systems. Entries 4 and 5 illustrate that one-step access to the 12-azasteroid nucleus can be achieved by employing a commercial enamine and readily accessible isocyanates as reaction partners. Entries 3 and 7 demonstrate that various functionalized enamines and isocyanates can also participate effectively in the ring-forming process. The relatively modest yield observed in entry 6 reflects the propensity of the isocyanate derived from cinnamic acid to suffer oligomerization in competition with acylation during reaction with enamines. This side reaction occurred to a lesser extent with some of the other examples as well. The pyridone moieties generated by using the transformation described in this paper are potentially versatile intermediates for synthesis, particularly in terms of their role in facilitating further carbon–carbon bond formation and oxidation level manipulation.[13]

Work is currently underway to exploit the considerable potential of this methodology for natural product synthesis.

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Registry No. 1, 5041-27-0; 2, 1125-99-1; 3, 13689-45-7; *trans*-PhCH=CHNCO, 33066-20-5; *trans*-PhCH=CHCO$_2$H, 140-10-3; 4-(1-methylethenyl)-1-isocyanatocyclohexene, 92525-48-9; 8-isocyanato-1,4-dioxaspiro[4.5]dec-7-ene, 92525-49-0; 1-isocyanatocyclopent-1-ene, 92525-50-3; 2-(pyrrolidin-1-yl)-3,4-dihydronaphthalene, 21403-95-2; 4-[2-(ethoxycarbonyl)-1-methyl-(*E*)-ethenyl]morpholine, 55212-82-3; 2-(pyrrolidin-1-yl)-3-methyl-1-cyclohexene, 75337-00-7; (−)-2-(1-methylethenyl)-1,2,3,4,5,6,7,8,9,10-decahydro-6-oxophenanthridine, 92525-51-4; 1,3,4,5,7,8,9,10-octahydro-2,6-phenanthridinedione 2,2-ethanediyl acetal, 92525-52-5; 7,8,9,10,11,12-hexahydrobenzo[*i*]phenanthridin-5(6*H*)-one, 92525-53-6; 6,7,8,9,10,11-hexahydrobenzo[*h*]-cyclopent[*c*]isoquinolin-5-one, 92525-54-7; 4-phenyl-5,6,7,8-tetrahydroisoquinolin-1(2*H*)-one, 92525-55-8; ethyl 4-methyl-2-oxo-5,6,7,8-tetrahydroquinoline-3(1*H*)-carboxylate, 92525-56-9; 10-methyl-1,3,4,5,7,8,9,10-octahydro-6(2*H*)-phenanthridinone, 92525-57-0; 1-cyclohexenecarboxylic acid, 636-82-8; 4-(1-methylethenyl)-1-carboxy-1-cyclohexene, 92525-58-1; 1,4-dioxaspiro[4.5]dec-7-ene-8-carboxylic acid, 92525-59-2; 1-cyclopentenecarboxylic acid, 1560-11-8.

Supplementary Material Available: Table of spectral and analytical details for the 2-pyridones in Table I (2 pages). Ordering information is given on any current masthead page.

(13) (a) Domagala, J. M. *J. Org. Chem.* **1984**, *49*, 126. (b) Kuzuya, M.; Mano, E; Adachi, M.; Noguchi, A.; Okuda, T. *Chem. Lett.* **1982**, 475.

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Nucleophilic Addition of Silyl Enol Ethers to Aromatic Nitro Compounds: A Facile Synthesis of α-Nitroaryl Carbonyl Compounds†

Summary: Silyl enol ethers and silyl ketene acetals add to aromatic nitro compounds in the presence of fluoride ion sources (e.g., tris(dimethylamino)sulfonium difluorotrimethylsilconate (TASF)) to give, after oxidation, α-nitroaryl carbonyl compounds.

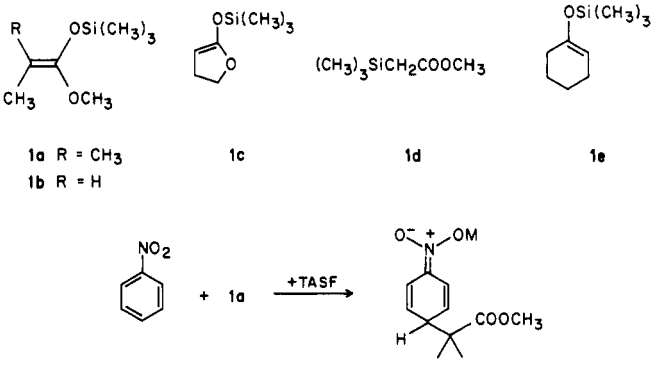
Sir: The synthetic utility of organosilicon reagents has been raidly expanding in the last few years.[1] Recently, we have reported that potent carbon nucleophiles with low basicity can be generated from silyl enol ethers and Lewis bases such as tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF) or bifluoride (TASHF$_2$).[1g] Thus, this reagent combination is compatible with Michael acceptors bearing active hydrogen atoms[2] and initiates "group transfer polymerization" of acrylic monomers.[3] In this communication we record our initial findings on the reactions of aromatic nitro compds. with silyl ketene acetals and silyl enol ethers.[4] In spite of the ready availability of aromatic nitro compounds, an efficient and general method to introduce alkyl side chains with useful functional groups to these compounds has not been developed.

Table I. Synthesis of α-(2-Nitroaryl) Carbonyl Compounds 5, from Nitroaromatics 4 and Silyl Reagents 1

		nitro compound		silyl reagent and yield of 5				
entry		X	Y	1a	1b	1c	1d	1e
1	4a	CH_3	H		44	43		
2	4b	Cl	H	51	58	55	50	50
3	4c	F	H		77	79		
4	4d	Cl	Cl		61			
5	4e	Cl	OCH_3	65				
6	4f	$C(CH_3)_2Cl$	H		31			
7	4-NITRO-2,1,3-BENZOTHIADIAZOLE[a]			64				
8	1-NITRONAPHTHALENE[a]				51	41		

[a] Addition occurs at positon ortho to the nitro group.

We find that nitrobenzene reacts with trimethylsilyl ketene acetal **1a** in THF/CH_3CN in the presence of 1 equiv of TASF.[5] The NMR spectrum of an equimolar mixture



1a R = CH_3 1c 1d 1e
1b R = H

2

M = TMS or TAS

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(4) (a) For other examples of additions of carbon nucleophiles to aromatic nitro compounds: Artamkina, G. A.; Egorov, M. P.; Beletskaya, I. P. *Chem. Rev.* **1982**, *82*, 427. (b) Addition of Grignard reagents: Bartoli, G.; Leardini, R.; Lelli, M.; Rosini, G. *J. Chem. Soc., Perkin Trans. 1*, **1977**, 884. Bartoli, G.; Leardini, R.; Medici, A.; Rosini, G. *Ibid.* **1978**, 692. Kienzle, F. *Helv. Chim. Acta* **1978**, *61*, 449. Bartoli, G.; Bosco, M.; Baccolini, G. *J. Org. Chem.* **1980**, *45*, 522. Bartoli, G.; Bosco, M. *Synthesis* **1980**, 616. Armillotta, N.; Bartoli, G.; Bosco, M.; Dalpozzo, R. *Ibid.* **1982**, 836. Bartoli, G.; Bosco, M.; Ciminale, F.; Dalpozzo, R. *J. Org. Chem.* **1982**, *47*, 5227. (c) Nucleophilic addition of heteroatom-stabilized carbon nucleophiles: Makosza, M.; Golinski, J. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 451; *Tetrahedron Lett.* **1978**, 3495. Makosza, M.; Golinski, J.; Pankowski, J. *Synthesis* **1983**, 40. See also: Hamana, M.; Iwasaki, G.; Saeki, S. *Heterocycles* **1982**, *17*, 177. Traynelis, V. J.; McSweeney, S. J. V. *J. Org. Chem.* **1966**, *31*, 243. Russel, G. A.; Weiner, S. A. *Ibid.* **1966**, *31*, 248.

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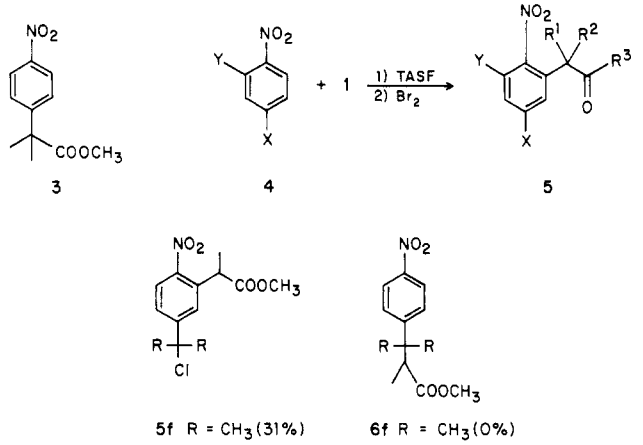
of the reagents at −60 °C exhibits signals characteristic of the formal Michael adduct **2** and nitrobenzene in a 2.5:1 ratio.[6] On warming the solution to 2 °C only observable species is **2**, and on recooling to −60 °C the mixture observed earlier is regenerated.

In situ oxidation of a rapidly cooled solution of **2** with an equivalent amount of bromine at −78 °C followed by usual workup and chromatographic purification affords **3** in 79% yield.[7] With less hindered ketene acetals **1b** and **1c**, ortho substitution predominates and 7:3 mixtures of ortho and para adducts are obtained.[8] C-Silylated methyl acetate **1d** also gives a mixture of ortho and para adducts in 49% yield in a ratio of 9 to 1.

Using this in situ oxidation procedure various substituted nitrobenzenes **4** can be readily converted to the corresponding α-nitroaryl carbonyl compounds[9] **5** in 40–80% yield (Table I). The ortho derivatives are valuable intermediates for the synthesis of indoles, oxindoles, and various other heterocycles.[10] Exclusive ortho addition can be achieved even with hindered ketene silyl acetals by the use of para-substituted nitrobenzenes (entries 2 and 5). It should be noted that there is *no* nuclear halogen substitution even when fluorine is the substituent (entries 2–5). Since the reduction of the resulting products **5** can be achieved with or without reducing the para halogen under catalytic or chemical reduction conditions, this method opens an exceptionally fast route to various indoles and oxindoles.[10a,e] Alternately the halogen can be later exchanged for various nucleophiles, providing unique opportunities in aromatic substitutions.



Even a typical $S_{RN}1$ substrate[11] **4f** gives only ring substitution product **5f**. No benzyl substitution product **6f** or other products of halide elimination were observed. The available evidence, thus, suggests that this surprisingly facile "Michael addition" proceeds via an electron pair mechanism and does not involve radical or single electron transfer processes.

The facile nitroarylation of carbonyl compounds described here makes use of readily available starting materials and is applicable to various substituted nitrobenzenes and nitro derivatives of heterocycles and condensed aromatic compounds. The scope and limitations of this reaction and further synthetic applications of α-nitroaryl carbonyl compounds will be reported in the near future.

Registry No. **1a**, 31469-15-5; **1b**, 34880-70-1; **1c**, 51425-66-2; **1d**, 2916-76-9; **1e**, 6651-36-1; **3**, 59115-08-1; **4a**, 99-99-0; **4b**, 100-00-5; **4c**, 350-46-9; **4d**, 611-06-3; **4e**, 6627-53-8; **4f**, 14500-58-4; **5** (R^1 = Y = H; R^2 = X = Me; R^3 = OMe), 92671-30-2; **5** (R^1 = Y = H; R^2,R^3 = CH_2CH_2O; X = Me), 92671-31-3; **5** (R^1 = R^2 = Me; R^3 = OMe; X = Cl; Y = H), 92671-32-4; **5** (R^1 = Y = H; R^2 = Me; R^3 = OMe; X = Cl), 86790-37-6; **5** (R^1 = Y = H; R^2,R^3 = CH_2CH_2O; X = Cl), 92671-33-5; **5** (R^1 = R^2 = Y = H; R^3 = OMe; X = Cl), 22908-29-8; **5** (R^1 = Y = H; R^2,R^3 = $(CH_2)_4$; X = Cl), 92671-34-6; **5** (R^1 = Y = H; R^2 = Me; R^3 = OMe; X = F), 92671-35-7; **5** (R^1 = Y = H; R^2,R^3 = CH_2CH_2O; X = F), 92671-36-8; **5** (R^1 = H; R^2 = Me; R^3 = OMe; X = Y = Cl), 92671-37-9; **5** (R^1 = R^2 = Me; R^3 = Y = OMe; X = Cl), 92671-38-0; **5** (R^1 = Y = H; R^2 = Me; R^3 = OMe; X = $C(CH_3)_2Cl$), 92671-39-1; TASF, 59218-87-0; $TASHF_2$, 85248-37-9; $PhNO_2$, 98-95-3; 4-nitro-2,1,3-benzothiadiazole, 6583-06-8; 1-nitronaphthalene, 86-57-7; 2-[1-(methoxycarbonyl)ethyl]-1-nitronaphthalene, 92671-40-4; 2-4,5-dihydro-2(3*H*)-oxofuran-3-yl]-1-nitronaphthalene, 92671-41-5; 5-[1-methyl-1-(methoxycarbonyl)ethyl]-4-nitro-2,1,3-benzothiadiazole, 92671-42-6.

† Contribution No. 3380.

(5) W. J. Middleton, *Org. Synth.*, in press. U.S. Patent 3940402, 1976.

(6) The NMR spectrum of **2** (THF-d_8/CD_3CN, 1:1, 2 °C, 360 MHz), inter alia, δ 1.08 (s, 6 H, CH_3's), 3.48 (m, 1 H, bisallylic H), 3.64 (s, 3 H, OCH_3), 4.88 (dd, J = 10 Hz, 5 Hz, 2 H H_3's), 6.95 (dd, J = 10 Hz, 2 Hz, 2 H, H_2's). The nature of M in **2** is uncertain at this time.

(7) To an equimolar mixture of the nitro compound and the silyl enol ether dissolved in THF (1 M) at −40 °C is added an equivalent amount of TASF solution in acetonitrile (1 M). The mixture is stirred for 30 to 60 min and an equivalent amount of Br_2 (or DDQ) is added at −78 °C. The products are isolated after warming to room temperature by the usual techniques. All compounds gave acceptable UV, IR, NMR, HRMS, and/or elemental analyses data.

(8) Silyl enol ethers in the presence of Lewis acids ($TiCl_4$, $Ti(OPr^i)_4$, $SnCl_4$) failed to effect the alkylations of nitrobenzenes. Alkali metal enolates of esters and ketones even in the presence of crown ethers are also ineffective.

(9) Current procedures for making these compounds will require more elaborate nitroaromatic precursors, often difficult or impossible to prepare. See, for example: (a) via nuclear substitution of halogen: Bourdais, J.; Germain, C. *J. Heterocycl. Chem.* **1976**, *13*, 1209. Wierenga, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 5621. (b) From nitroaryl acetic acids: Geyer, H. M., III; Martin, L. L.; Crichlow, C. A.; Dekow, F. W.; Ellis, D. B.; Kruse, H.; Setescak, L. L.; Worm, M. *J. Med. Chem.* **1982**, *25*, 340. (c) From nitrotoluenes: Garcia, E. E.; Fryer, R. I. *J. Heterocycl. Chem.* **1974**, *11*, 219.

(10) (a) For a leading reference to the use of these compounds in the synthesis of indoles: Raucher, S.; Koolpe, G. A. *J. Org. Chem.* **1983**, *48*, 2066 and references cited therein. (b) Synthesis of benzodiazepines: ref 9b. (c) Other examples from our work will be reported later.

(11) (a) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. (b) Russel, G. A.; Mudryk, B.; Jawdosiuk, M. *J. Am. Chem. Soc.* **1981**, *103*, 4610 and references cited therein. (c) Bunnet, J. F. *Acc. Chem. Res.* **1978**, 413.

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