22a). Kinetic Enolization. To a stirred solution of 15 mmol of LDA at −78 °C was added dropwise a solution of ketone, for example, **21a** (2.8 g, 15

mmol) in 20 mL of anhydrous THF. After the addition of the substrate was complete, the reaction mixture was stirred for an additional 20 min at −78 °C. TBDMSCl (2.25 g, 15 mmol) in 20 mL of THF was slowly introduced into the flask. The reaction mixture was warmed to room temperature with continued stirring for 3 h. Pentane (100 mL) was added, and the precipitated LiCl was removed by filtration through Celite. Concentration in vacuo followed by distillation under reduced pressure (85 °C/4 mmHg) gave the kinetic silyl enol ether **24a** (93%) essentially as a single regioisomer.

Thermodynamic Enolization. To a 100 mL round-bottom flask containing a stirring solution of ketone **21a** (2.8 g, 15 mmol) in DMF (50 mL) and ImH (2.10 g, 31 mmol) was introduced TBDMSCl (2.25 g, 15 mmol) dissolved in 20 mL of DMF. The contents were refluxed for 48 h. On cooling, it was diluted with ether (100 mL) and washed with cold saturated $NaHCO_3$ solution. The aqueous phase was reextrated with ether, and the combined organic extracts were washed rapidly and successively with dilute HCl (20 mL), saturated $NaHCO_3$ solution (20 mL), and water. After drying and concentration, distillation of the residue under reduced pressure gave the thermodynamically stable enol silyl ether **22a** in an overall yield of 80%.

General Irradiation Procedure. A typical photochemical reaction involved the irradiation of a mixture of silyl enol ethers (2 mmol) and DCN (0.06 g, 0.34 mmol) in 500 mL of CH_3CN/H_2O (4:1) for 3−4 h through Pyrex-filtered light (>280 nm, all light absorbed by enol ether only) using a 450 W Hanovia lamp without removing the dissolved oxygen. Removal of the solvent and silica gel (60−120 mesh) column chromatographic purification of the reaction mixture gave carbocyclic and spirocyclic products. The chemical purity of cyclized products was confirmed by GC analysis (methyl silicone, 25 m, 0.53 mm). DCN was recovered quantitatively (98%) at the end of the reaction.[13] During the irradiation of silyl enol ethers, a minor quantity (∼10−15%) of starting ketones were also formed, which have been shown to be formed by the thermal reversion of the enol silyl ethers by adequate control experiments.

7-Methoxy-1,2,3,4-tetrahydronaphthalen-2-one (18a). Yield: 72%. Viscous liquid. IR (neat): 2949, 1716, 1612, 1504, 1261, 1037, 732 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.05 (d, 1H, J = 9.75 Hz), 6.75 (dd, J_1 = 9.75 Hz, J_2 = 2.53 Hz, 1H), 6.60 (bs, 1H), 3.75 (s, 3H), 3.50 (s, 2H), 2.90 (t, J = 7.31 Hz, 2H), 2.45 (t, J = 7.31 Hz, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 210.23, 158.39, 134.24, 128.46, 128.20, 113.37, 112.16, 54.98, 44.76, 38.23, 27.20. HRMS (EI): 176.0836, (calcd for $C_{11}H_{12}O_2$ 176.0837. MS (*m*/*e*): 176 (M^+), 161 (5), 147 (10), 134 (100), 103 (17), 91 (25), 77 (17).

6,7-Dimethoxy-1,2,3,4-tetrahydronaphthalen-2-one (18b). Yield: 74%. Viscous liquid. IR ($CHCl_3$): 2939, 1716, 1510, 1514, 1465, 1338, 1247, 912 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.75 (s, 1H), 6.60 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.50 (s, 2H), 3.00 (t, J = 7.32 Hz, 2H), 2.55 (t, J = 7.32 Hz, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 209.92, 148.19, 147.99, 128.57, 125.26, 111.96, 111.67, 56.08, 44.03, 38.41, 28.09. HRMS (EI): 206.0937, calcd for $C_{12}H_{14}O_3$ 206.0942. MS (*m*/*e*): 206 (M^+), 191 (5), 178 (13), 164 (55), 147 (13), 135 (17), 121 (25), 107 (40), 91 (34).

1-(6-Methoxy-2,3-dihydro-1*H*-1-indenyl)-1-ethanone (23a). Yield: 70%. Viscous liquid. IR (neat): 2950, 1710, 1610, 1500, 1160 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.20 (d, J = 9.75 Hz, 1H), 6.80 (dd, J_1 = 9.75 Hz, J_2 = 2.80 Hz, 1H), 6.75 (s, 1H), 5.75 (t, J = 6.94 Hz, 1H), 3.80 (s, 3H), 2.75 (t, J = 7.31 Hz, 2H), 2.30−2.20 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 206.23, 158.07, 137.66, 128.23, 112.56, 109.97, 62.04, 55.20, 31.45, 28.18, 25.82. HRMS (EI): 190.0996, calcd for $C_{12}H_{14}O_2$ 190.0994. MS (*m*/*e*): 190 (M^+), 174 (68), 159 (100), 144 (38), 128 (46), 115 (51), 103 (13), 91 (23), 77 (19).

1-(5,6-Dimethoxy-2,3-dihydro-1*H*-1-indenyl)-1-ethanone (23b). Yield: 70%. Viscous liquid. IR (neat): 2930, 1710, 1590, 1495, 1250, 1150 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.80 (s, 1H), 6.70 (s, 1H), 5.75 (t, J = 6.94 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.70 (t, J = 7.32 Hz, 2H), 2.20 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 206.26, 148.35, 146.99, 136.33, 132.43, 110.18, 109.52, 62.04, 55.65, 54.78, 30.43, 26.95, 22.65. HRMS (EI): 220.1102, calcd for $C_{13}H_{16}O_3$ 220.1099. MS (*m*/*e*): 220 (M^+), 204 (100), 189 (74), 173 (15), 161 (16), 146 (15), 121 (20), 115 (40), 91 (20), 77 (18).

3-Methoxy-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cyclohepten-6-one (25a). Yield: 65%. Viscous liquid. IR (neat): 2940, 2260, 1700, 1610, 1500, 1050, 940 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.05 (d, 1H, J = 10 Hz), 6.70 (s, 1H), 6.65 (d, J = 10 Hz, 1H) 3.75 (s, 3H), 3.65 (s, 2H), 2.90 (t, 2H, J = 7.5 Hz), 2.55 (t, 2H, J = 7.5 Hz), 2.05 (m, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 208.95, 159.01, 141.81, 130.39, 125.64, 115.35, 111.56, 55.21, 49.19, 43.54, 33.25, 26.23. HRMS (EI): 190.1017, calcd for $C_{12}H_{14}O_2$ 190.0994. MS (*m*/*e*): 190 (M^+), 176 (4), 162 (24), 147 (22), 134 (100), 115 (11), 105 (18), 91 (49), 77 (39).

2,3-Dimethoxy-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cyclohepten-6-one (25b). Yield: 74%. Viscous liquid. IR (neat): 2950, 1700, 1615, 1520, 1460, 1360, 1270, 1120 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.75 (s, 1H), 6.70 (s, 1H), 3.90 (d, 6H, J = 4 Hz), 3.65 (s, 2H), 2.90 (t, 2H, J = 7.5 Hz), 2.55 (t, 2H, J = 7.5 Hz), 2.00 (m, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 208.97, 148.12, 147.79, 132.93, 125.48, 113.51, 113.24, 56.21, 55.91, 49.81, 44.05, 32.95, 26.93. HRMS (EI): 220.1118, calcd for $C_{13}H_{16}O_3$ 220.1099. MS (*m*/*e*): 220 (M^+), 192 (27), 177 (51), 164 (72), 149 (51), 121 (60), 107 (68), 91 (74), 77 (78).

1,2,3-Trimethoxy-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cyclohepten-6-one (25c). Yield: 72%. IR (neat): 2938, 1706, 1492, 1410, 1120 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.9−2.05 (m, 2H), 2.5−2.6 (t, 2H, J = 7.5 Hz), 2.8−2.9 (t, 2H, J = 7.5 Hz), 3.75 (s, 2H), 3.8−3.9 (m, 9H), 6.5 (s, 1H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 209.69, 152.35, 151.59, 141.21, 136.49, 119.90, 108.96, 61.57, 61.05, 56.23, 43.40, 41.47, 33.34, 26.67. HRMS (EI) 250.1198, calcd for $C_{14}H_{18}O_4$ 250.1205. MS (*m*/*e*): 250 (M^+), 219 (7), 190 (43), 161 (27), 147 (22), 134 (100), 105 (57), 91 (70), 77 (72).

2,3-Dimethoxy-6,7,8,9,10-pentahydro-5*H*-benzo[*a*]cycloocten-7-one (27). Yield: 70%. Mp: 86 °C. IR ($CHCl_3$): 3040, 2960, 1700, 1620, 1530, 1450, 1230, 1120 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.65 (s, 1H), 6.70 (s, 1H), 3.85 (d, 6H), 3.70 (s, 2H), 2.80 (t, 2H, J = 5.5 Hz), 2.35 (t, 2H, J = 5.5 Hz), 1.80 (m, 4H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 211.76, 148.68, 147.69, 133.13, 125.63, 113.38, 113.15, 56.03, 48.20, 41.12, 32.95, 31.33, 24.71. HRMS (EI): 234.1229, calcd for $C_{14}H_{18}O_3$ 234.1255. MS (*m*/*e*): 234 (100, M^+), 206 (63), 191 (54), 175 (68), 165 (46), 151 (24), 131 (24), 121 (44), 107 (37), 91 (49).

6′-Methoxyspiro[cyclohexane-1,1′-(2′,3′-dihydroindene)]-2,6-dione (34a). Yield: 71%. IR (neat): 3020, 2940, 1700, 1600, 1430, 1320, 1250, 1210, 1080, 1020 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.10 (d, J = 9.80 Hz, 1H), 6.75 (m, 2H), 3.80 (s, 3H), 3.05 (t, J = 7.50 Hz, 2H), 2.85 (m, 4H), 2.60 (t, J = 7.5 Hz, 2H), 2.15 (m, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 207.34, 160.19, 146.70, 132.52, 125.21, 112.89, 110.48, 77.89, 55.47, 38.38, 31.66, 17.85. HRMS (EI): 244.1068, calcd for $C_{15}H_{16}O_3$ 244.1099. MS (*m*/*e*): 244 (M^+), 162 (15), 141 (3), 127 (4), 111 (7), 97 (13), 91 (15), 85 (36), 71 (60), 57 (100).

6′-Methoxyspiro[cyclohexane-1,1′-(3′,4′-dihydro-2′*H*-naphthalene)]-2,6-dione (34b). Yield: 69%. IR (neat): 2950, 1720, 1700, 1620, 1510, 1480, 1250, 1180, 1120, 920, 740. cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ: 6.70 (m, 2H), 6.50 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.05−2.85 (m, 2H), 2.80−2.65 (m, 4H), 2.30−2.15 (m, 2H), 2.10−1.90 (m, 2H), 1.70−1.85 (m, 2H). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 209.85, 158.38, 139.64, 131.30, 125.31, 113.41, 112.59, 70.66, 55.04, 38.06, 34.14, 29.47, 18.88, 17.55. HRMS (EI): 258.1208, calcd for $C_{16}H_{18}O_3$ 258.1256. MS (*m*/*e*): 258 (M^+), 174 (100), 159 (28), 126 (15), 115 (22), 91 (15), 84 (86), 71 (22), 55 (61).

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