Nucleophilic Addition of Silyl Enol Ethers to Aromatic Nitro Compounds: Scope and Mechanism of Reaction[1]

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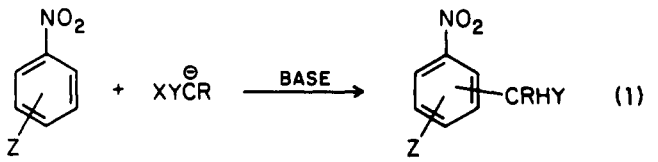
Abstract: In sharp contrast to alkali-metal enolates, silyl enol ethers and ketene silyl acetals add to aromatic nitro compounds in the presence of a fluoride ion source to give the intermediate dihydroaromatic nitronates, which can be observed by NMR. In situ oxidation of the intermediate with bormine or DDQ yields α-nitroaryl carbonyl compounds in moderate-to-high yields. The reaction is applicable to alkyl-, alkoxy-, and halogen-substituted nitrobenzenes as well as to heterocyclic and condensed nitroaromatic compounds. While substitution ortho to the nitro group predominates with sterically undemanding silyl reagents, para-substitution products are exclusively obtained with bulky reagents. However, by blocking the para position with an appropriate group such as chlorine, the addition can be directed to the ortho position. Halogen atoms of halogenated nitroaromatics and *p*-nitrocumenyl chloride are not displaced in the reaction, suggesting the absence of radical ion intermediates. Dihydroaromatic nitro derivatives can be isolated in some cases, such as anthracene and naphthalene systems which are less prone to rearomatize.

The use of silicon reagents in organic synthesis has been expanding rapidly in the past few years,[2-7] and versatile methods for carbon–carbon bond formations have been developed based on silyl enol ethers activated by fluoride ion sources. Various groups have reported alkylations,[3a,b] arylations,[3c] aldol condensations,[4] acylations,[5] and Michael additions.[6-8] Our own interest in this area originated with a notion that the nucleophilic reactivity of such reagent combinations might be distinctively different from that of the classical metal enolates and, in particular, that the enhanced nucleophilicity might be attained without significantly increasing basicity to lead to novel carbon–carbon bond-forming reactions. For example, we have reported (Scheme I) that trialkylketene silyl acetals can be added to α,β-unsaturated ketones in the presence of tris(dimethylamino)sulfonium difluorotrimethylsiliconate[9] (TASF) to give products equivalent to 1,4-additions of ester enolates.[7] This same reagent combination also initiates "group-transfer polymerization" of methacrylate monomers via sequential Michael additions[8] (Scheme I). In this paper, we wish to record our results on the fluoride-assisted addition of silyl enol ethers to aromatic nitro compounds. Oxidation of the resulting intermediate nitronate gives highly versatile α-nitroaryl carbonyl compounds.[10] This surprising "Michael" addition constitutes yet another example of the unusual carbon nucleophilicity of the silyl enol ether–fluoride combination. In most cases, the corresponding alkali-metal enolates give very poor yields of the addition products even in the presence of crown ethers.

In spite of the ready availability of aromatic nitro compounds, an efficient and general method to introduce alkyl side chains bearing useful functional groups to these compounds has not been developed. Even though σ-anionic complexes between aromatic polynitro compounds and enolates (Janovsky complexes) have been known for over 90 years, these have found no applications in synthesis.[10] Sulfur-mediated alkylations[11] and Grignard additions[12] are of limited value. The "vicarious" substitution of hydrogen[13] reported by Makosza et al. (eq 1) is not applicable for ketone, aldehyde, or tertiary ester enolate equivalents. Occasional com-



(1)

X = Cl, OR, SR

Y = $P(O)(OCH_3)_2$, SO_2Ph, CN, CO_2R

petitive aromatic displacements and regiochemical outcome often imposed by sterically demanding carbanionic species also limit the utility of this otherwise useful reaction.[13d]

Results

We find that nitrobenzene reacts with trimethylsilyl ketene acetal **1a** in THF/CH_3CN in the presence of 1 equiv of TASF. The NMR spectrum (vide infra) of an equimolar mixture of the reagents at −60 °C exhibits signals characteristic of the formal adduct **2** and nitrobenzene in a 2.5:1 ratio (eq 2). Quenching

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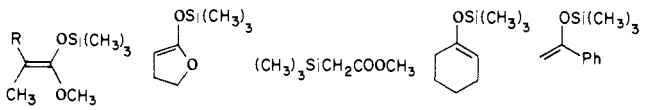
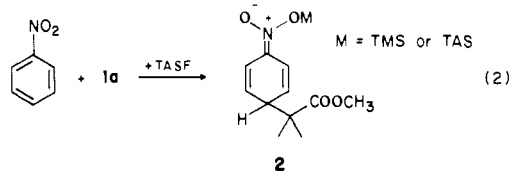


1a R = CH_3 1c 1d 1e 1f
1b R = H

a solution of **2** with mineral acid partially reverses the reaction and gives the nitro ester **3** and the azoxy compound **4** in 20% and 13% yield, respectively. In contrast, in situ oxidation of a rapidly



(2)

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cooled solution of **2** with an equivalent amount of bromine or DDQ at −78 °C followed by the usual workup and chromatographic separation afforded pure **3** in 79% yield without formation of the byproduct **4** (Scheme II). With less-hindered ketene acetals **1b** and **1c**, ortho substitution predominates and roughly 7:3 mixtures of ortho (**5**) and para (**6**) adducts (eq 3) are obtained (Table I). C-Silylated methyl acetate **1d** also gives a mixture of ortho and para adducts in 49% overall yield in a ratio of 9:1. With less-hindered silyl derivatives, there is a strong preference for ortho addition.

When this in situ oxidation procedure is used, various nitrobenzenes can be converted into the corresponding α-nitroaryl carbonyl compounds (eq 4) in 40–80% yields (Table II). Typically, to an equimolar mixture of the nitro compound and the silyl enol ether dissolved in THF (1 M) at low temperature is added an equivalent amount of TASF solution in dry acetonitrile. The mixture is stirred at that temperature for the appropriate time, and a stoichiometric amount of the oxidizing agent (bromine in cyclohexane or DDQ in THF) is added. After warming to room temperature, the product is isolated by the usual techniques. The reaction can also be carried out with tetra-*n*-butylammonium fluoride instead of TASF, albeit in lower yields.

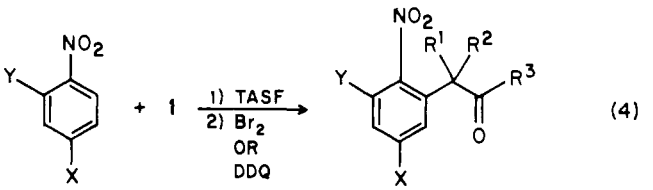

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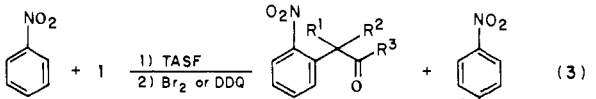
Table I. Addition of Silyl Reagents to Nitrobenzene



(3)

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SILYL REAGENT	PRODUCT R^1	R^2	R^3	YIELD (%)
1a	CH_3	CH_3	OCH_3	3 (79)
1b	H	CH_3	OCH_3	5b (36), 6b (16)
1c	H	$-CH_2CH_2O-$		5c (32), 6c (14)
1d	H	H	OCH_3	5d (44), 6d (5)
1e	H	$-CH_2CH_2CH_2CH_2-$		5e (6) 6e (11)

Table II. Synthesis of α-(2-Nitroaryl)carbonyl Compounds from Nitrobenzenes and Silyl Reagents (**1**)

ENTRY	NITRO COMPOUND IN EQ 4	X	Y	SILYL REAGENT AND YIELD α-ADDUCT 1a	1b	1c	1d	1e	1f
1	7	CH_3	H		7b (21)	7c (43)			
2	8	Cl	H	8a (51)	8b (58)	8c (55)	8d (67)	8e (50)	8f (35)
3	9	F	H		9b (77)	9c (79)			9f (38)
4	10	Cl	Cl		10b (61)			10e (30)	
5	11	Cl	OCH_3	11a (65)				11e (33)	
6	12	H	Cl				12d (51)[a]		
7	13	OCH_3	H		13b (84)				
8	14	CYCLOPROPYL	H		14b (74)				

[a] The para product, methyl-3-chloro-4-nitrobenzeneacetate was also obtained in 5% yield.

Table III. Addition of Silyl Reagents (**1**) to Polynuclear and Heterocyclic Aromatic Nitro Compounds

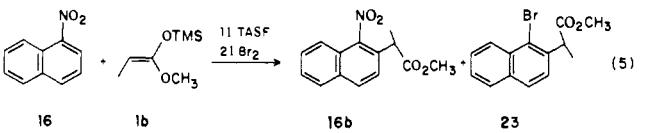
ENTRY NO		NITRO COMPOUND	SILYL REAGENT AND YIELD OF PRODUCT 1a	1b	1c	1d
1	16	1-NITRONAPHTHALENE[a]	25 (26)[b]	16b (51) 26 (67)[b]	16c (41)	-
2	17	2-NITRONAPHTHALENE[c]	0	17b (<5)	-	17d (66)
3	18	9-NITROANTHRACENE[d]	27 (56)[b]	28 (56)[b]		
4	19	4-NITRO-2,1,3-BENZOTHIADIAZOLE[e]	19a (64)	-	-	-
5	20	5-NITROISOQUINOLINE[a]	-	20b (50) 29 (74)[b]		
6	21	5-NITRO-1,2,3-BENZOTHADIAZOLE[e,f]	21a (5)	21b (46)	-	21d (75)
7	22	2-NITROTHIOPHENE[a]	30 (31)[b]			

[a] Yield of ortho adduct except in the case of 5-nitroisoquinoline where additional 10% para addition (**31**) is also observed. [b] Yield of dihydroaromatic adduct (see text). [c] Addition at position 1. [d] Addition at position 10. [e] Addition at position 4. [f] The author wishes to thank Dr. B. L. Chenard for experiments with this substrate. Details will be reported later.

It should be noted that nuclear halogen substituents are not displaced (entries 2–6). Even with the highly labile *p*-fluorine substituent (entry 3), no trace of substitution reaction was observed. This is in sharp contrast to the "Makosza" reaction[13b] where such competition does occur. Respectable yields of addition products in the reactions of hindered silyl derivatives **1a** and **1e** with various halogenated nitroaromatics (entry 2 and 5) clearly show the facility with which the addition proceeds. No displacement products were detected in any of these cases. Also note that α-C-silylated esters **1d** can also be used in this reaction.

The regiochemistry of addition is controlled by the size of the silicon reagent as seen in the case of nitrobenzene. The substitution pattern of the aromatic nucleus also plays a key part. For example, 2-chloronitrobenzene with methyl (trimethylsilyl)acetate (**1d**) gives methyl 3-chloro-2-nitrobenzeneacetate (**12d**, the ortho adduct) and methyl 3-chloro-4-nitrobenzeneacetate (the para adduct) in 51% and 5% yield, respectively. 3-Chloronitrobenzene (**15**) gives exclusively the ortho adduct **15d**. Note also that in this case, the ortho addition occurs at the more hindered, yet more electrophilic, position (Scheme III). More sterically demanding **1e** on the other hand adds to **15** to give the para adduct (**15e**) exclusively. Thus, bulkier silyl reagents react at the less-hindered position.

Nitronaphthalenes, nitroanthracene, and various heterocyclic nitro compounds can also be used in this reaction (Table III). With 1-nitronaphthalene and 5-nitroisoquinoline, the addition occurs predominantly at the ortho position. When 1-nitronaphthalene is reacted with **1b** in the presence of TASF (followed by bromine oxidation) in addition to 51% of the expected product **16b**, 15% yield of methyl α-methyl-1-bromonaphthaleneacetate (**23**) is also obtained (eq 5). This product apparently arises via



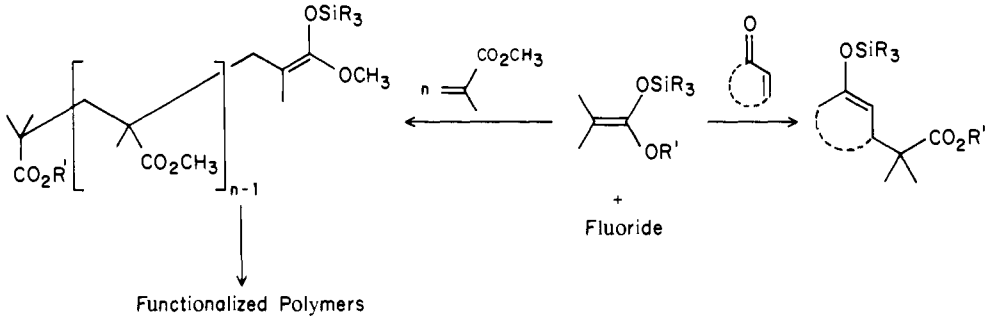
(5)

16 1b 16b 23

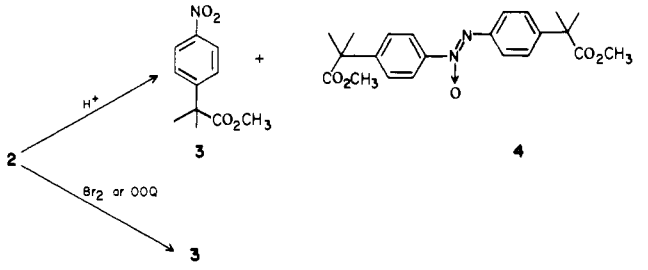
elimination of HNO_2 rather than HBr from the brominated intermediate. Preparation of the normal adduct **16b** is best achieved by DDQ oxidation of the intermediate nitronate.

The influence of the steric bulk of the silyl reagent is clearly contrasted by entries 2 and 6 in Table III. Very little reaction is seen with **1a** and 2-nitronaphthalene and 5-nitro-1,2,3-benzo-

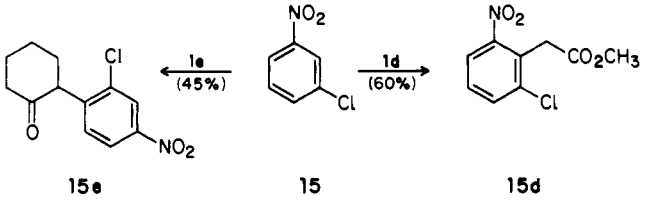
Scheme I



Scheme II

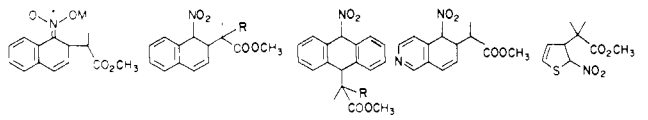


Scheme III



thiadiazole, since the only position which can be alkylated without destroying the aromaticity of both rings is hindered.

In systems not prone to aromatization, the initially formed nitronate adducts (for example **24**) can be isolated as the corresponding dihydroaromatic derivative by quenching the reaction mixture with a proton source rather than an oxidizing agent. The adducts **25–30** were isolated from the respective nitroaromatic precursors by this procedure. A mixture of diastereomers is

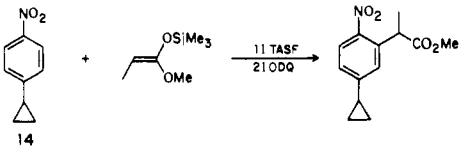


obtained in cases where chiral centers are generated in the reaction. However, recrystallized samples of adduct **26** appear to be a single isomer as judged by the 360-MHz ^{1}H NMR spectrum. We have previously observed distinct signals for diastereotopic $CH_3C(H)CO_2Me$ groups.[7] The stereochemistry remains to be established.

In the oxidative workup with bromine, the initial nitronate is brominated to give a dihydroaromatic derivative which aromatizes by elimination of HBr. With substituents which stabilize an extended conjugated system, occasionally one can isolate this intermediate even with nitrobenzene derivatives. For example, 4-chloro- and 4-methoxynitrobenzenes yield **32**, **33**, and **34** upon bromination workup[14] (Scheme IV). The doubling of CH_3CH doublets in **32b** clearly indicates diastereomerism at the newly created stereogenic centers. As in the case of the Grignard additions,[15] the bromination is expected to take place from the side opposite to the bulky alkyl ester side chain. Treatment of **32** with triethylamine readily converts it to the fully aromatic product.

In order to probe possible intervention of radical ion intermediates in this reaction, we have carried out additions on a typical "$S_{RN}1$ substrate",[16] *p*-nitrocumenyl chloride (**35a**) (Scheme V). It was expected that if electron transfer to **35a** was to take place, chloride would be eliminated and the products of benzylic substitution **36a** would result. Under these conditions, the dimer 4,4′-dinitrodicumenyl **38** could also be formed.[17] Under the reaction conditions we employed, no trace of benzylation or dimerization of either the nitro compound or the enolate was observed. However, benzylic substitution does compete with addition when unhindered *p*-nitrobenzyl chloride (**35b**) was used as the substrate.

Similarly 4-cyclopropylnitrobenzene (**14**) reacts with **1b** without any ring opening of the cyclopropane (eq 6). Radical intermediates would be expected to facilitate such a ring opening.



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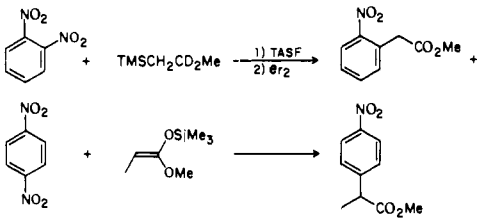
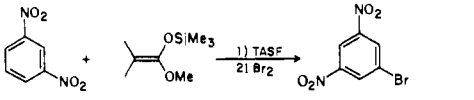
Only polynitro compounds show anomalous behavior. *o*-Dinitrobenzene, reacting with **1d**, gives 10% methyl 2-nitrobenzeneacetate and 37% methyl 3-nitrobenzeneacetate whereas *p*-dinitrobenzene yields a substitution product exclusively (eq 7 and 8).



Reacting with *m*-dinitrobenzene, **1a** yielded no trace of nucleophilic addition; instead, 3,5-dinitrobromobenzene was isolated as the sole product (eq 9). Mechanism of this very interesting



(9)

transformation remains speculative. However successful bromination of the highly electron-deficient substrate under mild conditions is noteworthy.

In light of successful additions of silyl enol ethers to α,β-unsaturated nitro compounds in the presence of Lewis acids reported by Yoshikoshi,[18] we attempted such additions to aromatic nitro

(14) For a related intermediate, see: Bartoli, G.; Bosco, M.; Melandri, A.; Bolcelli, A. C. *J. Org. Chem.* **1979**, *44*, 2087.

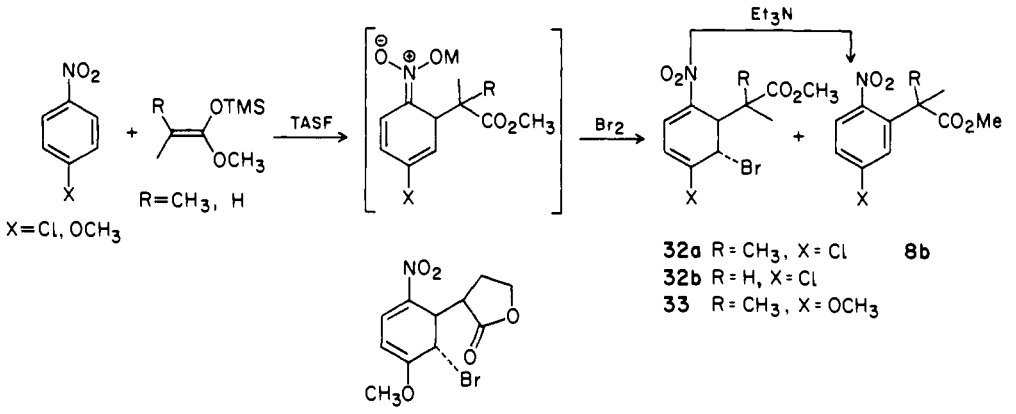
(15) Bartoli, G.; Bosco, M.; Forestl, E.; Pradella, G. *J. Org. Chem.* **1981**, *46*, 3109.

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

(17) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 725.

(18) Miyashita, M.; Yanami, Y.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679.

Scheme IV



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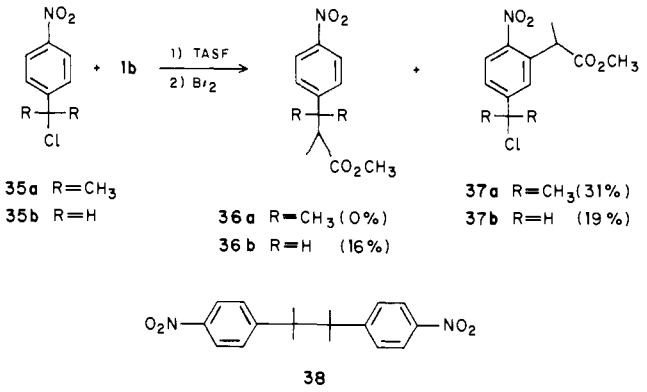
Scheme V



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compounds. No coupling products were detected upon treatment of **1b** and **1f** with nitrobenzene and 4-chloronitrobenzene in the presence of $SnCl_4$ (or $TiCl_4$) followed by oxidative workup.

Lithium enolates from methyl propionate, acetophenone, and cyclohexanone fail to add to aromatic nitro compounds under conditions where the fluoride-initiated reactions are successful. Similarly, addition of the potassium enolate of cyclohexanone to 4-chloronitrobenzene yielded several products, none of which corresponded to the 1:1 adduct. Reaction of the potassium enolate of methyl propionate with 4-chloronitrobenzene in the presence of 18-crown-6 yielded ~6% of the corresponding ortho adduct upon oxidative workup of the reaction with DDQ.

Finally, the reaction is unique for aromatic nitro compounds. Other electron-withdrawing substituents (CO_2Me, CN, and SO_2Ar, for example) do not activate the aromatic nucleus for nucleophilic addition.

The facile nitroarylation of carbonyl compounds described in this paper makes use of readily available starting materials and is applicable to various nitrobenzenes and nitro derivatives of heterocycles and condensed aromatic compounds. The resulting α-nitroaryl carbonyl compounds are highly useful intermediates, but available procedures for making these compounds have required more elaborate nitroaromatic precursors[19] which are often difficult or impossible to prepare. Since the aromatic halogens are not displaced under the alkylation conditions (see Table II), they can be replaced later by various nucleophiles. In addition, the nitro group can be reduced with or without concomitant reduction of halogens.[20,21] The resulting amino group can be transformed into various functionalities. These combinations of reactions thus provide unique opportunities in the synthesis of variously substituted aromatic compounds whose synthesis by classical methods would be circuitous.[21] Further applications of the α-nitroaryl carbonyl compounds for the synthesis of arylacetic and -propionic acids, indoles, and oxindoles will be reported later.

Discussion

Carbon nucleophiles generated by the reaction of silyl enol ethers and TASF are distinctly different from the corresponding alkali-metal enolates in their chemical reactivity. Recent theoretical studies[22] show that anion coordination to the silicon atom substantially enhances the nucleophilicity of silyl enol ethers without significantly increasing the basicity. Thus, the reagent combination may prove useful for reactions involving substrates or products which are sensitive to strongly basic alkali-metal enolates. In fact, base-sensitive substrates such as methyl vinyl ketones and cyclopentenone have been successfully used as Michael acceptors for silyl enol ethers in the presence of TASF.[7] The successful nitroarylation of silyl enol ethers may also be attributed partly to the essentially nonbasic reaction conditions under which many destructive events due to acid–base reactions of nitroaromatics can be effectively eliminated.

In a study of the aldol condensation of silyl enol ethers in the presence of TASF, Noyori concluded that the reaction proceeds via a highly dissociated and charge-separated (extended) transition state.[4b] This model correctly predicts the stereochemical outcome. It was further concluded that silylation of the aldolate is essential to drive the equilibrium to the product.

By contrast, in the "group-transfer polymerization" of methacrylates, we find that ketene trimethylsilyl acetals in the presence of fluoride ion sources add to α,β-unsaturated esters without dissociation of the TMS group.[8] The results of double-labeling/crossover experiments suggest that the migration of silicon along the growing polymer chain proceeds via the intermediacy of a hypervalent silicon intermediate. Such intermediates may be more general than commonly recognized in the electrophilic reaction of silyl enol ethers.

The mechanistic details of the nucleophilic addition to aromatic nitro compounds have largely remained unanswered. Both homolytic (single electron transfer followed by recombination of the radical pair) and heterolytic two-electron processes should be considered. Fyfe et al.,[23] based on the lack of CIDNP effect in the reaction of methoxide ion with 1-cyano-3,5-dinitrobenzene,

(19) 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. Ames, D. E.; Ribeiro, O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1073. Kraus, G. A.; Frazier, K. *Tetrahedron Lett.* **1978**, 3195. (b) From nitroarylacetic 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. K.; J. Heterocycl. Chem. **1974**, *11*, 219; Hengartner, U.; Batcho, A. D.; Blount, J. F. Leimgruber, W.; Larscheid, M. E.; Scott, J. W. *J. Org. Chem.* **1979**, *44*, 3748. (d) From 2-aminonitro compounds: Raucher, S.; Koolpe, G. A. *J. Org. Chem.* **1983**, *48*, 2066.

(20) (a) Kosak, J. R. In "Catalysis in Organic Synthesis"; Academic Press: New York, 1980. (b) Kraus, G. A.; Frazier, K. *Tetrahedron Lett.* **1978**, *19*, 3195. (c) Reference 19a, c, d, and others cited therein.

(21) Further examples from our work will be reported later.

(22) Dixon, D. A.; unpublished results.

(23) Fyfe, C. A.; Cocivera, M.; Damji, S. W. H. *J. Am. Chem. Soc.* **1975**, *97*, 5707.

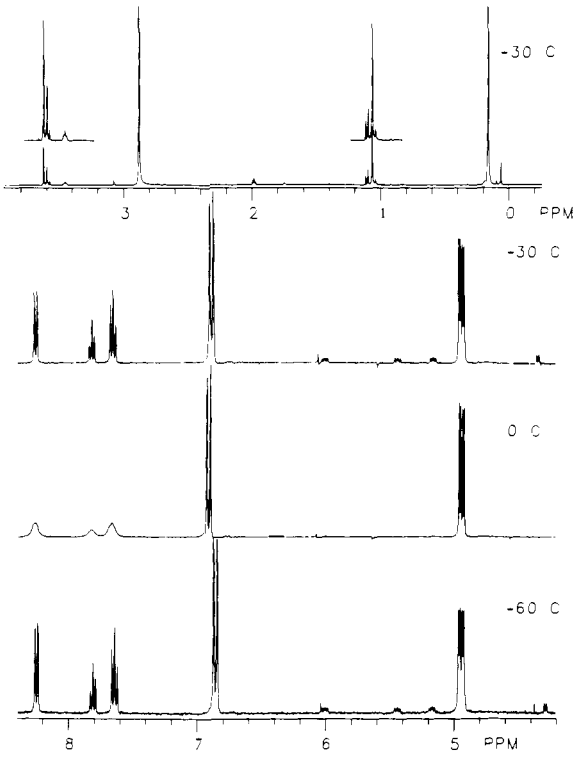

Figure 1. Temperature-dependent spectra of **1a** and nitrobenzene in the presence of 1 equiv of TASF in 1:1 CD_3CN/THF-d_8 (360 MHz). The spectral amplitude of the first trace is lower than the others.

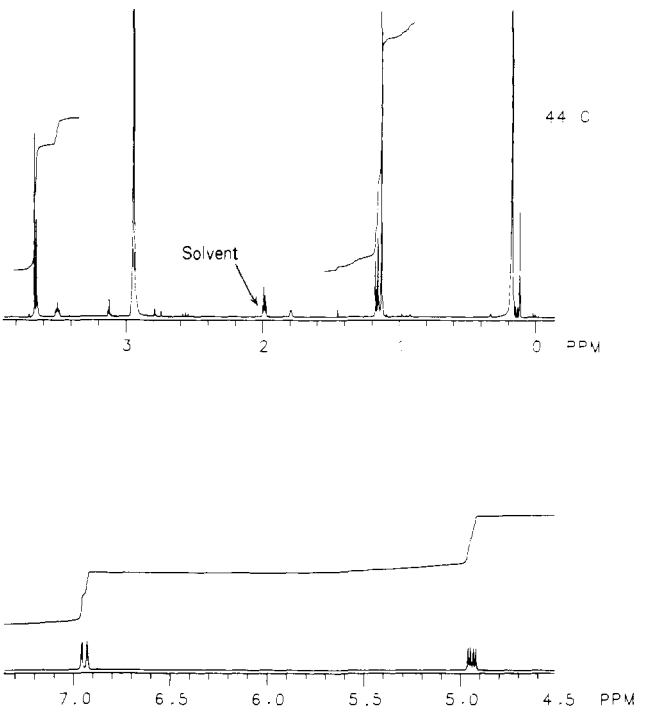

Figure 2. Spectrum of a 1:1 mixture of **1a** and nitrobenzene in the presence of 1 equiv of TASF at 44 °C.

have preferred an electron pair mechanism for such additions. It is, however, conceivable that the lifetime of the radical pair is too short on the time scale of the stopped-flow technique used by these workers. Chemical evidence for a single-electron-transfer (SET) pathway for the addition of Grignard reagents to aromatic nitro compounds has been provided by Bartoli et al.[24] When 5-hexenylmagnesium bromide reacts with 2-methoxy-1-nitronaphthalene, products of addition of both hexenyl as well as cyclopentylmethyl moieties are observed. Since the 5-hexenyl radical undergoes facile ring closure to the cyclopentylmethyl radical, this result is interpreted to mean an SET mechanism for these additions.

In the case of the fluoride-mediated additions of silyl enol ethers to aromatic nitro compounds, we favor a two-electron process. Chemistry of anionic σ complexes of the type **2** has attracted considerable attention in recent years.[25] Various intermediates derived from polynitro aromatic compounds have been characterized[26] even though such derivatives of nitrobenzene itself have remained largely speculative. They have been implicated as intermediates in aromatic nucleophilic substitution reactions.[13,27] Also, in our case, attempts to isolate the intermediate silyl nitronate (for example, **2**, M = TMS) were unsuccessful even when bulky (and hence hydrolytically more stable[28]) silyl derivatives were used in the reaction. Likewise, attempts to trap this intermediate with various electrophiles (aldehydes, alkylating agents, sulfur electrophiles, and *m*-CPBA) and dipolarophiles were unsuccessful.

To obtain further information on the intermediate, we have carried out low-temperature high-field NMR studies on the reaction of **1a** only a para adduct is formed, and this simplifies the spectrum. Thus, an equimolar mixture of nitrobenzene, **1a**, and TASF in 1:1 CD_3CN/THF-d_8 at −60 °C shows signals characteristic of a mixture of a hydroaromatic nitronate **2** and nitrobenzene in a ratio of 2.5:1 (Figure 1). The signals at 3.48 (m, 1 H, bis-allylic H_4), 4.88 (dd, J = 10, 5 Hz, 2 H, H_3's), and 6.95 (dd, J = 10, 2 Hz, 2 H, H_2's) were assigned on the basis of double-irradiation experiments. Irradiation of a peak at δ 6.95 sharpens the bis-allylic proton signal to a triplet (J = 5 Hz), and similarly the δ 3.48 signal becomes a broad singlet upon irradiation of the δ 4.88 peak. The nature of M in **2** remains uncertain at this time. Only one sharp singlet is observed for all the trimethylsilyl groups in the system. This is not surprising in view of the observations of Seebach[28] and Joffe[29] that the silyl groups in silyl nitronates undergo rapid exchange between the two oxygen atoms even in the absence of fluoride ion. Excess of fluoride present in our medium almost certainly will facilitate this process as well as other intermolecular silyl migrations.

When the solution is warmed to 0 °C, nitrobenzene peaks are considerably broadened, and at room temperature, they are barely visible. There is little change in the signals corresponding to the adduct. At 44 °C, the nitrobenzene peaks disappear completely (Figure 2). The integration of the signals corresponding to the adduct with respect to the residual protons in the deuterated acetonitrile clearly shows that there is no significant change in the concentration of the adduct as a function of temperature. Thus, the broadening of the nitrobenzene signal is *not* likely due to a reversible equilibrium involving **2**. Significantly, the reaction mixture can be cooled back to −30 °C to regenerate the spectrum observed earlier. Prolonged keeping at room temperature deteriorates the sample. Acetonitrile, being a relatively acidic solvent, can, in principle, take part in any of the several schemes one can envision for the reaction. Therefore, we repeated the above experiments with THF-d_8/pyridine-d_5 as the solvent and confirmed the observations made earlier. With a catalytic amount of TASF in CD_3CN and THF-d_8, nitrobenzene reacts with **1a** to the extent of fluoride ion availability. Surprisingly, a spectrum of a 1:1 mixture of nitrobenzene and **1a** at −60 °C in the presence of 0.20 M equiv of TASF shows, in addition to nitrobenzene and **2**, the starting ketene acetal for at least up to 2 h. This confirmed our earlier experimental observation that a stoichiometric amount of

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(25) For leading references see: (a) ref 10. (b) Strauss, M. J. *Acc. Chem. Res.* **1974**, *7*, 181.
(26) For example, see: Kovar, K. A.; Breitmaier, E. *Chem. Ber.* **1978**, *111*, 1646 and references cited there.
(27) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273.
(28) Colvin, E. W.; Beck, A. K.; Bastani, B.; Seebach, D.; Kai, Y.; Dunitz, J. D. *Helv. Chim. Acta* **1980**, *63*, 697.
(29) Kashutina, M. V.; Joffe, S. L.; Tartakovskii, V. A. *Dokl. Akad. Nauk. SSSR* **1974**, *218*, 109.

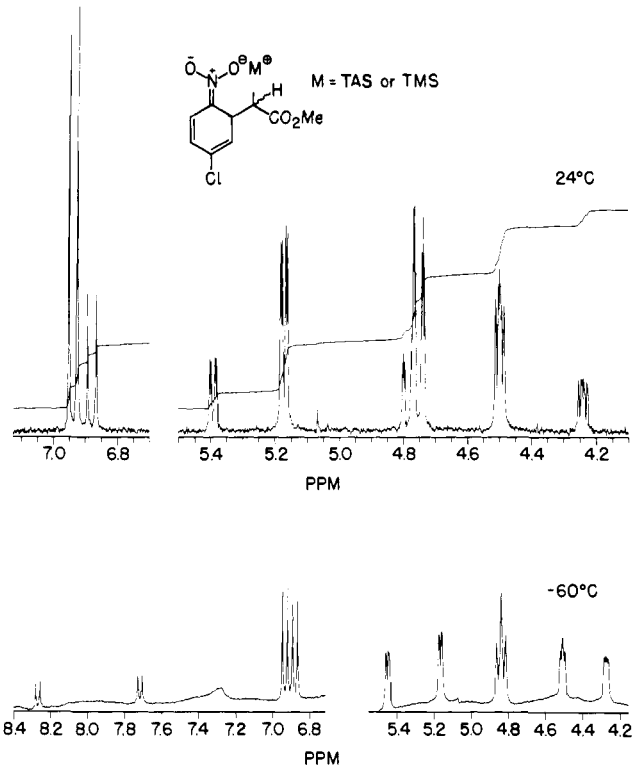
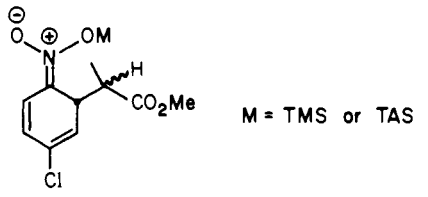


Figure 3. Spectrum (360 MHz) of a mixture of **1b** and 4-chloronitrobenzene (1:1 THF-d_8/CD_3CN).

fluoride ion is needed for the reaction. In a separate experiment, it can be shown that TASF itself does not add to nitrobenzene.

Ketene silyl acetal **1b** adds to 4-chloronitrobenzene to give an intermediate **39** similar to **2**. Based on the spectral data at −60 °C, a 1:1 ratio of *p*-chloronitrobenzene to the adduct(s) is observed (Figure 3). The ratio of diastereomers is 1:1 as calculated by



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peak integration of the appropriate signals in the ^1H NMR spectrum. This ratio changes to 1:2.8 at room temperature. Broadening of the 4-chloronitrobenzene peaks at room temperature is also observed as in the case of nitrobenzene in the previous experiment.

Further, since we can observe the ^1H NMR spectrum of the intermediate Meisenheimer-type complex **2**, a reversible electron-transfer process is unlikely. For comparison, in the addition of lithium ethylthiolate to *o*-nitrotoluene, formation of paramagnetic intermediates causes the aromatic signals to disappear completely.[30] Electron-transfer processes similar to this may indeed be responsible for the temperature dependence of the PMR spectrum of a mixture of nitrobenzene, **1a**, and TASF (vide supra). *Notably, under the typical reaction conditions (−40 to −60 °C) there is no significant broadening of the aromatic protons.*

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam Acculab 8 or Nicolet Model 7199FT spectrometer. UV spectra were recorded on a Cary 17 spectrophotometer. NMR spectra were obtained on a Varian EM-390, IBMNR80, or Nicolet 360WB spectrometer, and chemical shifts are reported from tetramethylsilane and were recorded in $CDCl_3$ solutions unless otherwise indicated. Gas chromatography was done on a Hewlett-Packard 5710A model. Unless otherwise specified, a glass column 6 ft × $^1/_8$ in. containing 3% SP2100 on Supelcoport 60/80 support was used with temperature programming.

All solvents were purified by standard procedures and were freshly distilled. Acetonitrile was refluxed with calcium hydride and was distilled fresh and was dried further with molecular sieve of 3 Å for each reaction. Acetonitrile-d_3 and THF-d_8 were dried with activated molecular sieve of 3 Å.

The ketene silyl acetals and silyl enol ethers were prepared according to procedures reported in the literature.[31] Aromatic nitro compounds except 4-nitrophenylcyclopropane and 4-nitrocumenyl chloride were purchased commercially and were purified by either recrystallization or distillation.

TASF[9] is extremely hygroscopic: rigorous exclusion of water from all solvents and reagents was followed in all experiments involving TASF and/or silyl enol ethers. TASF was weighed out in a dry polyethylene glovebag. Unless otherwise mentioned, all experiments were carried out under nitrogen atmosphere.

Reaction of 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (1a) with Nitrobenzene, Acidic Workup. A mixutre of 2.37 mL (23.25 mmol) of nitrobenzene and 4.72 mL (23.25 mmol) of **1a** in 10 mL of anhydrous THF was added to a solution of 5.50 g (20 mmol) of TASF dissolved in 20 mL of THF and 10 mL of pyridine at −5 to 0 °C. The mixture was allowed to warm to room temperature and stirred for 3.5 h. About 10 mL of concentrated HCl was added (exothermic reaction), and the product was extracted with three 75-mL portions of ether. The ether extract was washed with saturated sodium bicarbonate and water. Drying, concentrating, and isolating products was followed by column chromatography on silica gel (20% ether/hexanes). The following fractions were isolated and identified. Conversion to the coupled products was 67%. Fraction 1: 1.232 g, nitrobenzene. Fraction 2: methyl α,α-dimethyl-4-nitrobenzeneacetate (**3**), 1.026 g (20%); IR (KBr) 1732, 1520, 1345 cm^{-1}; ^1H NMR δ 1.65 (s, 6 H), 3.70 (s, 3 H), 7.55 (d, J = 9 Hz, 2 H), 8.20 (d, J = 9 Hz, 2 H). Fraction 3: azoxy compound **4**, 0.607 g (13%); mp 93–96 °C; UV (EtOH) 332 nm (ε 20300), 270 (8880), 235 (10000); IR (KBr) 1728, 1465, 1265, 1155 cm^{-1}; ^1H NMR δ 1.60 (s, 6 H), 3.65 (s, 3 H), 7.45 (m, 2 H), 8.20 (t, J = 8 Hz, 2 H); HRMS, found 207.0889 ($M^+ - C_{11}H_{13}NO_2$), calcd for $C_{11}H_{13}NO_3$ 207.0896.

Reaction of 1a with Nitrobenzene, Bromine Workup: Methyl α,α-Dimethyl-4-nitrobenzeneacetate (3). To a mixture of 1.02 mL (10 mmol) of nitrobenzene and 2.14 mL (10.75 mmol) of **1a** in 15 mL of THF at −78 °C was added 2.751 g of TASF dissolved in 5 mL of acetonitrile. The dropping funnel containing TASF solution was washed down with 5 mL of THF. The cold bath was removed and the reaction warmed to −10 °C and maintained at −10 °C for 1 h. After the solution was cooled to −78 °C, 0.512 mL (10 mmol) of bromine in 2 mL of cyclohexane was added dropwise. The cold bath was removed, and the mixture was brought to room temperature. Stirring was continued for 1 h. Twenty milliliters of saturated sodium bisulfite was added, and the product was extracted into ether. Isolation by flash chromatography[32] on silica gel yielded 1.824 g (79%) of the para adduct identified by comparison of physical properties with those of a sample prepared earlier.

General Procedures for Nucleophilic Alkylation of Aromatic Nitro Compounds. Procedure A. This procedure is essentially the same as for the addition of **1b** to nitrobenzene described below. Typically, 10 mmol (2.751 g) of TASF in 3 mL of anhydrous THF and 3 mL of anhydrous acetonitrile was added dropwise to a solution of 10 mmol of the nitro compound and 10.50 mmol of the silyl reagent dissolved in 10–15 mL of anhydrous THF and maintained at −78 °C. The last traces of TASF were washed down with an additional 5 mL of THF, and the mixture was stirred at that temperature overnight (18–21 h). From a dropping funnel was added 9–10 mmol of bromine dissolved in 3–5 mL of cyclohexane. The reaction was stirred for 10 min at −78 °C and subsequently was warmed to room temperature. The product(s) was extracted into ether after adding excess saturated sodium bisulfite solution. Purified products were isolated by flash chromatography and identified by spectroscopic techniques. As shown in one of the following examples (**8e**), in the case of 4-substituted nitrobenzenes, addition of excess triethylamine following the addition of bromine facilitates the HBr elimination from the intermediate dihydroaromatic adduct.

Two typical examples follow.

Addition of 1b to Nitrobenzene. A solution of 5.11 mL (50 mmol) of nitrobenzene and 9.69 mL (52.5 mmol) of **1b** in 75 mL of anhydrous

(30) Benedetti, F.; Marshall, D. R.; Stirling, C. J. M.; Leng, J. L. *J. Chem. Soc., Chem. Commun.* **1982**, 918.

(31) (a) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59. (b) Ainsworth, C.; Kuo, Y.-N. *Ibid.* **1972**, *46*, 73. (c) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(32) Still, W. C.; Mitra, A.; Kahn, M. *J. Org. Chem.* **1978**, *43*, 2923.

THF was cooled to −78 °C, and a solution of 13.755 g (50 mmol) of TASF in 15 mL of anhydrous acetonitrile and 15 mL of THF was added at such a rate that the temperature did not go above −75 °C. The last traces of TASF were washed down from the dropping funnel with 2 mL of acetonitrile. The mixture was stirred at −78 °C overnight (21 h) and treated with a solution of 2.50 mL (48.81 mmol) of bromine in 10 mL of cyclohexane. After 15 min at −78 °C, the mixture was warmed to room temperature and stirred for 1 h. Fifty milliliters of saturated KH_2PO_4 solution was added, and the product was extracted with four 100-mL portions of ether. The ether extract was washed with saturated sodium chloride, dried, and concentrated. Sublimation on a Kugelrohr oven gave 5.46 g (52%) of a mixture of ortho and para adducts in a ratio of 7:3 as determined by gas chromatography (3% SE30, 6 ft × $^1/_8$ in. glass column, 130 °C). We were unable to separate the two compounds by column chromatography completely.

The reaction can be worked up with iodine or DDQ instead of bromine, albeit in lower yield (22%). Ortho adduct, methyl α-methyl-2-nitrobenzeneacetate (**5b**): UV (EtOH) 254 nm (4100); IR (neat) 1745, 1520, 1350 cm^{-1}; ^{1}H NMR δ 1.60 (d, J = 7 Hz, 3 H), 3.60 (s, 3 H), 4.30 (q, J = 7 Hz, 1 H), 7.30–8.00 (m, 4 H); HRMS, found 209.0701 (M^+), calcd for $C_{10}H_{11}NO_4$ 209.0688. Para adduct, methyl α-methyl-4-nitrobenzeneacetate (**6b**): UV (EtOH) 268 nm (9970); IR (neat) 1740, 1525, 1350, 1210 cm^{-1}; ^{1}H NMR δ 1.50 (d, J = 6 Hz, 3 H), 3.65 (s, 3 H), 3.80 (q, J = 6 Hz, 1 H), 7.45 (d, J = 8 Hz, 2 H), 8.20 (d, J = 8 Hz, 2 H); HRMS, found 209.0701 (M^+), calcd for $C_9H_{11}NO_4$ 209.0688.

2-(5-Chloro-2-nitrophenyl)cyclohexanone (8e). A mixture of 1 mL (5.33 mmol) of **1e** and 0.788 g (5 mmol) of 1-chloro-4-nitrobenzene in 20 mL of THF was placed in a 100-mL flask fitted with an addition funnel. A solution of 1.375 g (5 mmol) of TASF in 1 mL of 1:1 THF/acetonitrile was added dropwise over 10 min at −78 °C. The mixture was stirred overnight at −78 °C. At −78 °C, 0.250 mL (5 mmol) of bromine was added dropwise, and the mixture was warmed to room temperature. Two equivalents (1.40 mL) of triethylamine was then added, and the reaction mixture was stirred for 1 h. Addition of sodium bisulfite, extraction into ether, and isolation yielded the crude product containing the starting material and the expected product. The coupled product was isolated by column chromatography on silica gel: yield, 0.632 g (50%); UV (EtOH) 268 nm (5770); IR (neat) 1720, 1530, 1350 cm^{-1}; ^{1}H NMR δ 1.50–2.75 (br, m, 8 H), 4.10–4.50 (br, m, 1 H), 7.33 (s, 1 H), 7.39 (dd, J = 8, 1 Hz, 1 H) 7.97 (dd, J = 8, 1 Hz, 1 H); HRMS, found 207.0548 ($M^+ - NO_2$), calcd for $C_{12}H_{12}OCl$ 207.0576.

Using the general procedure A, the following compounds were prepared.

3-(2-Nitrophenyl)oxacyclopentan-2-one (5c): mp 112–117 °C dec; UV (EtOH) 340 nm (450), 257 (5260); IR (KBr) 1765, 1580, 1360 cm^{-1}; ^{1}H NMR δ 2.10–3.05 (m, 2 H), 4.20–4.70 (m, 3 H), 7.25–7.90 (m, 3 H), 8.05 (m, 1 H); HRMS, found 208.0580 (M^+ + 1), calcd for $C_{10}H_{10}NO_4$ 208.0610, 161.0605 ($M^+ - NO_2$), calcd 161.0602. Anal. C, H, N.

3-(4-Nitrophenyl)oxacyclopentan-2-one (6c): mp 76–78 °C; UV (EtOH) 340 nm (335), 267 (10 640); IR (KBr) 1765, 1605, 1495, 1520, 1350 cm^{-1}; ^{1}H NMR δ 2.25–3.00 (m, 2 H), 3.95 (dd, J = 11, 9 Hz, 1 H), 4.20–4.70 (m, 2 H), 7.50 (d, J = 8 Hz, 2 H), 8.20 (d, J = 8 Hz, 2 H); HRMS, found 207.0525 (M^+), calcd for $C_{10}H_9NO_4$ 207.0531, 163.0623 ($M^+ - CO_2$) calcd 163.0634.

Methyl 2- and 4-nitrobenzeneacetates (5d and 6d): ratio 9/1; structure confirmed by comparison of spectral properties with those of authentic samples (Aldrich).

2-(2-Nitrophenyl)cyclohexanone (5e): UV (EtOH) 258 nm (4840); IR (KBr) 1710, 1525, 1350 cm^{-1}; ^{1}H NMR δ 1.25–2.75 (m, 8 H), 4.20–4.50 (m, 1 H), 7.25–7.75 (m, 3 H), 8.00 (m, 1 H); HRMS, found 219.0903 (M^+), calcd for $C_{12}H_{13}NO_3$ 219.0895.

2-(4-Nitrophenyl)cyclohexanone (6e): IR (KBr) 1710, 1523, 1345 cm^{-1}; ^{1}H NMR δ 1.25–2.75 (m, 8 H), 3.80 (m, 1 H), 7.25 (d, J = 9 Hz, 2 H), 8.15 (d, J = 9 Hz, 2 H); HRMS, found 219.0892 (M^+), calcd for $C_{12}H_{13}NO_3$ 219.0895.

Methyl α-Methyl-5-chloro-2-nitrobenzeneacetate (8b): IR (neat) 1740, 1525, 1350 cm^{-1}; ^{1}H NMR δ 1.60 (d, J = 6 Hz, 3 H), 3.63 (s, 3 H), 4.33 (q, J = 6 Hz, 1 H), 7.40 (dd, J = 8, 2 Hz, 1 H), 7.46 (s, 1 H), 7.93 (d, J = 8 Hz, 1 H); HRMS, found 197.0355 ($M^+ - NO_2$), calcd for $C_{10}H_{10}O_2$ 197.0369, 184.0161 ($M^+ - CO_2Me$), calcd 184.0165.

3-(5-Chloro-2-nitrophenyl)oxacyclopentan-2-one (8c): mp 93 °C; UV (EtOH) 340 nm (910), 268 (6860); IR (KBr) 1748, 1529, 1349 cm^{-1}; ^{1}H NMR δ 2.20–3.05 (m, 2 H), 4.15–4.60 (m, 3 H), 7.40 (s, 1 H), 7.50 (d, J = 9 Hz, 1 H), 8.03 (d, J = 9 Hz, 1 H); HRMS, found 242.0168, (M^+ + 1), calcd for $C_{10}H_9NO_4Cl$ 242.0219, 195.0199 ($M^+ - NO_2$), calcd for $C_{10}H_8O_2Cl$ 195.0213. Anal. C, H, N.

Methyl 5-Chloro-2-nitrobenzeneacetate (8d): mp 56 °C; IR (neat) 1740, 1515, 1340 cm^{-1}; ^{1}H NMR δ 3.73 (s, 3 H), 4.00 (s, 2 H), 7.36 (d, J = 1 Hz, 1 H), 7.43 (dd, J = 8, 1 Hz, 1 H), 8.07 (d, J = 8 Hz, 1 H); HRMS, found 197.9973 ($M^+ - OCH_3$), calcd for $C_8H_5NO_3Cl$ 197.9958.

2-(5-Chloro-2-nitrophenyl)-1-phenylethanone (8f): mp 120–121 °C; UV (EtOH) 275 nm (9550), 243 (19 700); IR (KBr) 1685, 1565, 1340 cm^{-1}; ^{1}H NMR δ 4.75 (s, 2 H), 7.25–7.50 (m, 5 H), 7.80–8.20 (m, 3 H); HRMS, found 229.0421 ($M^+ - NO_2$), calcd for $C_{14}H_{10}OCl$ 229.0420. Anal. C, H, N, Cl.

Methyl α-Methyl-5-fluoro-2-nitrobenzeneacetate (9b): IR (neat) 1750, 1540, 1355 cm^{-1}; ^{1}H NMR δ 1.56 (d, J = 7 Hz, 3 H), 3.70 (s, 3 H), 4.43 (q, J = 7 Hz, 1 H), 7.16 (m, 2 H), 8.06 (dd, J = 7, 5 Hz, 1 H); HRMS, found 196.0405 ($M^+ - OCH_3$), calcd for $C_9H_7NO_3F$ 196.0409, 181.0663 ($M^+ - NO_2$), calcd 181.0665. Procedure B (vide infra) gave 77% yield of product.

3-(5-Fluoro-2-nitrophenyl)oxacyclopentan-2-one (9c): mp (EtOH) 130–133 °C; UV (EtOH) 340 nm (380), 262 (5180); IR (KBr) 1775, 1585, 1480, 1535, 1360 cm^{-1}; ^{1}H NMR δ 2.15–3.05 (m, 2 H), 4.30–4.80 (m, 3 H), 7.05–7.45 (m, 2 H), 8.00–8.45 (m, 1 H); ^{19}F NMR 102.69 (m); HRMS, found 226.0502 (M^+ + 1), calcd for $C_{10}H_9NO_4F$ 226.0516, 179.9513 ($M^+ - NO_2$), calcd 179.0508. Procedure B gave 79% yield of **9c**.

2-(5-Fluoro-2-nitrophenyl)-1-phenylethanone (9f): IR (KBr) 3080, 3060, 2920, 2860, 1690, 1620, 1590, 1480, 1525, 1345 cm^{-1}; ^{1}H NMR δ 4.70 (s, 2 H), 7.00–8.35 (m, 8 H); HRMS, found 260.0701 (M^+ + 1), calcd for $C_{14}H_{11}NO_3F$ 260.0723, 213.0723 ($M^+ - NO_2$), calcd 213.0716.

Methyl α-Methyl-3,5-dichloro-2-nitrobenzeneacetate (10b): IR (neat) 1740, 1585, 1560, 1540, 1360 cm^{-1}; ^{1}H NMR δ 1.57 (d, J = 8 Hz, 3 H), 3.73 (s, 3 H), 3.73 (q, J = 8 Hz, 1 H), 7.40 (s, br, 2 H); HRMS, found 245.9703 ($M^+ - OCH_3$), calcd for $C_9H_6NO_3Cl_2$ 245.9724, 230.9969 ($M^+ - NO_2$, calcd for $C_{10}H_9O_2Cl_2$ 230.9979. Procedure B (−10 °C, 1 h) gave 61% yield.

Methyl α-Methyl-1-nitronaphthalene-2-acetate (16b): mp (EtOH) 68–71 °C; UV (EtOH) 360 nm (580), 319 (1130), 267 (5100), 223 (90 650); IR (KBr) 3060, 1740, 1635, 1605, 1525, 1510, 1355 cm^{-1}; ^{1}H NMR (360 MHz) δ 1.60 (d, J = 7 Hz, 3 H), 3.68 (s, 3 H), 3.95 (q, J = 7 Hz, 1 H), 7.52 (d, J = 10 Hz, 1 H), 7.55–7.67 (m, 2 H), 7.72 (dm, J = 8 Hz, 1 H), 7.88 (dm, J = 8 Hz, 1 H), 7.97 (d, J = 8 Hz, 1 H); HRMS, found 259.0819 (M^+) calcd for $C_{14}H_{13}NO_4$. 259.0844, 213.0905 ($M^+ - NO_2$), calcd 213.0916.

Methyl α-Methyl-1-bromonaphthalene-2-acetate (23): ^{1}H NMR δ 1.57 (d, J = 8 Hz, 3 H), 3.67 (s, 3 H), 4.60 (q, J = 8 Hz, 1 H), 7.25–8.60 (m, 6 H); GCMS, m/e 294 ($C_{14}H_{13}{}^{81}BrO_2$), 292 ($C_{14}H_{13}{}^{79}BrO_2$), 233, 235 ($M^+ - C_2H_3O_2$) (equal intensity for both sets of peaks). **16b** and **23** were separated by GLPC on an SE30 column (3%, $^1/_8$ in. × 6 ft).

From *p*-Nitrocumenyl Chloride. Methyl α-Methyl-5-(2-chloro-2-propyl)-2-nitrobenzeneacetate (37a): IR (neat) 1740, 1525, 1325 cm^{-1}; ^{1}H NMR δ 1.60 (d, J = 8 Hz, 3 H), 1.97 (s, 6 H), 3.67 (s, 3 H), 4.33 (q, J = 8 Hz, 1 H), 7.60 (d, J = 9 Hz, 1 H), 7.67 (s, 1 H), 7.90 (d, J = 9 Hz, 1 H); HRMS, found 250.1067 ($M^+ - Cl$), calcd for $C_{13}H_{16}NO_4$ 250.1079, 239.0832 ($M^+ - NO_2$), calcd 239.0838. Anal. C, 54.01 (calcd, 54.62); H, 5.61 (5.64); N, 4.82 (4.90); Cl, 13.36 (12.41).

Methyl α-Methyl-5-(chloromethyl)-2-nitrobenzeneacetate (37b): IR (neat) 1740, 1535, 1350 cm^{-1}; ^{1}H NMR δ 1.60 (d, J = 8 Hz, 3 H); 3.67 (s, 3 H), 4.33 (q, J = 8 Hz, 1 H), 4.63 (s, 2 H), 7.43 (dm, J = 9 Hz, 1 H), 7.53 (s, br, 1 H), 7.93 (d, J = 9 Hz, 1 H); HRMS, found 211.0521 ($M^+ - NO_2$), calcd for $C_{11}H_{12}O_2Cl$ 211.0525, 198.0310 ($M^+ - CO_2CH_3$), calcd 198.0322.

Methyl 2-Methyl-3-(4-nitrophenyl)propionate (36b): IR (neat) 1735, 1520, 1345 cm^{-1}; ^{1}H NMR δ 1.20 (d, J = 7 Hz, 3 H), 2.55–3.20 (m, 3 H), 3.60 (s, 3 H), 7.30 (d, J = 8 Hz, 2 H), 8.10 (d, J = 8 Hz, 2 H); HRMS, found 223.0850 (M^+), calcd for $C_{11}H_{13}NO_4$ 223.0845.

Procedure B. In procedure B, the experiment was repeated as in A, except upon addition of TASF, the reaction mixture was warmed to −40–0 °C and then was stirred for 1–2 h before adding cyclohexane solution of bromine at −78 °C.

A typical experiment follows.

3-(1-Nitronaphth-2-yl)oxacyclopentan-2-one (16c). To a solution of 1.73 g (10 mmol) of 1-nitronaphthalene and 1.67 mL (10.5 mmol) of **1c** in 20 mL of THF at −78 °C was added 2.751 g (10 mmol) of TASF dissolved in 5 mL of acetonitrile. The reaction mixture was brought to −10 °C (inside temperature), stirred for 1 h, and subsequently cooled to −78 °C. A solution of 0.510 mL (10 mmol) of bromine in 5 mL of cyclohexane was added. The bath was removed after 10 min, and the mixture was warmed to room temperature over 1 h. Twenty-five milliliters of water was added and the product extracted with four 50-mL portions of ether. The combined organic phase was washed with 20 mL of water, dried, and concentrated. Column chromatography on silica using 20% ethyl acetate in hexane yielded 1.054 g (41%) of the adduct. A portion was recrystallized from methanol: mp 149–152 °C; UV (EtOH) 355 nm (800), 320 (1370), 260 (5190), 223 (97 150); IR (KBr) 3060, 2970, 2900, 1770, 1600, 1570, 1500, 1525, 1360 cm^{-1}; ^{1}H NMR δ 2.05–3.00 (m, 2 H), 3.90–4.55 (m, 3 H), 7.10–8.00 (m, 6 H); HRMS,

found 257.0676 (M^+), calcd for $C_{14}H_{11}NO_4$ 257.0688. Anal. C, H, N.

The following compounds were prepared by procedure B.

Methyl α-Methyl-5-methyl-2-nitrobenzeneacetate (7b): UV (EtOH) 271 nm (6000); IR (neat) 1735, 1610, 1585, 1340 cm^{-1}; HRMS, found 223.0853 (M^+), calcd for $C_{11}H_{13}NO_4$ 223.0844.

3-(5-Methyl-2-nitrophenyl)oxacyclopentan-2-one (7c): UV (EtOH) 272 nm; IR (KBr) 1770, 1610, 1590, 1520, 1340 cm^{-1}; ^1H NMR δ 2.40 (s, 3 H), 2.70 (m, 2 H), 4.37 (m, 3 H), 7.06 (s, br, 1 H), 7.23 (dm, J = 9 Hz, 1 H), 7.95 (d, J = 9 Hz, 1 H); HRMS, found 175.0754 ($M^+ - NO_2$), calcd for $C_{11}H_{11}O_2$ 175.0759.

Methyl α,α-Dimethyl-5-chloro-3-methoxy-2-nitrobenzene-1-acetate (11a): mp 125–127 °C; UV (EtOH) 285 nm (2190); IR (KBr) 3090, 2980, 2950, 2880, 2840, 1740, 1590, 1570, 1535, 1365, 1265 cm^{-1}; ^1H NMR δ 1.60 (s, 6 H), 3.70 (s, 3 H), 3.85 (s, 3 H), 7.05 (s, 2 H); HRMS, found 241.0637 ($M^+ - NO_2$), calcd for 241.0631, 228.0428 ($M^+ - CO_2Me$), calcd 228.0427.

Methyl α,α-Dimethyl-4-nitro-2,1,3-benzothiadiazole-1-acetate (19a): mp 134–136 °C; IR (KBr) 1745, 1610, 1535, 1520, 1355, 1245 cm^{-1}; ^1H NMR δ 1.80 (s, 6 H), 3.63 (s, 3 H), 7.76 (d, J = 8 Hz, 1 H), 8.59 (d, J = 8 Hz, 1 H): HRMS, found 281.0460 (M^+), calcd for $C_{11}H_{11}N_3O_4S$ 281.0470. Anal. C, H, N, S.

Procedure C. To a mixture of 10 mmol of the nitro compound and 10.50 mmol of the silicon reagent in 25 mL of anhydrous THF at −78 °C was added 10 mmol of TASF dissolved in 5 mL of acetonitrile and 3 mL of THF. The mixture was brought to −40 to −20 °C and was further stirred for 1–2 h. DDQ was then added as a solid or in THF, and the reaction mixture was brought to room temperature. The product was extracted into ether after adding excess water, and the combined ether extracts were washed with 5% sodium hydroxide and then saturated sodium chloride. Drying, concentrating and flash column chromatographing on silica gel gave purified products, which were identified by the usual techniques.

Three typical preparations are described below.

Methyl 3-Chloro-2-nitrobenzeneacetate (12d): To 1.575 g (10 mmol) of 1-chloro-2-nitrobenzene and 1.92 mL (10.5 mmol) of methyl (trimethylsilyl)acetate in 10 mL of THF was added 2.751 g (10 mmol) of TASF dissolved in 3 mL of acetonitrile at −70 °C. The addition funnel was washed down with 3 mL more of acetonitrile, and the mixture was brought to −40 °C. To this reaction mixture was added 2.53 g (10 mmol) of solid DDQ, and the reaction was brought up to room temperature and was further stirred for 60 min. The product was extracted into ether, and the combined ether extracts were washed with 5% sodium hydroxide and then brine. Drying, concentrating, and chromatographing on silica gel yielded **12d** as the major product: 1.16 g (51%); IR (neat) 1740, 1600, 1570, 1535, 1365 cm^{-1}; ^1H NMR (360 MHz) δ 3.68 (s, 2 H), 3.70 (s, 3 H), 7.34 (dd, J = 7, 2 Hz, 1 H), 7.38–7.50 (m, 2 H); HRMS, found 229.0129 (M^+) calcd for $C_9H_8NO_4Cl$ 229.0141.

GLPC analysis of the crude product showed *no trace* of Cl displacement as ascertained by comparison of retention times with those of an authentic product. Minor amounts of a product have been identified as methyl 3-chloro-4-nitrobenzeneacetate: ^1H NMR (360 MHz) 3.72 (s, 3 H), 4.05 (s, 2 H), 7.35 (d, J = 2 Hz, 1 H), 7.45 (dd, J = 8, 2 Hz, 1 H), 8.10 (d, J = 8 Hz). GC/MS confirmed this assignment.

Methyl α-Methyl-5-cyclopropyl-2-nitrobenzeneacetate (14b). To 1.63 g (10 mmol) of 4-nitrocyclopropylbenzene[33] and 1.95 mL (10.1 mmol) of **1b** in 25 mL of THF at −78 °C was added 2.751 g (10 mmol) of TASF dissolved in 5 mL of CH_3CN. The reaction mixture was warmed to −40 °C and maintained at that temperature for 30 min. To this was added 2.53 g of DDQ dissolved in 20 mL of THF. The reaction was brought to room temperature and was further stirred for 30 min. Eighty milliliters of water and 150 mL of ether were added, and the organic layer was separated. The aqueous layer was extracted with three 60-mL portions of ether and the combined ether extract was dried and concentrated. The product was isolated by flash chromatography on silica by using 20% ether/hexanes as the solvent: yield, 1.84 g (74%); IR 3080, 3000, 2950, 2880, 2840, 1740, 1610, 1520, 1490, 1345, 1200 cm^{-1}; ^1H NMR δ 0.80 (m, 2 H), 1.20 (m, 2 H), 1.55 (d, J = 7 Hz, 3 H), 1.95 (m, 1 H), 3.75 (s, 3 H), 4.40 (q, J = 7 Hz, 1 H), 7.10 (m, 2 H), 7.90 (d, J = 8 Hz, 1 H); HRMS, found 203.1072 ($M^+ - NO_2$) calcd for $C_{13}H_{15}O_2$ 203.1072.

2-(2-Chloro-4-nitrophenyl)cyclohexanone (15e). A mixture of 3.152 g (20 mmol) of 3-chloronitrobenzene and 3.94 mL (21 mmol) of **1e** in 40 mL of THF was cooled to −78 °C under nitrogen. A solution of 5.502 g (20 mmol) of TASF dissolved in 5 mL of acetonitrile and 3 mL of THF was dropped in with vigorous stirring. The mixture was warmed to −30 to −20 °C and stirring was continued for 1 h. To the reaction mixture was added 4.54 g of DDQ dissolved in 20 mL of anhydrous THF at −30 °C. The cold bath was removed, and the mixture was allowed to come to room temperature and was further stirred for 1 h. Fifty milliliters of water was added followed by 100 mL of ether. The ether layer was separated, and the aqueous layer was extracted with more ether (60 mL × 4). The combined ether extract was washed with 60 mL of 5% sodium hydroxide and was subsequently dried and concentrated. Column chromatography on silica gel yielded a solid which was recrystallized from 95% ethanol: yield, 45%; mp 93–95 °C; IR (KBr) 3100, 1710, 1590, 1515, 1525, 1345 cm^{-1}; ^1H NMR (360 MHz) 1.75–2.63 (m, 8 H), 4.20 (dd, J = 12, 5 Hz, 1 H), 7.41 (d, J = 9 Hz, 1 H), 8.13 (dd, J = 8, 2 Hz, 1 H), 8.26 (d, J = 2 Hz, 1 H); HRMS, found 218.0820 (M^+ − Cl), calcd for $C_{12}H_{12}NO_3$ 218.0817. Anal. C, H, N.

The following adducts were prepared according to procedure C.

2-(3,5-Dichloro-2-nitrophenyl)cyclohexanone (10e): mp 98–101 °C; IR (KBr) 3080, 2950, 2500, 2870, 1715, 1540, 1365 cm^{-1}; ^1H NMR (360 MHz) δ 1.70–2.60 (m, 8 H); 3.60 (dd, J = 12, 4 Hz, 1 H), 7.24 (d, J = 2 Hz, 1 H), 7.44 (d, J = 2 Hz, 1 H); HRMS, found 241.0182 ($M^+ - NO_2$), calcd for $C_{12}H_{11}OCl_2$ 241.0187. Anal. C, H, N.

2-(5-Chloro-3-methoxy-2-nitrophenyl)cyclohexanone (11e): mp 144–146 °C; IR (KBr) 3080, 3020, 2960, 2940, 2860, 1715, 1530, 1370 cm^{-1}; ^1H NMR (360 MHz) δ 1.70–2.60 (m, 8 H), 3.60 (dd, J = 13, 5 Hz, 1 H), 3.88 (s, 3 H), 6.88 (d, J = 2 Hz, 1 H), 6.94 (J = 2 Hz, 1 H); HRMS, found 237.0682 ($M^+ - NO_2$), calcd for $C_{13}H_{14}O_2Cl$ 237.0682. Anal. C, H, N.

Methyl α-Methyl-5-methoxy-2-nitrobenzeneacetate (13b): mp 60–62 °C IR (KBr) 3100, 3030, 3010, 1730, 1510, 1335, 1240 cm^{-1}; ^1H NMR (360 MHz) δ 1.60 (d, J = 7 Hz, 3 H), 3.67 (s, 3 H), 4.41 (q, J = 7 Hz, 1 H), 6.87 (dd, J = 9, 3 Hz, 1 H), 6.91 (d, J = 3 Hz, 1 H), 8.07 (d, J = 9 Hz, 1 H); HRMS, found 239.0792 (M^+), calcd for $C_{11}H_{13}NO_5$ 239.0793. Anal. C, H, N.

Methyl 2-chloro-6-nitrobenzeneacetate (15d): IR (KBr) 1745, 1605, 1530, 1350 cm^{-1}; ^1H NMR (360 MHz) δ 3.74 (s, 3 H), 4.18 (s, 2 H), 7.42 (t, J = 8 Hz, 1 H), 7.70 (dd, J = 8, 1 Hz, 1 H), 7.94 (dd, J = 8, 1 Hz, 1 H); HRMS, found 197.9950 ($M^+ - OCH_3$), calcd 197.9958.

Methyl 2-Nitronaphthalene-1-acetate (17d): mp 102–104 °C; IR (KBr) 1735, 1620, 1595, 1505, 1520, 1345 cm^{-1}; ^1H NMR (360 MHz) δ 3.74 (s, 3 H), 4.41 (s, 2 H), 7.68 (m, 2 H), 7.95 (m, 3 H), 8.14 (m, 1 H); HRMS, found 245.0691 (M^+), calcd for $C_{13}H_{11}NO_4$ 245.0688. Anal. C, H, N.

Methyl α-Methyl-5-nitroisoquinoline-6-acetate (20b): mp 84–86 °C; IR (KBr) 1735, 1630, 1590, 1570, 1495, 1525, 1360 cm^{-1}; ^1H NMR (360 MHz) δ 1.65 (d, J = 7 Hz, 3 H), 3.70 (s, 3 H), 4.05 (q, J = 7 Hz, 1 H), 7.59 (d, J = 6 Hz, 1 H), 7.70 (d, J = 8 Hz, 1 H), 8.15 (d, J = 8 Hz, 1 H), 8.69 (d, J = 6 Hz, 1 H), 9.34 (s, 1 H); HRMS, found 260.0797 (M^+), calcd for $C_{13}H_{12}N_2O_4$ 260.0803. Anal. C, H, N.

Methyl α-Methyl-5-nitroisoquinoline-8-acetate (31): mp 79 °C; IR (KBr) 1735, 1620, 1590, 1570, 1490, 1515, 1335 cm^{-1}; ^1H NMR (360 MHz) δ 1.75 (d, J = 7 Hz, 3 H), 3.71 (s, 3 H), 4.74 (q, J = 7 Hz, 1 H), 7.70 (d, J = 8 Hz, 1 H), 8.49 (d, J = 8 Hz, 1 H), 8.52 (dd, J = 6, 1 Hz, 1 H), 8.80 (d, J = 6 Hz, 1 H), 9.68 (s, 1 H); HRMS, found 260.0797 (M^+), calcd for $C_{13}H_{12}N_2O_4$ 260.0797. Anal. C, H, N.

Methyl α-Methyl-5-nitro-1,2,3-benzothiadiazole-4-acetate (21b): mp 87.5–90 °C; IR (KBr) 1743, 1720, 1523, 1341 cm^{-1}; ^1H NMR δ 1.90 (d, J = 7 Hz, 3 H), 1.90 (d, J = 7 Hz, 3 H), 3.60 (s, 3 H), 5.40 (q, J = 7 Hz, 1 H), 8.25 (ABq, J = 17, 9 Hz, 2 H). Anal. C, H, N (sublimed sample, 70 °C/0.03 nm).

Methyl 5-Nitro-1,2,3-benzothiadiazole-4-acetate (21d): mp 96–98 °C; IR (KBr) 1734, 1521, 1345, 1200, 1180 cm^{-1}; ^1H NMR δ 3.80 (s, 3 H), 5.07 (s, 2 H), 8.35 (ABq, J = 24, 8 Hz, 2 H). Anal. C, H, N (sublimed, 85 °C/0.03 nm).

Reaction of TASF with 4-Chloronitrobenzene. After a mixture of 0.779 g (5 mmol) of 4-chloronitrobenzene and 1.375 g (5 mmol) of TASF in 15 mL of THF and 3 mL of acetonitrile was stirred for 2.50 h at −78 °C, 0.250 mL (5 mmol) of bromine in 3 mL of cyclohexane was added. Stirring was continued for 15 min, the bath was removed, and the products were extracted into ether after adding 20 mL of saturated sodium bisulfite. The dried organic layer was concentrated and analyzed by ^1H and ^{19}F NMR as well as GC. Only starting 4-chloronitrobenzene was detected. No fluorine incorporation had occurred.

Use of Tetra-*n*-butylammonium Fluoride for the Preparation of 3. To a mixture of 1.02 mL (10 mmol) of nitrobenzene and 2.40 mL (12 mmol) of **1a** in 10 mL of THF was added 10 mL (10 mmol) of a 1 N solution of Bu_4NF. The mixture was warmed to −10 to −20 °C and stirred for 1 h. It was subsequently cooled to −78 °C, and 0.51 mL (10 mmol) of bromine in 10 mL of cyclohexane was added. The cold temperature bath was removed, and 30 mL of saturated sodium bisulfite was added. Extraction with ether and isolation of the product by standard techniques yielded 0.576 g (26%) of product identified by comparison of spectral properties with those of an authentic sample prepared by using TASF instead of Bu_4NF.

(33) Ketcham, R.; Cavestri, R.; Jambotkar, D. *J. Org. Chem.* **1963**, *28*, 2139.

Methyl α-Methyl-5-fluoro-2-nitrobenzeneacetate (9b) Using *n*-Bu_4NF. When the procedure described in the previous experiment was used, the title compound was prepared in 11% yield. The structure was confirmed by comparison of spectral properties with those of an authentic sample prepared by the TASF method.

Reaction of *m*-Dinitrobenzene with 1a. To a mixture of 3.362 g (20 mmol) of *m*-dinitrobenzene and 4.20 mL (20 mmol) of **1a** was added 5.50 g of TASF dissolved in 20 mL of acetonitrile at −70 °C. The mixture was warmed to −20 to −15 °C and stirred at that temperature for 1 h. After the solution was cooled to −78 °C, 1.00 mL of bromine in 10 mL of cyclohexane was added with stirring. The mixture was stirred at room temperature for 1 h and then 40 mL of sodium bisulfite was added and the product was extracted into ether (50 mL × 4). Chromatography of the product on silica gel using ethyl acetate/hexane solvent system yielded 0.844 g (17%) of 1,3-dinitro-5-bromobenzene as a solid in addition to 2.30 g of the starting material. No trace of coupling products was detected: ^{1}H NMR δ 8.70 (d, J = 3 Hz, 2 H), 9.00 (t, J = 3 Hz, 1 H), HRMS, found 245.9275 (M^+), calcd for $C_6H_3BrN_2O_4$ 245.9276.

In the absence of the ketene silyl acetal, only the starting material was recovered in 96% yield.

Reaction of 1b with *p*-Dinitrobenzene. The general procedure B was used for the reaction of **1b** with *p*-dinitrobenzene. The product was chromatographed on silica gel. Only coupled product isolated was identified as methyl α-methyl-4-nitrobenzeneacetate (21%) by comparison of physical properties with those of an authentic sample and GC retention times. No addition product was obtained.

Reaction of 1d with *o*-Dinitrobenzene. A solution of 2.751 g (10 mmol) of TASF in 5 mL of dry acetonitrile was added to a mixture of 1.688 g (10 mmol) of 1,2-dinitrobenzene and 1.64 mL (10 mmol) of **1d** dissolved in 15 mL of THF at −70 °C. The reaction was warmed to −20 °C and was stirred for 1 h. After the mixture was cooled to −70 °C, 0.50 mL of bromine in 5 mL of cyclohexane was added, and the cold bath was removed. After 20 mL of water was added, the product was extracted into ether. Isolation and chromatography on silica using ethyl acetate/hexanes as solvent gave two fractions. The first fraction 0.669 g) was identified as a mixture of methyl 2-nitrobenzeneacetate (22%) and methyl 3-nitrobenzeneacetate (78%). The second fraction (0.248 g) was clean methyl 3-nitrobenzeneacetate as confirmed by the following data and GCMS. Total yield of coupled product 0.92 g (47%). Retention times of products: ortho 11.87 min (3% SP2100 on 60/80 Supelcoport, 6 ft × $^1/_8$ in. glass column, 100 °C/4 min increased to 230 °C at 16 °C/min rate), meta 12.32 min. Methyl 3-nitrobenzeneacetate: IR (neat) 1735, 1529, 1350 cm^{-1}; ^{1}H NMR (360 MHz) δ 3.72 (s, 3 H), 3.77 (s, 2 H), 7.51 (t, J = 8 Hz, 1 H), 7.65 (d, J = 8 Hz, 1 H), 8.11 (dm, J = 8 Hz, 1 H), 8.16 (s, br, 1 H). Comparison of properties with those of authentic methyl esters prepared from commercially available (Aldrich) nitrobenzeneacetic acids confirmed the structures.

Reaction of 1b with 4-Chloronitrobenzene with a Catalytic Amount of TASF. Procedure A with a catalytic amount of TASF (0.20 equiv) gave only 7.5% yield of expected product **8b**, as opposed to 58% with a stoichiometric amount of fluoride.

Methyl α,α-Dimethyl-6-bromo-5-chloro-2-nitro-2,4-cyclohexadiene-1-acetate (32a). To a mixture of 0.788 g (5 mmol) of 4-chloronitrobenzene and 1.02 mL (5.01 mmol) of **1a** in 10 mL of anhydrous THF was added 1.389 g (5.05 mmol) of TASF in 2 mL of acetonitrile and 2 mL of THF at −78 °C. The mixture was stirred overnight at −78 °C and then at −20 to −30 °C for 30 min. Subsequently 0.240 mL (4.70 mmol) of bromine was added, the cold bath was removed, and stirring was continued for 40 min. The products were extracted into ether after adding 20 mL of saturated sodium bisulfite and 20 mL of water. Drying of the ether layer, concentrating, and chromatographing on silica gel using 20% ether/hexanes yielded two products. The desired product **32a** was isolated in 41% (0.695 g) yield: mp 76–77 °C; UV (EtOH) 340 nm (610), 268 (6660); IR (KBr) 1735, 1600, 1566, 1522, 1342 cm^{-1}; ^{1}H NMR δ 1.15 (2s, 6 H), 3.70 (s, 3 H), 4.20 (s, br, 1 H), 4.90 (s, br, 1 H), 6.30 (d, J = 7 Hz, 1 H), 7.55 (d, J = 7 Hz, 1 H); HRMS, found 290.9806 ($M^+ - NO_2$), calcd for $C_{11}H_{13}O_2ClBr$ 290.9787, 258.0533 (M^+ − Br), calcd 258.0532; CIMS M^+ = 337 containing 1 Cl and 1 Br. The other product was identified as **8a**.

Preparation of Methyl α-Methyl-6-bromo-5-chloro-2-nitro-2,4-cyclohexadiene-1-acetate (32b). To a solution of 0.779 g (5.00 mmol) of 4-chloronitrobenzene and 0.930 mL (5.04 mmol) of **1b** in 15 mL of anhydrous THF was added 1.3479 g (4.90 mmol) of TASF in 4 mL of THF and 2 mL of acetonitrile in 10 min at −78 °C. The mixture was stirred for 45 min at −78 °C. A solution of 0.250 mL (4.88 mmol) of bromine in 2 mL of cyclohexane was added and the mixture was stirred for 15 min. After warming to room temperature, 20 mL of saturated sodium bisulfite was added. Extraction with four 50-mL portions of ether and isolation of the product mixture gave three compounds which were separated by column chromatography. Fraction 1 was starting material, 0.0767 g. Fraction 2, the addition product **8b**, was identified by comparison of physical properties with those of a sample previously prepared. Fraction 3 was the dihydro adduct, **32b**, 0.233 g (14%): UV (EtOH) 340 nm (1030), 266 (7690); IR (KBr) 1740, 1525, 1345 cm^{-1}; ^{1}H NMR δ 1.15 (d, J = 7 Hz), 1.22 (d, J = 7 Hz), together 3 H, 2.83 (m, 1 H), 3.67 (s), 3.74 (s) together 3H, 3.97 (d, m, J = 5 Hz), 4.15 (dm, J = 5 Hz) together 1 H, 4.90 (s, br), 5.00 (s, br) together 1 H, 6.30 (d, m, J = 6 Hz), 6.34 (d, m, J = 6 Hz) together 1 H, 7.48 (d, J = 6 Hz), 7.55 (d, J = 6 Hz) together 1 H; HRMS, found 197.0366 ($M^+ - HBrNO_2$), calcd for $C_{10}H_{10}O_2Cl$ 197.0369. CIMS M^+ = 323 (also showed the presence of 1 Cl, 1 Br, and an odd number of N).

Elimination of HBr from 32b. A solution of 0.110 g (0.34 mmol) of **32b** in 3 mL of CH_2Cl_2 was stirred with 0.200 mL (0.74 mmol) of triethylamine for 4 h. Thin-layer chromatography showed a presence of trace amounts of starting material and the elimination product. Fifteen milliliters of 2.5 N HCl was added followed by 40 mL of methylene chloride. The organic phase was separated and washed with saturated chloride and water. Concentration gave 0.083 g of the dehydrobromination product identified as **8b** by GC and ^{1}H NMR spectroscopy.

3-(6-Bromo-5-methoxy-2-nitro-2,4-cyclohexadienyl-1-oxacyclopentan-2-one (34). A two-necked flask fitted with a thermometer and dropping funnel is charged with 1.53 g (10 mmol) of *p*-nitroanisole and 2 mL (12 mmol) of **1c** in 30 mL of anhydrous THF. To the mixture at −78 °C was added 2.75 g (10 mmol) of TASF dissolved in 5 mL of acetonitrile. The mixture was warmed to −15 °C, stirred for an hour, and then cooled to −78 °C. A solution of 0.500 mL (9.7 mmol) of bromine dissolved in 10 mL of cyclohexane was added below −70 °C. After stirring for 15 min at −78 °C, the mixture was warmed to room temperature and the product was extracted into ether from aqueous solution. The combined ether extract was washed with saturated sodium bisulfite and water. Concentration and isolation of the product by column chromatography (1:1 ethyl acetate/hexane; silica) yielded 1.25 g (40%) of **34**: mp 130–140 °C dec; UV (EtOH) 370 nm (8750); IR (KBr) 3080, 2980, 2960, 2910, 2840, 1755, 1640, 1555, 1320 cm^{-1}; ^{1}H NMR δ 2.00–3.05 (m, br, 3 H), 3.87 (s, 3 H), 3.97 (dd, J = 8 Hz, 1 H), 4.05–4.45 (m, br, 2 H), 4.60 (dd?, J = 2, 2 Hz, 1 H), 5.50 (dd, J = 6, 2 Hz, 1 H), 7.80 (d, J = 6 Hz, 1 H); HRMS, found 3.16.9781 (M^+), calcd for $C_{11}H_{12}NO_5Br$ 316.9898, 237.0637 (M^+ − HBr), calcd 237.0636. Anal. C, H, Br.

Methyl α,α-Dimethyl-6-bromo-5-methoxy-2-nitro-2,4-cyclohexadiene-1-acetate (33). The procedure reported for the preparation of **34** using **1a** instead of **1c** as the starting material gave 2.313 g (69%) of the adduct **33**: mp 115–116 °C; UV (EtOH) 375 nm (8725); IR (KBr) 3080, 3020, 2990, 2960, 1725, 1645, 1565, 1320 cm^{-1}; ^{1}H NMR δ 1.12 (s, 3 H), 1.18 (s, 3 H), 3.67 (s, 3 H), 3.76 (s, 3 H), 4.13 (s, 1 H), 4.67 (s, 1 H), 5.22 (d, J = 8 Hz, 1 H), 7.76 (d, J = 8 Hz, 1 H); HRMS, found 333.0165 (M^+), calcd for $C_{12}H_{16}NO_5Br$ 333.0211. Anal. C, H, Br.

Methyl α,α-Dimethyl-1-nitro-1,2-dihydronaphthalene-2-acetate (25). To a solution of 0.833 g (3.03 mmol) of TASF in 20 mL of anhydrous THF and 5 mL of pyridine was added a mixture of 1.732 g (10 mmol) of 1-nitronaphthalene and 2.03 mL (10.20 mmol) of **1a** dropwise at −10 °C. The mixture was allowed to warm to room temperature with the bath in place (3.5 h). Ten milliliters of 1 N HCl was added, and the mixture was stirred for 5 min. The product was extracted into ether with three 50-mL portions. The combined ether extract was dried, concentrated, and chromatographed on silica using 20% ethyl acetate/hexane as solvent. The first fraction contained 0.6115 g of unconverted starting material. The second component contained 0.711 g (26%) of the desired product **25** which was recrystallized from ether/hexanes: mp 74.5–76.5 °C; UV (EtOH) 300 nm (1200), 290 (1576), 259 (8965), 217 (29 336), 211 (27 280) (1,2-dihydronaphthalene chromaphore); IR (KBr) 1720, 1540, 1360, 1600, 1490 cm^{-1}; ^{1}H NMR (360 MHz) δ 1.03 (s, 3 H), 1.20 (s, 3 H), 3.60 (s, 3 H), 3.62 (dt, J = 5, 1 Hz, 1 H), 5.53 (d, J = 1 Hz, 1 H), 5.93 (dd, J = 9, 5 Hz, 1 H), 6.70 (d, J = 9 Hz, 1 H), 7.18 (d, J = 15 Hz, 1 H), 7.25–7.42 (m, 3 H); HRMS, found 228.1152 ($M^+ - HNO_2$), calcd for $C_{15}H_{16}O_2$ 228.1150, 169.1000 ($M^+ - (HNO_2 + C_2H_3O_2)$), calcd 169.1017.

DDQ Treatment of 25. A mixture of 0.060 g (0.22 mmol) of **25** and 0.200 g (0.88 mmol) of DDQ was refluxed in benzene for 18 h. Benzene was removed on the rotary, and the product was filtered through silica gel using 80% ether/petroleum ether as solvent: yield of HNO_2 elimination product, 0.043 g (86%); IR (KBr) 1730, 1630, 1600, 1505, 1145 cm^{-1}; ^{1}H NMR (360 MHz) δ 1.68 (s, 6 H), 3.65 (s, 3 H), 7.40–7.50 (m, 3 H), 7.75–7.85 (m, 4 H); HRMS, found 228.1145 (M^+), calcd for $C_{15}H_{16}O_2$ 228.1150, 169.1000 ($M^+ - CO_2CH_3$), calcd 169.1017.

Methyl α-Methyl-1-nitro-1,2-dihydronaphthalene-2-acetate (26). To a solution of 1.737 g (10 mmol) of 1-nitronaphthalene and 1.90 mL (10.28 mmol) of **1b** in 25 mL of anhydrous THF was added 2.751 g (10 mmol) of TASF in 10 mL of acetonitrile at −78 °C in 10 min. The mixture was stirred for 22 h at −78 °C. A mixture of 2 mL of glacial

acetic acid and 15 mL of hexane was added at −78 °C followed by 10 mL of saturated potassium hydrogen phosphate. The mixture was warmed to room temperature. The product was extracted into ether, dried, and concentrated. Column chromatography on silica gel yielded 0.9492 g of pure material as the first fraction. A second contaminated fraction was recrystallized from ether/hexane to get 0.8154 g more of the addition product **26**: total yield of crystalline material, 1.7646 g (67%); mp 98 °C; UV (EtOH) 300 nm (1130), 290 (1530), 258 (8530) (1,2-dihydronaphthalene chromaphore); IR (KBr) 1730, 1600, 1495, 1550, 1360, 1170 cm^{-1}; ^1H NMR (360 MHz) δ 1.40 (d, J = 7 Hz, 3 H), 2.78 (m, 1 H), 3.15 (m, 1 H), 3.80 (s, 3 H), 5.75 (d, J = 7 Hz, 1 H), 5.90 (d, m, J = 10 Hz, 1 H), 6.60 (dd, J = 10, 4 Hz, 1 H), 7.20–7.45 (m, 4 H); HRMS, found 215.1036 ($M^+ - NO_2$), calcd for $C_{14}H_{15}O_2$ 215.1082. Anal. C, H, N.

Further purification of the mother liquor by careful chromatography gave 0.1424 g (5%) of another pure adduct, possibly the 1,4-isomer: IR (KBr) 1730, 1550, 1360 cm^{-1}; ^1H NMR δ 1.13 (d, J = 7 Hz, 3 H), 2.40 (m, 1 H), 3.60 (m, 1 H), 3.60 (s, 3 H), 5.40 (d, J = 1 Hz, 1 H), 6.09 (dd, J = 11, 5 Hz, 1 H), 6.63 (d, J = 11 Hz, 1 H), 7.05–7.40 (m, 4 H). Even though the recrystallized product is a single isomer, the crude mixture of products indicate multiplicities of CH_3 and other signals, clearly showing geometric and/or diastereomeric isomerism. The structures of none of these products have been conclusively established.

Methyl α,α-Dimethyl-9-nitro-9,10-dihydroanthracene-10-acetate (27). A solution of 1.115 g (5 mmol) of 9-nitroanthracene and 1.01 mL (5 mmol) of **1a** in 20 mL of anhydrous THF was treated with 1.375 g (5 mmol) of TASF dissolved in 3 mL of acetonitrile at −78 °C. After addition of TASF was completed, the reaction mixture was brought to −10 °C and stirred for 1 h. Ten milliliters of water was added and the product was extracted into ether. The organic layer was washed with saturated sodium chloride solution, dried, and concentrated. Trituration with methanol yielded 0.900 g (56%) of **27** as pale-yellow crystals, mp 159–163 °C dec; UV (EtOH) 335 nm (1985), 300 (965), 275 (1450), 268 (1580), 250 (2080); IR (KBr) 1710, 1543 cm^{-1}; ^1H NMR δ 0.93 (s, 6 H), 3.70 (s, 3 H), 4.47 (s, 1 H), 6.26 (s, 1 H), 7.25–7.90 (m, 8 H); HRMS, found 279.1383 ($M^+ - NO_2$), calcd for $C_{19}H_{19}O_2$ 279.1385. Anal. C, H, N.

Methyl α-Methyl-9-nitro-9,10-dihydroanthracene-10-acetate (28). To a solution of 0.757 g (3.39 mmol) of 9-nitroanthracene and 0.663 mL (3.56 mmol) of **1b** in 20 mL of anhydrous THF was added 0.941 g (3.42 mmol) of TASF in 2 mL of anhydrous acetonitrile at −78 °C. The mixture was stirred for 24 h at −78 °C. Ten milliliters of saturated KH_2PO_4 and 20 mL of water were added, and the product was extracted into ether. The combined ether extract was washed with water, dried, and concentrated. The major product (0.491 g, 56%) was isolated by column chromatography of silica using 20% ether/hexane as the solvent. Addition of a small amount of ether to the major fraction yielded **28** as a light-yellow solid: UV (EtOH) 274 nm (1200), 267 (1370); IR (KBr) 1720, 1552 cm^{-1}; ^1H NMR δ 1.10 (d, J = 7 Hz, 3 H), 2.73 (dq, J = 7, 9 Hz, 1 H), 3.53 (s, 3 H), 4.26 (d, J = 9 Hz, 1 H), 6.50 (s, 1 H), 7.20–7.35 (m, 8 H); HRMS 265.1212 ($M^+ - NO_2$), calcd for $C_{18}H_{17}O_2$ 265.1229. The crude product showed multiplicities of CH_3 and other signals indicating geometric/diastereomeric mixtures. Upon crystallization, however, only one of these products came out of solution.

The ether soluble component was identified as an aromatic ester arising from the elimination of the elements of HNO_2 from **28**. An authentic sample of this adduct was prepared as described in the next experiment.

Elimination of HNO_2 from 28. A mixture of 0.100 g of **28** and 5 g of silica was stirred overnight in 20 mL of methylene chloride. The silica was filtered off, and the product was chromatographed on a thick plate using 30% ether/hexanes as the solvent, yield 0.073 g (86%); the product was identified as methyl α-methyl-10-anthraceneacetate: IR (KBr) 1732 cm^{-1}; ^1H NMR δ 1.83 (d, J = 7 Hz, 3 H), 3.57 (s, 3 H), 5.10 (q, J = 7 Hz, 1 H), 7.50 (m, 4 H), 8.10 (m, 4 H), 8.40 (s, br, 1 H); HRMS, found 264.1154 (M^+), calcd for $C_{18}H_{16}O_2$ 264.1151, 205.100 ($M^+ - C_2H_3O_2$), calcd 205.1017.

Methyl α-Methyl-5,6-dihydro-5-nitroisoquinoline-6-acetate (29). A flame-dried 50-mL flask fitted with an addition funnel was charged with 0.872 g (500 mmol) of 5-nitroisoquinoline and 0.95 mL (5.1 mmol) of **1b**. An acetonitrile solution of 1.40 g (5.09 mmol) of TASF was slowly added to the reaction mixture in 15 min at −78 °C. The mixture was stirred for 22 h at that temperature. One milliliter of acetic acid in 5 mL of hexane was added, and the reaction was warmed to room temperature. After 30 min, 40 mL of water was added. The solid which precipitated out was collected and analyzed: yield, 0.972 g (74%); IR (KBr) 3400, 1710, 1650, 1630, 1350 cm^{-1}; ^1H NMR (80 MHz, Me_2SO-d_6) inter alia δ 0.87 (d, J = 8 Hz, 3 H), 3.23 (m, 1 H), 3.63 (s, 3 H), 4.63 (t, J = 5 Hz, 1 H), 5.69 (dd, J = 9, 5 Hz, 1 H), 6.53 (d, J = 9 Hz, 1 H), 7.83 (s, 1 H), 7.90 (d, J = 7 Hz, 1 H), 8.60 (d, J = 7 Hz, 1 H). The material is poorly soluble even in Me_2SO and hence suggests a Zwitterionic structure. The acidic proton is too broad (?) to be observed: HRMS, found 231.0769 ($M^+ - OCH_3$), calcd for $C_{12}H_{11}N_2O_3$ 231.0769, 215.0948 ($M^+ - NO_2$), calcd for $C_{13}H_{13}NO_2$ 215.0946, 156.0795 ($M^+ - (HNO_2 + C_2H_3O_2)$), calcd for $C_{11}H_{10}N$ 156.0814.

Air Oxidation of 29. A mixture of 1 g of **29** in 50 mL of 1,2-dichloroethane and 2 mL of triethylamine was refluxed for 4 h with no precaution for exclusion of air. Seventy-five milliliters of methylene chloride and 50 mL of water were added, and the product was extracted into methylene chloride. The combined methylene chloride layer was washed with saturated KH_2PO_4, dried, and concentrated. Two major products isolated by column chromatography on silica using 40% ethyl acetate/hexanes corresponded to **20b** and **31** in a ratio of 10:1, respectively. These compounds were identified by samples previously prepared by the direct oxidation of the nitronate with DDQ. (See Table III.)

NMR Experiments. Reaction of Nitrobenzene with 1a. To a mixture of 11.90 μL (0.116 mmol) of nitrobenzene and 24.20 μL (0.116 mmol) of **1a** in 1:1 THF-d_8 and CD_3CN in a dry NMR tube was added 0.032 g (0.116 mmol) of TASF in CD_3CN at −70 °C. The mixture was shaken well and then transferred into the probe of a Nicolet 360WB NMR spectrometer, and the spectra were recorded at various temperatures. (See Figures 1 and 2 and Discussion section.)

Reaction of 4-Chloronitrobenzene with 1b. To a solution of 0.055 g (0.35 mmol) of 4-chloronitrobenzene and 68 μL (0.36 mmol) of **1b** in 0.44 mL of THF-d_8 in a dry NMR tube was added 0.096 g (35 mmol) of TASF in 0.10 mL of CD_3CN. The mixture was shaken well, and NMR spectra were run at various temperatures (Figure 3). On the basis of the spectral data reported below in addition to the starting 4-chloronitrobenzene, the reaction mixture contained the diastereomeric adducts **39** in a ratio of 1:1 at −60 °C.

Reaction Mixture at Room Temperature. The above reaction mixture was maintained at −70 °C overnight and was warmed to the probe temperature (24 °C) in 20 min, and the spectrum was recorded. *In addition to the complete disappearance of starting 4-chloronitrobenzene, there is a change in the ratio of major to minor adduct*, the present ratio being 1:2.8. **Major Isomer**: ^1H NMR ((360 MHz) −60 °C to room temperature, 20 min, THF-d_8–CD_3CN) δ 1.015 (d, J = 9 Hz, 3 H, benzylic CH_3), 2.70 (m, 1 H) 3.60 (s, 3 H, CH_3O), 4.50 (ddm, J = 6, 4 Hz, 1 H, H_6), 4.75 (dm, J = 10 Hz, 1 H, olefinic H_3), 5.17 (dd, J = 6, 2 Hz, 1 H, H_5), 6.94 (d, J = 10 Hz, 1 H, H_2). **Minor Isomer**: NMR δ 1.012 (d, J = 9 Hz, 3 H, benzylic CH_3), 2.70, (m, 1 H), 3.46 (s, 3 H, OCH_3), 4.25 (ddm, J = 6, 4 Hz, H_6), 4.79 (d, m, J = 10 Hz, 1 H, H_3), 5.40 (dd, J = 6, 2 Hz, 1 H, H_5), 6.88 (d, J = 10 Hz, 1 H, H_2).

Preparation of 4-Nitrocumenyl Chloride (35a). Excess chlorine oxide[34] in carbon tetrachloride (40 mL of a 40% solution) was added to a solution of 5 g (30.5 mmol) of 4-nitrocumene (Fluka) in CCl_4, and the mixture was stirred for 2 days. Subsequently the solution was dried, and the solvent and excess Cl_2O were removed on the rotary. Distillation 75 °C, 0.4 mm) yielded 5.14 g (85%) of **35a** identical in every respect with the sample described in the literature.[35]

Reaction of 4-Chloronitrobenzene with Potassium Enolate of Cyclohexanone. To a suspension of 0.170 g (4.24 mmol) of mineral oil-free KH in 3 mL of THF at 0 °C was added 0.439 mL (4.23 mmol) of cyclohexanone in 5 mL of THF.[36] The mixture was stirred for 1 h at 0 °C and was subsequently cooled to −78 °C, and 0.669 g (4.24 mmol) of 4-chloronitrobenzene in 5 mL of THF was dripped in. After the solution was stirred at −78 to −40 °C for 2 h, 0.962 g (4.23 mmol) of DDQ in 3 mL of THF was added and the mixture was brought to room temperature. Thirty milliliters of saturated sodium chloride was added, and the product was extracted into ether (50 mL × 4). The ether extract was washed with 60 mL of 6% sodium hydroxide and then was concentrated after drying. TLC (ether/hexanes) showed several spots and very little if any of the expected product (**8e**).

Reaction of 4-Chloronitrobenzene with Potassium Enolate of Methyl Propionate in the Presence of 18-Crown-6. To a suspension of 0.256 g (6.38 mmol) of mineral oil-free KH in 3 mL of THF was added 0.615 mL (6.38 mmol) of methyl propionate in 5 mL of THF at −50 °C. To the mixture was added 0.30 g of dried 18-crown-6, and the temperature was brought up to −30 °C. A solution of 1.005 g (6.40 mmol) of 4-chloronitrobenzene in THF was slowly added, the reaction was stirred for 1 h at −40 °C, and 1.44 g (6.34 mmol) of DDQ in THF was added. The reaction was brought to room temperature and worked up as in the previous experiment. Column chromatography on silica using 10% ether/hexanes yielded about 6% of the expected product (**8b**).

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Addition of Lithium Ester Enolates to Nitrobenzenes. Lithium enolates prepared from methyl propionate and γ-butyrolactone with LDA were reacted with nitrobenzene (−78 to 3 °C), 4-chloronitrobenzene (−20 °C, 2 h), 4-fluoronitrobenzene (−20 °C, 90 min), and 4-nitroanisole (−20 °C, 2 h), and the reaction mixtures were oxidized with bromine. No trace of coupling products were detected in any of these cases.

Registry No. 1a, 31469-15-5; **1b**, 34880-70-1; **1c**, 51425-66-2; **1d**, 2916-76-9; **1e**, 6651-36-1; **1f**, 13735-81-4; **3**, 59115-08-1; **4**, 97522-00-4; **5b**, 30096-07-2; **5c**, 97522-01-5; **5d**, 30095-98-8; **5e**, 68614-38-0; **6b**, 50415-69-5; **6c**, 97522-02-6; **6d**, 2945-08-6; **6e**, 52648-78-9; **7b**, 92671-30-2; **7c**, 92671-31-3; **8a**, 92671-32-4; **8b**, 86790-37-6; **8c**, 92671-33-5; **8d**, 22908-29-8; **8e**, 92671-34-6; **8f**, 80805-54-5; **9b**, 92671-35-7; **9c**, 92671-36-8; **9f**, 97522-03-7; **10b**, 92671-37-9; **10e**, 97522-04-8; **11a**, 92671-38-0; **11e**, 97522-05-9; **12d**, 77158-65-7; **13b**, 97522-07-1; **14b**, 97522-08-2; **15**, 121-73-3; **15d**, 97522-09-3; **15e**, 97522-10-6; **16**, 86-57-7; **16a**, 97522-19-5; **16b**, 92671-40-4; **16c**, 92671-41-5; **17**, 581-89-5; **17b**, 97522-11-7; **17d**, 97522-12-8; **18**, 602-60-8; **19**, 6583-06-8; **19a**, 92671-42-6; **20**, 607-32-9; **20b**, 97522-13-9; **21**, 13599-78-5; **21a**, 97522-14-0; **21b**, 97522-15-1; **21d**, 97522-16-2; **22**, 609-40-5; **23**, 97522-17-3; **25**, 97522-18-4; **26**, 97522-20-8; **26** (1,4 isomer), 97522-21-9; **27**, 97522-22-0; **28**, 97522-23-1; **31**, 97522-24-2; **30**, 97522-26-4; **31**, 97522-25-3; **32a**, 97522-27-5; **32b**, 97522-28-6; **33**, 97522-29-7; **34**, 97522-30-0; **35a**, 14500-58-4; **35b**, 100-14-1; TASF, 59218-87-0; Bu_4NF, 429-41-4; nitrobenzene, 98-95-3; 1-chloro-4-nitrobenzene, 100-00-5; *m*-dinitrobenzene, 99-65-0; 1,3-dinitro-5-bromobenzene, 18242-39-2; *p*-nitroanisole, 100-17-4; methyl α-methyl-10-anthraceneacetate, 79938-37-7; 4-nitrocumene, 1817-47-6; cyclohexanone, 108-94-1; methyl propionate, 554-12-1; δ-butyrolactone, 96-48-0; 1-methyl-4-nitrobenzene, 99-99-0; 1-fluoro-4-nitrobenzene, 350-46-9; 1,3-dichloro-4-nitrobenzene, 611-06-3; 1-chloro-3-methoxy-4-nitrobenzene, 6627-53-8; 1-chloro-2-nitrobenzene, 88-73-3; 1-cyclopropyl-4-nitrobenzene, 6921-44-4; methyl 3-chloro-4-nitrobenzeneacetate, 97522-06-0; 1,2-dinitrobenzene, 528-29-0; methyl 3-nitrobenzeneacetate, 10268-12-9; 1,4-dinitrobenzene, 100-25-4.

Photocyclization of *o-tert*-Butylbenzophenone

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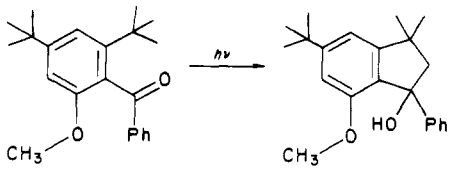
Abstract: UV irradiation of *o-tert*-butylbenzophenone as a solid or in solution from 77 K to room temperature results in its quantitative cyclization to 1-phenyl-3,3-dimethyl-1-indanol. The quantum efficiency is 0.04 in hydrocarbon solvents and 1 in methanol. Laser flash spectroscopy reveals the intermediacy of the expected 1,5-biradical, which has a lifetime in methanol of 43 ns from −100 to 25 °C but only 4 ns in toluene. This biradical is formed from a very reactive triplet, which has a lifetime greater than 10 ns only in alcohols below −70 °C. The variation of triplet lifetime with temperature (−70 to −130 °C) indicates an activation energy of 2.30 kcal/mol and an *A* factor of $10^{10.6}$ s^{-1} for δ-hydrogen abstraction by the triplet. Room temperature quenching of the cyclization indicates a rate constant $\geq 10^9$ M^{-1} s^{-1}. This exceptionally fast example of δ-hydrogen abstraction results from the ketone existing exclusively in a conformation ideal for internal hydrogen abstraction and may represent tunnelling. X-ray analysis of the crystal reveals that the *tert*-butylphenyl ring is twisted 69° from coplanarity with the carbonyl and that two of the *tert*-butyl hydrogens are within bonding distance of the oxygen. Oxygen and nitroxides increase the product quantum yield and decrease the biradical lifetime. This effect of paramagnetic additives is similar to that observed for 1,4-biradicals, but the solvent effect on biradical lifetimes is larger than usual.

The photochemistry of *o-tert*-butylphenyl ketones has been a subject of some confusion. Beckett and Porter originally reported that *o-tert*-butylbenzophenone (OTBBP) undergoes photodisappearance in 2-propanol and assumed that it was being photoreduced by solvent.[2] Neckers reported that 2,4,6-tri-*tert*-butylacetophenone photocyclizes inefficiently by presumedly slow δ-hydrogen abstraction.[3] O'Connell reported briefly that 2,4-di-*tert*-butyl-6-methoxybenzophenone photocyclizes to a 3,3-dimethyl-1-indanol derivative.[4] This report is striking because it suggests that *tert*-butyl primary hydrogens may be more reactive than methoxy hydrogens, when in fact anisole is known to be six times more reactive than *tert*-butylbenzene toward alkoxy radicals.[5] More recently, Bergmark and Kennedy reported that 2,5-di-*tert*-butylvalerophenone is stable to UV irradiation.[6] They ascribed this lack of reactivity to very rapid and totally reversible δ-hydrogen abstraction. These conclusions are unusual since δ-hydrogen abstraction normally is very slow.[7]



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Our combined interests in biradicals[8-12] and conformational effects on intramolecular reactions[13] prompted us to investigate the photobehavior of OTBBP as completely as possible. We report here our findings, which confirm all the earlier observations and most of the puzzling earlier conclusions, especially that of very rapid triplet δ-hydrogen abstraction, and reveal unusually large conformational and solvent effects on triplet hydrogen abstraction and on biradical decay.

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