Chemoselectivity in the Michael Addition of Silyl Enol Ethers in Lithium Perchlorate–Diethyl Ether Medium. Evidence for Facile Silyl Group Transfer to Michael Acceptors

V. Geetha Saraswathy and S. Sankararaman*

Department of Chemistry, Indian Institute of Technology, Madras - 600 036, India

Received January 17, 1995[⊗]

The silyl enol ethers from cyclohexanone and cyclopentanone underwent efficient 1,4-addition to β-nitro- and β,β-dicyanostyrenes in 5 M lithium perchlorate/diethyl ether (LPDE) at ambient temperature to give the corresponding Michael adducts in good yields and with moderate stereoselectivity. The reaction was found to be highly chemoselective in that α,β-unsaturated carbonyl compounds failed to undergo Michael addition with the silyl enol ethers under identical conditions. The experimental evidence suggests that the mechanism involves transfer of the silyl group from the silyl enol ether to the Michael acceptor. The silyl enol ethers reacted with *p*-benzoquinone in 5 M LPDE to give benzofuran derivatives in good yields. Reaction with chloranil yielded the corresponding O-alkylated products while with DDQ, the corresponding C-alkylated products were obtained in excellent yields and with high regio- and stereoselectivities.

Organic reactions involving polar transition states or intermediates are profoundly influenced by the medium as well as by additives such as salts, as evident from the seminal contribution by Winstein on solvolysis reactions.[1,2] The use of lithium perchlorate in diethyl ether (LPDE) as a medium for synthetic transformations[3] has attracted attention largely due to the enhanced rate and selectivity observed in Diels–Alder and other cycloadditions,[4] Michael additions,[5,6] rearrangements,[7] and aldol condensations.[6] The lithium ion in ether is a mild Lewis acid, and at high concentration it can act as an effective catalyst. Thus the LPDE medium not only imparts selectivity but also offers the convenience of carrying out the reactions under essentially neutral reaction and workup conditions. Recently, we have reported the chemoselective conversion of aldehydes and acetals to dithioacetals in 5 M LPDE.[8] Our continued interest in exploiting this medium for selective synthetic transformations has resulted in the investigation of Michael addition reactions of silyl enol ethers. Grieco[5] has reported the conjugate addition of ketene silyl acetals to hindered α,β-unsaturated carbonyl compounds in LPDE, which are otherwise difficult to do under standard Lewis acid catalyzed (Mukaiyama–Michael reaction[9]) conditions. In this paper we wish to report our findings on the chemo- and stereoselectivity of Michael additions involving silyl enol ethers.

Results and Discussion

The reactions were carried out in 5 M LPDE using 1-[(trimethylsilyl)oxy]cyclopentene (**1**) and 1-[(trimethylsilyl)oxy]cyclohexene (**2**) as the Michael donors.

Reaction of silyl enol ethers **1** and **2** with various β-nitro- and β,β-dicyanostyrenes **3** (2 equiv) in 5 M LPDE afforded the corresponding Michael adducts **5** and **6**, respectively, in good yields and modest diastereoselectivity (Table 1). α,β-Unsaturated carbonyl compounds are conventional Michael acceptors, and addition of enolates or silyl enol ethers provides a convenient method for the synthesis of 1,5-dicarbonyl compounds.[10] However, attempted Michael reactions between enol ether **2** (or **1**) and acceptors such as benzalacetone (**3g**), 3-benzylideneacetylacetone (**3h**), benzalacetophenone (**3i**), and cyclohex-2-enone (**3j**) in 5 M LPDE yielded only cyclohexanone (or cyclopentanone) and in all these cases the Michael acceptor remained intact.

Quinones are more powerful Michael acceptors than α,β-unsaturated carbonyl compounds. Addition of silyl enol ethers to quinones under Lewis acid catalyzed conditions is known to yield fused benzofuran derivatives by a sequence involving Michael addition followed by cyclization.[11,12] The alkylation of quinones with allylsilanes[13] and ketene silyl acetals[14] have been reported in LPDE medium. Addition of **1** (2 mmol) to a solution of

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1995.

(1) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988; pp 121–281. Isaacs, N. S. *Physical Organic Chemistry*; ELBS Longman: Essex, 1987; Ch. 5, pp 171–209.

(2) Winstein, S. *Quart. Rev.* **1969**, *23*, 141. Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597. Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169.

(3) Grieco, P. A. *Aldrichimica Acta* **1991**, *24*, 61. Waldmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1306.

(4) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595. Forman, M. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 2761. Fohlisch, B.; Krimmer, D.; Gehrlach, E.; Kashammer, D. *Chem. Ber.* **1988**, *121*, 1585. Srisiri, W.; Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* **1993**, *58*, 4185. Grieco, P. A.; Handy, S. T.; Beck, J. P. *Tetrahedron Lett.* **1994**, *35*, 2663.

(5) Grieco, P. A.; Cooke, R. J.; Henry, K. J., Jr.; VanderRoest, J. M. *Tetrahedron Lett.* **1991**, *32*, 4665.

(6) Reetz, M. T.; Fox, D. N. A. *Tetrahedron Lett.* **1993**, *34*, 1119. Ipaktschi, J.; Heydari, A. *Chem. Ber.* **1993**, *126*, 1905.

(7) Grieco, P. A.; Clark, J. D.; Jagoe, C. T. *J. Am. Chem. Soc.* **1991**, *113*, 5488. Grieco, P. A.; Collins, J. L.; Henry, K. J., Jr. *Tetrahedron Lett.* **1992**, *33*, 4735. Palani, N.; Balasubramanian, K. K. *Tetrahedron Lett.* **1993**, *34*, 5001.

(8) Geetha Saraswathy, V.; Sankararaman, S. *J. Org. Chem.* **1994**, *59*, 4665.

(9) Mukaiyama, T. In *Challenges in Organic Synthesis*; Baldwin, J. E., Ed.; Clarendon Press: Oxford, 1990; p 177. Mukaiyama, T. *Org. React.* **1982**, *28*, 203. Mukaiyama, T.; Murakami, M. *Synthesis* **1987**, 1043.

(10) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin Cummings: Menlo Park, 1972, pp 595–621. Jung, M. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press, New York, 1991; Vol. 4, pp 1–67.

(11) Finley, K. T. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; John Wiley: New York, 1974; Vol. 2, p 877.

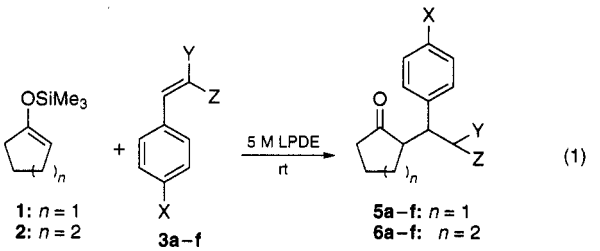
(12) Mukaiyama, T.; Sagawa, Y.; Kobayashi, S. *Chem. Lett.* **1987**, 2169.

(13) Ipaktschi, J.; Heydari, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 313.

(14) Ipaktschi, J.; Heydari, A. *Chem. Ber.* **1992**, *125*, 1513.

0022-3263/95/1960-5024$09.00/0

Table 1. Michael Addition of Silyl Enol Ethers to β-Nitro- and β,β-Dicyanostyrenes in 5 M LPDE

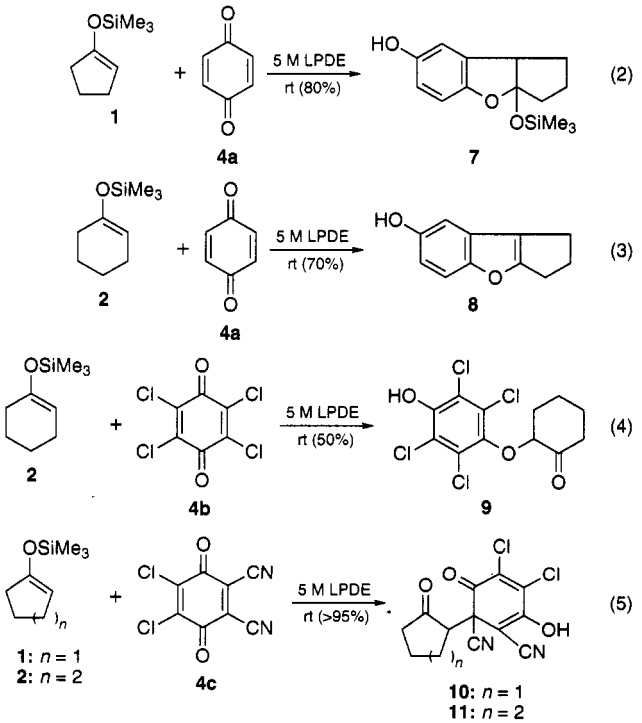


(1)

donor		acceptor X	Y	Z	product	reaction time	yield[a] (%)	ratio of diastereomers[b]
1	**3a**	H	NO_2	H	**5a**	15 min	85	2.0:1
2	**3a**				**6a**	45 min	85	1.6:1
1	**3b**	Cl	NO_2	H	**5b**	15 min	85	1.8:1
2	**3b**				**6b**	45 min	65	1.6:1
1	**3c**	Me	NO_2	H	**5c**	45 min	79[c]	1.6:1
2	**3c**				**6c**	4 h	75[c]	2.5:1
1	**3d**	OMe	NO_2	H	**5d**	60 min	75[c]	2.0:1
2	**3d**				**6d**	14 h	68[c]	1.3:1
1	**3e**	H	CN	CN	**5e**	2 h	85	3.5:1
2	**3e**				**6e**	3 h	80	2.0:1
1	**3f**	NO_2	CN	CN	**5f**	1 h	84	2.0:1
2	**3f**				**6f**	3 h	78	2.0:1

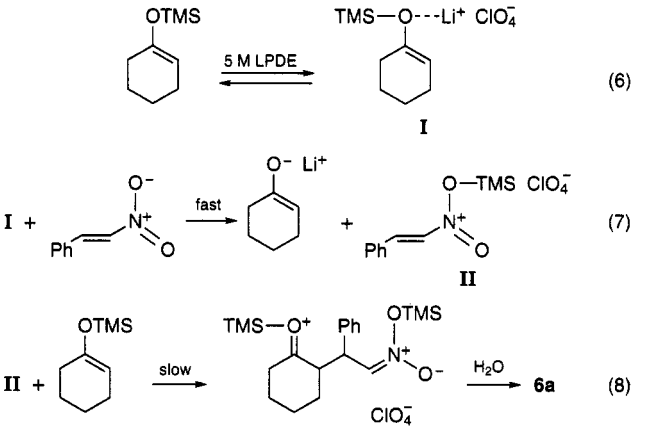
[a] Isolated yield (%) of the product. [b] From the integration of the 400 MHz ^{1}H-NMR spectrum. [c] With 3 equiv of the donor.

4a (2 mmol) in 5 M LPDE yielded **7** in 80% yield as a colorless crystalline solid (eq 2), while the reaction of **2** with **4a** gave **8** in 70% yield (eq 3). The solubility of chloranil (**4b**) was poor in 5 M LPDE solution and reaction with **2** yielded the O-alkylated product **9** in 50% yield after 2h, based on the unrecovered chloranil (eq 4). DDQ (**4c**) reacted with **1** and **2** in 5 M LPDE and within 15 min yielded the corresponding C-alkylated products **10** and **11**, respectively, in nearly quantitative yields (eq 5).



Mechanism of Michael Addition of Silyl Enol Ethers to β-Nitro- and β,β-Dicyanostyrenes in LPDE. The Michael additions described above for the nitro- and cyanostyrenes required a minimum of 2 equiv of the silyl enol ether to obtain the Michael adducts in good yields. When only 1 equiv of the silyl enol ether was used, rapid desilylation occurred within 10 min to yield the corresponding carbonyl compound and the unreacted Michael acceptor, after aqueous workup. It must be emphasized that the silyl enol ethers **1** and **2**, in the absence of Michael acceptor, were quite stable in 5 M LPDE for several hours.

Scheme 1



The generally accepted mechanism for the Lewis acid-catalyzed Michael addition of silyl enol ethers to Michael acceptors involves the complexation of the Lewis acid to the Michael acceptor followed by the 1,4-addition of the silyl enol ether.[15,16] The above mechanism requires only 1 equiv of the silyl enol ether. Lithium ion is a mild Lewis acid in ether and it shows enhanced selectivity compared to the conventional Lewis acids such as BF_3 and $TiCl_4$.[8] In the present study, for the Michael addition of the nitro- and cyanostyrenes we propose a mechanism (Scheme 1) involving an initial complexation of the silyl enol ether to the lithium ion (eq 6). Evidence for such complexation comes from IR spectroscopic studies. Thus, the C=C stretching frequency of the silyl enol ether **2**, which appears at 1667 cm^{-1} in ether, is shifted to 1660 cm^{-1} in 5 M LPDE, consistent with the coordination of the lithium ion to the oxygen of the silyl enol ether. Such a complexation would make the silyl enol ether a poor Michael donor, but desilylation would be facilitated. Such Lewis acid-mediated desilylation of silyl enol ether has been observed previously by NMR spectroscopy from **1** using $TiCl_4$ as the Lewis acid.[17] In contrast, it has been found from IR spectroscopic studies that the nitro stretching frequencies in β-nitrostyrene (**3a**) are not affected by the lithium ion in LPDE. Thus the nitro stretching frequencies of **3a** which appear at 1522 and 1322 cm^{-1} in ether remained unchanged in 5 M LPDE at 1520 and 1324 cm^{-1}, respectively. Similarly, in the case of β,β-dicyanostyrene, the cyano stretching frequency remained unchanged at 2240 cm^{-1} in both ether and in 5 M LPDE. We attribute the mild Lewis acidity of lithium ion for the

(15) Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Chem. Lett.* **1986**, 1017. Miyashita, M.; Yanami, T.; Kumazawa, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1984**, *106*, 2149. For an electron transfer mechanism involving ketene silyl acetal and Lewis acid-coordinated Michael acceptor see Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **1991**, *113*, 4028.

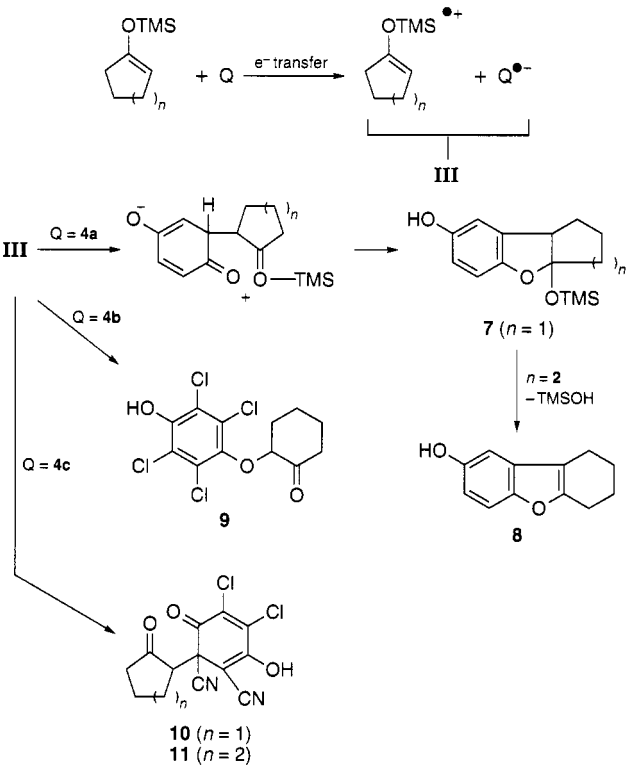
(16) Seebach, D.; Brook, M. A. *Helv. Chim. Acta* **1985**, *68*, 319. Brook, M. A.; Seebach, D. *Can. J. Chem.* **1987**, *65*, 836. Blarer, S. J.; Schweizer, W. B.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 1637.

(17) Nakamura, E.; Shimada, J -i.; Horiguchi, Y.; Kuwajima, I. *Tetrahedron Lett.* **1983**, *24*, 3341.

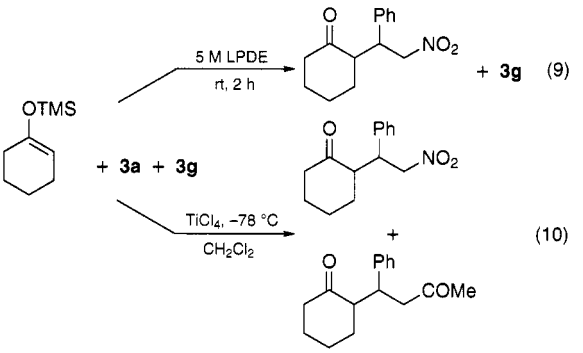
chemoselective complexation in that it complexes with the most basic of the substrates among the silyl enol ether and the nitro- and cyanostyrenes. On the basis of these IR spectroscopic studies and other experimental observations (*vide infra*), we propose the mechanism depicted in Scheme 1. We presume that the lithium enolate which is the product of desilylation does not further undergo Michael reaction because its nucleophilicity in 5 M LPDE medium is highly reduced due to ion pairing. The decrease in the nucleophilicity of carbanions due to ion pairing with a cation, especially such as Li^+, is amply demonstrated in the literature.[18] Addition of a 1:1 mixture of **1** (1 mmol) and **2** (1 mmol) to **3a** (1 mmol) in 5 M LPDE yielded a 2.5:1 mixture of adducts **5a** and **6a**. In another experiment **1** and **2** (1 equivalent of each) were added in sequence. Thus, to a stirred solution of **3a** (1 mmol) in 5 M LPDE was added silyl ether **1** (1 mmol) and after 10 min, **2** (1.3 mmol) was added and the mixture was stirred for 1 h. The crude product consisted of adducts **5a** and **6a** in the ratio 2.2:1, respectively. When the addition was reversed, namely addition of **2** followed by **1** (1 mmol each) to **3a** (1 mmol) the adducts **5a** and **6a** were formed in the ratio 6.6:1, respectively. These experiments not only show that the desilylation is a rapid step, but also indicate that the first equivalent of the silyl enol ether is consumed in the silyl transfer reaction and that only the second equivalent is used for the actual Michael addition. These experiments also reveal the relative rates of Michael addition of **1** and **2** to **3a** in that the silyl ether **1** adds much faster than **2** as supported by the data in Table 1. Since the desilylation reaction is very rapid when only 1 equiv of the silyl enol ether is used, formation of a mixture of Michael adducts in these reactions implies that the initially formed cycloalkanone enolate equilibrates with the second equivalent of the silyl enol ether.

Unlike nitro- and cyanostyrenes, α,β-unsaturated carbonyl compounds failed to undergo Michael reaction even with excess of the silyl enol ether. From IR spectroscopic studies it is clear that the lithium ion coordinates to the carbonyl oxygen.[8] Although α,β-unsaturated carbonyl compounds are weaker Michael acceptors compared to nitro- and cyanostyrenes, no chemoselectivity is observed in the presence of conventional Lewis acid catalysts such as $TiCl_4$, $Sn(OTf)_2$, or TMSOTf. For example, Mukaiyama–Michael reactions are generally carried out at −78 °C and nitro olefins[16,19] as well as α,β-unsaturated carbonyl compounds[20] react alike with silyl enol ethers to give the corresponding Michael adducts.[12,15] In LPDE, lithium ion being mildly Lewis acidic, it is possible to observe chemoselectivity in the Michael addition. In a competitive experiment carried out with a 1:1 mixture of **3a** and **3g** (1 mmol each) with **2** (3 mmol) only the Michael adduct from **3a**, namely **6a**, was obtained, and **3g** was recovered quantitatively (eq 9). However, when the reaction was carried out with $TiCl_4$ in CH_2Cl_2 at −78 °C no chemoselectivity was observed, both **3a** and **3g** reacted with **2** to give the corresponding Michael adducts

Scheme 2



(eq 10). The more reactive ketene silyl acetal, however, undergoes Michael addition to α,β-unsaturated ketones in LPDE.[5] These reactions have been reported to require an excess of the ketene silyl acetal, presumably, due to competing desilylation in LPDE.



Mechanism of Reaction of Silyl Enol Ethers with Quinones. Quinones are known to form electron donor–acceptor (EDA) complexes[21] and undergo electron transfer reaction with silyl enol ethers.[21,22] Evidence for the formation of the EDA complexes in the present study comes from the observation of transient colors during the addition of the silyl enol ether to the quinones in LPDE. The observed products (**9**–**11**, eqs 4, 5) are reminiscent of the products arising from the charge transfer photochemistry of **4b** with **2**.[22] The LPDE medium should favor formation of the ion radical intermediates arising from an initial electron transfer from the silyl enol ethers to the quinones, and the formation of the products can be explained on the basis of the radical pair coupling reactions as depicted in Scheme 2. It must be empha-

(18) Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; John Wiley: New York, 1975; pp 96–132. The reactivity of carbanion is reduced due to the formation of triple ions and ion aggregates with $LiClO_4$. See Jackman, L. M.; Lange, B. C. *Tetrahedron* **1977**, *33*, 2737. Reutov, O. A.; Kurts, A. L. *Russ. Chem. Rev.* **1977**, *46*, 1040.

(19) Stevens, R. W.; Mukaiyama, T. *Chem. Lett.* **1985**, 855.

(20) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1993**, *58*, 2647, Narasaka, K.; Soai, K.; Aikawa, T.; Mukaiyama, T. *Bull. Chim. Soc. Jpn.* **1976**, *49*, 779, Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Chem. Lett.* **1986**, 1017.

(21) Bhattacharya, A.; DiMichele, L. M.; Dolling, U.-H.; Grabowski, E. J. J.; Grenda, V. J. *J. Org. Chem.* **1989**, *54*, 6118.

(22) Bockman, T. M.; Perrier, S.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2*, **1993**, 595.

sized that the Michael addition to the quinones in LPDE requires only 1 equiv of the silyl enol ether unlike the nitro- and cyanostyrene cases. Also the formation of **7** clearly indicates that these reactions do not proceed through a silyl group transfer mechanism.

Conclusions

The Michael addition of silyl enol ethers **1** and **2** to various β-nitro- and β,β-dicyanostyrenes have been carried out in 5 M LPDE at ambient temperature under essentially neutral reaction and workup conditions to yield the corresponding adducts in good yields but low to moderate diastereoselectivity. α,β-Unsaturated carbonyl compounds failed to undergo Michael addition under the same conditions. Unlike the conventional Lewis acid catalysts, the LPDE medium can impart high chemoselectivity in the Michael reaction due to the mild Lewis acidity of the lithium ion in ether. The stoichiometry of the reaction and other experimental evidence suggests that 1 equiv of the silyl enol ether is used in the transfer of the silyl group to the Michael acceptor and only the second equivalent is effective in undergoing the Michael addition. Silyl enol ethers **1** and **2** reacted with *p*-benzoquinone in 5 M LPDE to give the corresponding benzofuran derivatives **7** and **8**, respectively, in good yields. Reaction with chloranil yielded the O-alkylated product **9**, while with DDQ, the C-alkylated products **10** and **11** were obtained. Formation of these products is explained by an initial electron transfer step from the silyl enol ether to the quinone followed by the radical coupling of the resulting ion radical pair.

Experimental Section

Materials. Preparation of 5 M LPDE has been described previously.[8] Starting materials **1** and **2**,[23] **3a–d**,[24] **3e–f**,[25] **3g–i**,[26] and **4a**[27] were prepared according to literature procedures and were purified by distillation or recrystallization and characterized by mp, IR, ^{1}H-NMR, and MS data. Ketone **3j** and quinones **4b,c** were commercial samples and were purified by distillation (**3j**) or recrystallization prior to use.

General Procedure for the Michael Addition of Silyl Enol Ethers to β-Nitro- and β,β-Dicyanostyrenes. In a typical experiment β-nitrostyrene (**3a**) (0.26 g, 1.74 mmol) was dissolved in 5 M LPDE (3 mL) under N_2 atmosphere. To the resulting pale yellow solution was added silyl ether **2** (0.6 g, 3.5 mmol) from a syringe, and the mixture was stirred at rt. The reaction was followed by TLC. After 45 min (refer Table 1) the TLC showed the absence of the starting materials. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and cooled in an ice bath, and then ice cold water (10 mL) was added (exothermic!). The aqueous and organic layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was dried over anhyd Na_2SO_4, and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (60–120 mesh) using ethyl acetate and hexane (3:7 v/v) as the eluent to yield **7a** (0.36 g, 1.45 mmol, 85%). The product was further purified by recrystallization from ether and hexane.

The same procedure was adopted for acceptors **3b–f** and **4a–c**. In the case of **3d** 3 equiv of the silyl enol ether (**1** or **2**) were employed, while in the case of **4a–c** only 1 equiv of the silyl enol ether was used to obtain the products in good yields. Compounds **5a** and **5d**,[28] **6a–d**,[16,28] **6e,f**,[29] **8**[30], **9–11**[21,22] are known and in the present study they were characterized by IR, ^{1}H and ^{13}C-NMR, and mass spectroscopic data.

2-[1-(4-Chlorophenyl)-2-nitroethyl]cyclopentanone (5b): yield 0.46 g, 1.7 mmol, 85% from 2 mmol of **3b**; IR (neat) 1742, 1558, 1382 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ isomer I: 7.31 (m, 2H), 7.10 (m, 2H), 5.30 (dd, 1H, *J* = 12.7, 5.4 Hz), 4.65 (dd, 1H, *J* = 12.7, 10.2 Hz), 3.65 (dt, 1H, *J* = 9.28, 5.3 Hz), 2.5–1.5 (m, 7H); isomer II: 7.31 (m, 2H), 7.10 (m, 2H), 4.9 (d of AB quartet, 2H, *J* = 12.9, 9.68, 5.86 Hz), 3.75 (dt, 1H, *J* = 8.8, 5.4 Hz), 2.5–1.5 (m, 7H); ^{13}C-NMR ($CDCl_3$) δ 218.7 (s), 218.1 (s), 136.1 (s), 135.8 (s), 133.7 (s), 133.6 (s), 129.8 (d), 129.3 (d), 129.0 (d), 77.9 (t), 77.0 (t), 51.3 (d), 50.2 (d), 43.4 (d), 43.3 (d), 39.1 (t), 38.5 (t), 28.1 (t), 26.9 (t), 20.4 (t), 20.1 (t); MS (70 eV, EI) *m/z* 269 (6), 267 (12), 235 (15), 233 (34), 222 (23), 220 (60), 208 (32), 194 (52), 192 (100), 179 (22), 177 (32), 127 (25), 125 (54).

2-[1-(4-Methylphenyl)-2-nitroethyl]cyclopentanone (5c): yield 0.3 g, 1.2 mmol, 79% from 1.5 mmol of **3c**; IR (neat) 1731, 1555, 1379 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ isomer I: 7.05 (m, 4H), 5.25 (dd, 1H, *J* = 12.7, 5.37 Hz), 4.67 (dd, 1H, *J* = 12.7, 10.26 Hz), 3.65 (dt, 1H, *J* = 9.3, 5.42 Hz), 1.5–2.5 (m, 7H), 2.3 (s, 3H); isomer II: 7.05 (m, 4H), 5.0 (dd, 1H, *J* = 12.9, 9.0 Hz), 4.93 (dd, 1H, *J* = 12.9, 6.35 Hz), 3.77 (ddd, 1H, *J* = 10.05, 6.35 Hz), 1.5–2.5 (m, 7H), 2.3 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 219.1 (s), 218.6 (s), 137.5 (s), 137.4 (s), 134.7 (s), 134.4 (s), 129.6 (d), 129.5 (d), 128.3 (d), 127.9 (d), 78.4 (t), 77.3 (t), 51.5 (t), 50.5 (t), 43.8 (d), 43.6 (d), 39.2 (t), 38.5 (t), 28.1 (t), 26.9 (t), 21.0 (q), 20.5 (t), 20.2 (t); MS (70 eV, EI) *m/z* 247 (M^+, 9.5), 202 (48), 201 (100), 188 (33), 183 (61), 174 (98), 157 (95), 146 (90), 130 (80), 83 (90); HRMS calcd for $C_{14}H_{17}NO_3$ 247.12082, found 247.11914.

2-(2,2-Dicyano-1-phenylethyl)cyclopentanone (5e): yield 0.5 g, 2.1 mmol, 85% from 2.5 mmol of **3e**; IR (neat) 2256, 1734 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ isomer I: 7.4–7.18 (m, 5H), 5.48 (d, 1H, *J* = 4.4 Hz), 3.2 (dd, 1H, *J* = 10.9, 4.4 Hz), 2.8 (m, 1H), 2.2 (m, 2H), 2.0 (m, 3H), 1.4 (m, 1H); isomer II: 7.4–7.18 (m, 5H), 5.23 (d, 1H, *J* = 11.2 Hz), 3.5 (dd, 1H, *J* = 11.2, 4.4 Hz), 2.8 (m, 1H), 2.1 (m, 2H), 1.9 (m, 3H), 1.45 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 219.6 (s), 219.3 (s), 135.3 (s), 135.0 (s), 129.3 (d), 128.9 (d), 128.4 (d), 128.2 (d), 112.0 (s), 111.8 (s), 49.2 (d), 48.3 (d), 47.2 (d), 46.4 (d), 39.4 (t), 38.4 (t), 29.2 (t), 27.3 (t), 27.0 (d), 26.2 (d), 20.3 (t), 19.7 (t); MS (70 eV, EI) *m/z* 238 (M^+, 6), 173 (30), 155 (26), 145 (58), 129 (38), 119 (58), 117 (45), 91 (100); HRMS calcd for $C_{15}H_{14}N_2O$ 238.1106, found 238.1104.

2-[2,2-Dicyano-1-(4-nitrophenyl)ethyl]cyclopentanone (5f): yield 0.3 g, 1.1 mmol, 84% from 1.3 mmol of **3f**; IR (KBr) 2256, 1740, 1523, 1353 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ isomer I: 8.3 (d, 2H, *J* = 8.8 Hz), 7.6 (d, 2H, *J* = 8.8 Hz), 5.6 (d, 1H, *J* = 4.9 Hz), 3.4 (dd, 1H, *J* = 10.9, 4.6 Hz), 2.82 (dt, 1H, *J* = 7.8, 11.7 Hz), 2.55 (m, 1H), 2.3 (m, 1H), 2.0 (m, 3H), 1.42 (m, 1H); isomer II: 8.26 (d, 2H, *J* = 9 Hz), 7.46 (d, 2H, *J* = 9 Hz), 5.25 (d, 1H, *J* = 11 Hz), 3.7 (dd, 1H, *J* = 10.3, 5.4 Hz), 2.92 (m, 1H), 2.4 (m, 1H), 2.2–1.5 (m, 5H); ^{13}C-NMR ($CDCl_3$) δ 218.5 (s), 148.4 (s), 148.3 (s), 142.4 (s), 142.3 (s), 129.9 (d), 129.7 (d), 124.5 (d), 124.4 (d), 111.9 (s), 111.8 (s), 111.7 (s), 111.5 (s), 49.6 (d), 48.2 (d), 46.8 (d), 46.3 (d), 39.1 (t), 38.4 (t), 29.3 (t), 27.6 (t), 26.7 (d), 26.2 (d), 20.3 (t), 19.8 (t); HRMS calcd for $C_{15}H_{13}N_3O_3$ 283.0956, found 283.0911.

2,3-Dihydro-5-hydroxy-2,3-trimethylene-2-[(trimethylsilyl)oxy]benzofuran (7): yield 0.42 g, 1.6 mmol, 80% from 2 mmol of **4a**; mp 71–72 °C; IR (KBr) 3392, 1612, 1459, 1209 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.4–6.6 (m, 3H), 5.3 (br, s, 1H, D_2O exch), 3.31 (d, 1H, *J* = 8.8 Hz), 2.1 (m, 2H), 1.85 (m, 1H), 1.6 (m, 2H), 1.45 (m, 1H), 0.05 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 152.7 (s), 149.8 (s), 132.0 (s), 122.2 (s), 114.4 (d), 112.1 (d), 108.8 (d),

(23) House, H. O.; Czuba, L. J.; Gall, M.; Olmstaed, H. D. *J. Org. Chem.* **1969**, *34*, 2324.
(24) Worrall, D. E. *Organic Synthesis*; Wiley: New York, 1932; Collect. Vol. I, p 413.
(25) Carson, R. B.; Stoughton, R. W. *J. Am. Chem. Soc.* **1928**, *50*, 2825. Sturz, H. G.; Noller, C. R. *J. Am. Chem. Soc.* **1949**, *71*, 2949.
(26) *Vogel's Text Book of Practical Organic Chemistry*, 5th ed.; ELBS Longman: Essex, 1989; p 1033. McEntee, M. E.; Pinder, A. R. *J. Chem. Soc.* **1957**, 4419.
(27) Vliet, E. B. in ref 28, p 482.
(28) Moorjani, M. C.; Trivedi, G. K. *Ind. J. Chem.* **1978**, *16B*, 405.
(29) Mohamed, M. M.; El Hashash, M. A.; El Naggar, A.; Said, F.; Ali, W. M. *Pak. J. Sci. Ind. Res.* **1980**, *23*, 169, *Chem. Abstr.* **1981**, *95*, 150124u.
(30) Domschke, G. *Z. Chem.* **1964**, *4*, 29. *Chem. Abstr.* **1964**, *60*, 7973g. Zavyalov, S. I.; Kondrateva, G. V.; Gunar, V. I. *Izv. Akad. Nauk. SSSR. Ser. Khim.* **1964**, part II, 2086. *Chem. Abstr.* **1965**, *62*, 7714g.

53.3 (d), 41.1 (t), 33.4 (t), 24.2 (t), 1.3 (q); MS (70 eV, EI) 264 (M^+, 3), 192 (62), 136 (100); HRMS calcd for $C_{14}H_{20}O_3Si$ 264.1181, found 264.1155.

Competitive Michael Addition Reaction. To a solution containing **3a** (0.15 g, 1 mmol) and **3g** (0.15 g, 1 mmol) in 5 M LPDE (5 mL) was added silyl ether **2** (0.51 g, 3 mmol), and the mixture was stirred at ambient temperature for 2 h. The reaction was worked up as described above to yield a crude product (0.63 g) which consisted of the adduct **6a**, unreacted **3g**, and cyclohexanone. The mixture was separated by preparative TLC, and the products were characterized by IR and ^{1}H-NMR spectroscopic techniques and also by TLC comparison with authentic samples. The Michael adduct corresponding to the addition of silyl ether **2** to **3g**, namely 2-[1-(3-oxo-1-phenyl)butyl]cyclohexanone (**6g**), was absent.

The competitive experiment with $TiCl_4$ was performed following the literature procedure.[20] Silyl ether **2** (0.51 g, 3 mmol) was added to a mixture containing $TiCl_4$ (0.57 g, 3 mmol), **3a** (0.15 g, 1 mmol), and **3g** (0.15 g, 1 mmol) in CH_2Cl_2 at −78 °C, and the mixture was stirred for 1 h and worked up. Analysis of the product by TLC, IR, and ^{1}H-NMR revealed the absence of starting materials and formation of the adducts **6a** and **6g** which was further confirmed by comparative TLC using authentic samples.

Acknowledgment. Financial support from CSIR and DST, New Delhi, is gratefully acknowledged. One of us (V.G.S) thanks CSIR, New Delhi, for a Senior Research Fellowship. We thank Mr. K. Sriram for his contributions during the initial stages of this work and the Regional Sophisticated Instrumentation Centre, IIT, Madras, for spectroscopic data. We gratefully acknowledge constructive criticism and valuable suggestions from one of the anonymous referees.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **5b**, **5c**, **5e**, **5f**, and **7** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO950106Q