3.40–3.51 (m, 1 H, OCH), 2.95 (br s, 1 H, OH), 1.55–1.81 (m, 4 H, $OCH_2CH_2CH_2$), 1.13–1.55 (m containing a large singlet at 1.27 and singlet shoulders at 1.32 and 1.36, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, CH_3); IR (neat) 3390 (m), 2910 (s), 2880 (s), 1452 (m), 1370 (m), 1295 (w), 1240 (m), 1195 (m), 1050 (s), 890 (w), 705 cm^{-1} (w); high-resolution mass spectrum (CI) calcd for $C_{17}H_{34}O_3$ 286.2508, found 286.2493.

2-Methyl-2-[3-(methylsulfonyl)propyl]-4-decyl-1,3-dioxolane (4c). According to a standard procedure,[12] 20.2 g (70.4 mmol) of **8** was converted into 21.5 g (85%) of **4c**, which decomposed rapidly at 25 °C and slowly at 0 °C. It was used without further purification: ^1H NMR ($CDCl_3$) δ 4.21–4.31 (m, 2 H, CH_2OSO_2), 3.96–4.15 (m, 2 H, OCH_2), 3.39–3.53 (m, 1 H, OCH), 3.01 (s, 3 H, CH_3SO_2O), 1.69–1.95 (m, 4 H, $OCH_2CH_2CH_2$), 1.12–1.53 (m containing a large singlet at 1.26 and singlet shoulders at 1.31 and 1.35, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, CH_3); IR (neat) 2910 (s), 2850 (m), 1460 (w), 1350 (s), 1170 (s), 1040 (w), 965 (m), 910 (m), 810 (m), 710 cm^{-1} (w).

[3-(4-Decyl-2-methyl-1,3-dioxolan-2-yl)propyl]trimethylammonium Methanesulfonate (1c). A solution of 21.5 g (58.9 mmol) of **4c** in 50 mL of 25% (w/v) Me_3N–MeOH was allowed to stand for 4 days at 25 °C. Then an additional 50 mL of Me_3N–MeOH was added, and the solution was refluxed for 6 h under an Me_2CO–dry ice condenser. Rotary evaporation, followed by drying at 85 °C (0.1 mmHg) left a residue that was recrystallized from 9:1 (v/v) and then from 19:1 (v/v) EtOAc–MeOH to yield 17.9 g (72%) of **1c**: mp 140–144 °C (sealed tube); ^1H NMR ($CDCl_3$) δ 3.96–4.16 (m, 2 H, OCH_2), 3.35–3.55 (m + s at 3.34, 12 H total, $(CH_3)_3N$, NCH_2, and OCH), 2.72 (s, 3 H, $CH_3SO_3^-$), 1.55–1.91 (m, 4 H, $NCH_2CH_2CH_2$), 1.12–1.55 (m containing a large singlet at 1.26 and singlet shoulders at 1.31 and 1.35, 21 H total, $(CH_2)_9$ and $OCCH_3$), 0.88 (t, 3 H, CH_3); IR (Nujol) 1185 (s), 1110 (w), 1040 (s), 950 (w), 895 (w), 825 (w), 760 cm^{-1} (s); high-resolution mass spectrum (FAB) calcd for $C_{20}H_{42}NO_2$[13] 328.3215, found 328.3234. Anal. Calcd for $C_{21}H_{45}NO_5S \cdot 0.5H_2O$: C, 58.30; H, 10.72. Found: C, 58.42, 58.39; H, 10.50, 10.49.

Hydrolysis of Micellar 1c. A solution of 191 mg (0.450 mmol) of **2c** in 50 mL of 5% aqueous HCl was prepared and immediately extracted with 25 mL of Et_2O. The mixture foamed but cleanly separated into two layers within 15 min. The aqueous layer was further extracted with five 15 mL-portions of Et_2O with 15 min between extractions. The combined extracts were dried (Na_2SO_4) and rotary evaporated to yield 94 mg (103%) of crude **3**, mp 58–59 °C (lit.[14] mp 60–61 °C). The aqueous solution was rotary evaporated to give 114 mg of a yellow oil which by ^1H NMR (D_2O) contained **2c** (**2a**).

Hydrolysis of 1c in a Microemulsion. A microemulsion composed of 1.02 g (2.41 mmol) of **1c**, 1.03 g of 1-butanol, 0.40 g of hexane, and 7.60 g of 0.01 M $NaHCO_3$ was equilibrated at 40 °C.[15] Then 5 mL of 5% HCl was added, and the mixture was extracted with 5 mL of Et_2O. Clean separation of layers occurred within 5 min, and the aqueous layer was then extracted immediately with three 5-mL portions of Et_2O and 1 h later with 5 mL of Et_2O. The combined Et_2O extracts were dried (Na_2SO_4) and yielded 267 mg (56%) of **3**, mp 58.0–59.5 °C. After the aqueous layer sat overnight at 25 °C, it was extracted with three 5-mL portions of Et_2O. The combined extracts were dried (Na_2SO_4) and yielded 173 mg (36%) of **3**, mp 57.5–59.0 °C.

For both this and the above hydrolysis, control extractions were performed with the substitution of H_2O for 5% HCl. In each case, persistent emulsions did not form. This behavior is fortuitous and not to be generally expected.[1e,4b,16]

Acknowledgement is made to the U.S. Army Research Office, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Marathon Oil Company for support of this research.

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Supplementary Material Available: Spectral data (^1H NMR and IR) for **1d** and the preparation and characterization of **2a**, **2b**, **2c**, (4-oxopentyl)trimethylammonium tetraphenylborate, and tetramethylammonium methanesulfonate (3 pages). Ordering information is given on any current masthead page.

Reaction of 1,1,1-Trichloro-3-nitro-2-propene with Furans: A Reexamination

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We have recently examined the chemistry of 1,1,1-trichloro-3-nitro-2-propene (**1**).[3-5] Burkett and Wright[3] report that furan (**2a**), 2,5-dimethylfuran (**2b**), and 2-chlorobutadiene with **1** give only starting materials under a variety of conditions. Other workers[6] have reported on the facile reaction of nitroethylene with furans, and a report has appeared[7] on the reaction of 2,3,4,5-tetramethylfuran with **1**. In contrast to the results of Burkett and Wright we find that equimolar amounts of **1** and furans **2a–c** condense at room temperature in the absence of solvents to give Diels–Alder adducts cleanly and in good yield (Scheme I).

Furan (**2a**) and **1** are observed (by ^1H NMR) to react slowly, reaching an equilibrium at 90% conversion after 14 days at room temperature. Two products are observed to form in a ratio of 1.2:1, and the ratio does not change throughout the course of the reaction. The adducts **3a** and **4a** may be separated by preparative liquid chromatography in 45% and 41% isolated yields, respectively. Their structures are assigned by consideration of the coupling of the protons adjacent to the nitro and trichloromethyl groups with the adjacent bridgehead protons. Thus the $CHNO_2$ signal of **3a** at 4.65 is a doublet with J = 4.4 Hz and the $CHCCl_3$ signal at 4.48 is a double doublet with J = 4.4 and 4.4 Hz. Since endo protons in bicyclo[2.2.1]-heptanes couple with their adjacent bridgehead protons with J = 0–2 Hz and exo protons couple with J = 4–7 Hz,[6] the $CHCCl_3$ proton must be exo, and the $CHNO_2$ proton must be endo, consistent with structure **3a**. The nitroolefin **1** is trans, and the coupling of 4.4 Hz is consistent with the expected 3–6 Hz trans coupling in substituted bicyclo-[2.2.1]heptanes.[6]

Condensation of 2,5-dimethylfuran (**2b**) and **1** reaches equilibrium at 81% conversion after 11 days. A single product is observed in the ^1H NMR throughout the course of the reaction; however, no structural assignment can be made from analysis of the spectrum. The product crystallizes after chromatography, and an X-ray crystal structure analysis (Figure 1) results in assignment of structure **3b**.

The reaction of 2-methylfuran (**2c**) and **1** is much faster, reaching 83% conversion after 4 h. A 4:1 ratio of **3c** and **4c** is formed, and this ratio does not vary throughout the course of the reaction. The structures are assigned by ^1H

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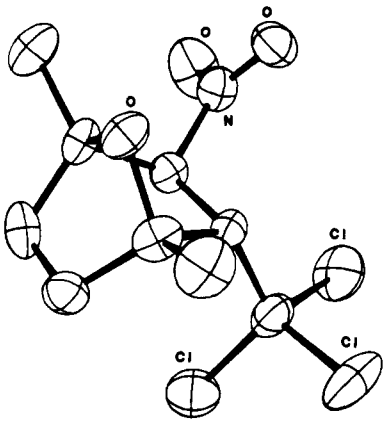
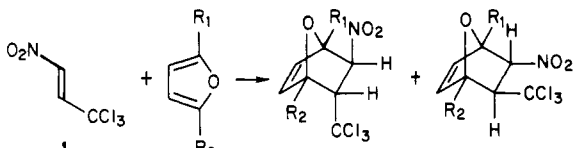


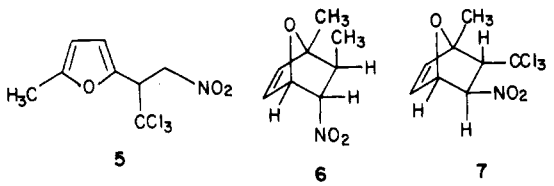
Figure 1. Result of single-crystal X-ray structure determination on dimethylfuran adduct **3b**.

Scheme I



	R_1	R_2	ratio 3:4		
a:	H	H	45	:	41
b:	CH_3	CH_3	100	:	0
c:	CH_3	H	75	:	25

NMR as for **3a** and **4a**. With extended reaction times **3c** and **4c** are converted to furan **5**, reaching 46% conversion



in 2 months at 5 °C. Complete conversion to **5** is achieved by treating a chloroform solution of **3c** and **4c** with a small amount of trifluoroacetic acid for 24 h, thereby confirming that regioisomers **6** and **7** are not present. A similar result has been reported, and a plausible mechanism proposed, for the reaction of furans and nitroethylene.[6]

Upon attempted distillation of **3c** and **4c** we observe only starting materials **1** and **2c**. It is possible that Burkett and Wright[3] similarly brought about a retro-Diels–Alder reaction upon attempted distillation of their reactions. An attempted reaction of **1** and 2-chlorobutadiene in xylene showed only starting materials by ^{1}H NMR after 1 month at room temperature.

The high regioselectivity in the reaction of **1** with **2c** is in accord with that reported for 3-nitroacrylates[8] and nitroethylene[6] with various dienes. The increasing tendency toward endo trichloromethyl stereochemistry with increasing substitution at the terminal positions of the furan diene may be compared with similar reactions of 3-nitroacrylates with furan, which gives an unspecified mixture,[9] and nitroethylene with **2a–c** where the *endo*-nitro stereochemistry is favored.[6] The report on the reaction of **1** with 2,3,4,5-tetramethylfuran gives no data on the stereochemistry of the adduct.[7] The nature of the endo-directing effect of substituents in the Diels–Alder reaction is poorly understood.[10,11] Our results are in accord with a stereochemical explanation[12–16] where a steric interaction occurs between the trichloromethyl group and the oxygen lone pairs and the alkyl substituents of the furan when the dienophile approaches the diene with the trichloromethyl group exo.

One of the earlier reports includes a description of the reaction of nitroethylene with furan and 2-methylfuran and states that the reactivity of 2-methylfuran is much greater, in accord with our results for **1**.[7,17] That the monosubstituted furan **2c** reacts faster than **2a** may be rationalized by increased electron density in the diene, and that **2c** reacts faster than **2b** may be rationalized by decreased steric hindrance, but the particular pattern of reactivity observed here does not appear to fit well with these arguments.

In conclusion, our observations on the reaction of 3,3,3-trichloro-1-nitro-1-propene pose some intriguing questions. The increased propensity for the trichloromethyl group to be endo with increasing substitution, or indeed for a substituent with no π-bonds to prefer the endo position at all, requires a more sophisticated explanation than the classical "orbital overlap" rationale. The remarkably higher reactivity of 2-methylfuran toward both **1** and nitroethylene[7] is also difficult to rationalize. Further research may shed light on this topic.

Experimental Section

^{1}H NMR spectra were obtained on a Varian EM-360 spectrometer operating at 60 MHz. Chemical shifts (δ) are reported in parts per million downfield of tetramethylsilane external standard (neat samples) or internal standard (chloroform-*d* samples). Coupling constants (J) are in hertz. Liquid chromatography was carried out on a Waters Prep-500 unit using dual silica gel columns. The nitroolefin **1** was prepared by literature methods.[1] Furans **2a–c** were purchased from Aldrich Chemical Co. and used without further purification.

Reaction of Furan (2a) with 1. 5-*exo*-Nitro-6-*endo*-(trichloromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (3a) and 5-*endo*-Nitro-6-*exo*-(trichloromethyl)-7-oxabicyclo[2.2.1]-hept-2-ene (4a). A mixture of 3.40 g (0.05 mol) of furan (**2a**) and 9.52 g (0.05 mol) of **1** was allowed to stand at ambient temperature for 22 days; an aliquot was analyzed by ^{1}H NMR periodically. After 14 days integration of starting material and product signals revealed 90% conversion to products **3a** and **4a** with a product ratio of 52:48. Liquid chromatography using 20:1 pentane:ether gave 5.3 g (41% yield) of **4a** at 2.9–3.2 column volumes and 5.8 g (45% yield) of **3a** at 4.0–5.0 column volumes. **3a**: white crystalline solid, mp 69–71 °C; ^{1}H NMR (neat) 6.65 (b m, 2 H), 5.37 (m, 2 H), 4.65 (d, J = 4.4, 1 H), 4.48 (dd, J = 4.4, 4.4, 1 H). Anal. Calcd for $C_7H_6Cl_3NO_3$: C, 32.53; H, 2.34; N, 5.42. Found: C, 32.92; H, 2.68; N, 5.27. **4a**: white crystalline solid, mp 64–64.5 °C; ^{1}H NMR (neat) 6.9 (dd, J = 2, 6, 1 H), 6.45 (dd, J = 1.5, 6, 1 H), 5.53 (bd, J = 5, 1 H), 5.28 (b s, 1 H), 5.2 (dd, J = 4.5, 5, 1 H), 3.63 (d, J = 4.5, 1 H). Anal. Calcd for $C_7H_6Cl_3NO_3$: C, 32.53; H, 2.34; N, 5.42. Found: C, 32.55; H, 2.35; N, 5.41.

Reaction of 2,5-Dimethylfuran (2b) with 1. 1,4-Dimethyl-5-*exo*-nitro-6-*endo*-(trichloromethyl)-7-oxabicyclo-[2.2.1]hept-2-ene (3b). A mixture of 4.8 g (0.05 mol) of 2,5-di-

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(17) Although ref 7 states that nitroethylene does not react at all with furan, ref 6 describes this reaction as complete in 24 h.

methylfuran (**2b**) and 9.52 g (0.05 mol) of **1** was allowed to stand at ambient temperature for 21 days; an aliquot was analyzed by ^{1}H NMR periodically. After 11 days integration of starting material and product signals revealed 81% conversion to a single product, and the reaction proceeded no further thereafter. Purification of the reaction mixture by liquid chromatography (pentane) gave 10.02 g (70% yield) of **3b** as a white crystalline solid: mp 69–70 °C; ^{1}H NMR (neat) 6.4 (AB q, J = 5, 2, 2 H), 4.73 (d, J = 4.4, 1 H), 4.17 (d, J = 4.4, 1 H), 1.87 (s, 3 H), 1.5 (s, 3 H). Anal. Calcd for $C_9H_{10}Cl_3NO_3$: C, 37.73; H, 3.52; N, 4.89. Found: C, 37.76; H, 3.56; N, 4.85.

X-ray crystallographic data for 3b ($C_9H_{10}Cl_3N_1O_3$): M_r 254.55; space group $P2_1/n$; Cu radiation, wavelength 1.54184 Å; cell dimensions a = 7.002 (4) Å, b = 20.355 (15) Å, c = 9.389 (5) Å, and β = 106.86 (5)°. The structure was solved by direct methods (program MULTAN) and also by Patterson search method (program VECMAT). Least-squares refinements brought the final discrepancy (R) factor down to 0.0788 for 1208 observed reflections. No significant features in the difference Fourier map were found at this stage. A listing of the structure factors and atomic coordinates has been included in the supplementary material section.

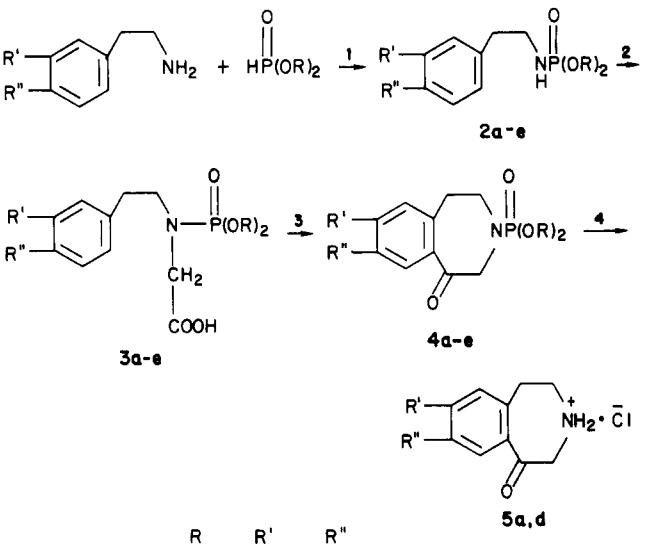
Reaction of 2-Methylfuran with 1. A mixture of 4.10 g (0.05 mol) of 2-methylfuran (**2c**) and 9.52 g (0.05 mol) of **1** was allowed to stand at ambient temperature. After 4 h analysis by ^{1}H NMR revealed a conversion of 83%, and no further conversion to bicyclic products occurred thereafter. A 4:1 ratio of **3c** and **4c** was observed by ^{1}H NMR. **3c**: 6.62 (dd, J = 2, 5, 1 H), 6.28 (d, J = 5, 1 H), 5.12 (m, 1 H), 4.6 (d, J = 4.4, 1 H), 4.47 (dd, J = 4.4, 4.4, 1 H), 1.52 (s, 3 H). **4c**: 6.78 (dd, J = 2, 5, 1 H), 6.15 (d, J = 5, 1 H), 5.12 (m, 1 H), 4.92 (d, J = 4.4, 1 H), 3.68 (d, J = 4.4, 1 H), 1.82 (s, 3 H). Upon standing for longer periods, conversion of the products to a new product was observed. The ^{1}H NMR spectrum of this product was identical with that of **5** obtained below.

2-Methyl-5-[2-nitro-1-(trichloromethyl)ethyl]furan (5). A chloroform solution of the crude mixture of **3c**, **4c**, and starting materials obtained above was treated at room temperature with 3 drops of trifluoroacetic acid. The solution turned dark immediately. After standing overnight the solution was washed with aqueous sodium bicarbonate solution, dried over anhydrous sodium sulfate, filtered, and evaporated to give a dark oil. The product was purified by evaporative distillation to give 5.0 g of **5** as a yellow oil which slowly solidified: mp 26–27 °C; ^{1}H NMR ($CDCl_3$) 6.38 (d, J = 4, 1 H), 5.93 (b, 1 H), 5.47–4.43 (m, 3 H), 2.1 (s, 3 H). Anal. Calcd for $C_8H_8Cl_3NO_3$: C, 35.26, H, 2.96, N, 5.24. Found: C, 35.34, H, 2.98, N, 5.12.

Registry No. 1, 763-16-6; **2a**, 110-00-9; **2b**, 625-86-5; **2c**, 534-22-5; **3a**, 92315-06-5; **3b**, 92315-07-6; **3c**, 92315-08-7; **4a**, 92418-53-6; **4c**, 92418-54-7; **5**, 92315-09-8.

Supplementary Material Available: Tables of X-ray crystallographic atomic coordinates for dimethylfuran adduct **3b** (4 pages). Ordering information is given on any current masthead page.

Scheme I[a]



	R	R'	R"
a	CH_3	-OCH_2O-	
b	C_2H_5	-OCH_2O-	
c	*i*-Pr	-OCH_2O-	
d	*i*-Pr	OCH_3	OC_2H_5
e	*n*-Bu	-OCH_2O-	

[a] 1. CCl_4, $(C_2H_5)_3N$; 2. NaH, $ClCH_2COOH$ in THF; 3. $SnCl_4$, $(CF_3CO)_2O$; 4. HCl(g) in THF.

Phosphoryl as a Novel Amino Protecting Group for Friedel–Crafts Acylation of *N*-[2-(3,4-Dialkoxyphenyl)ethyl]glycine

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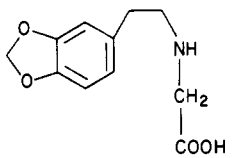
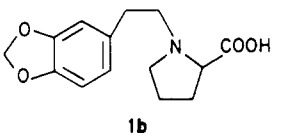
The family Cephalotaxaceae contains so far only one known genus with eight species and possibly two to three varieties mostly native to China.[1] Some ester alkaloids of cephalotaxus have shown significant activity in a variety of experimental leukemia systems. This has stimulated many groups in the world to develop total syntheses of these alkaloids.[2] Some of the promising starting materials for synthesis of the parent cephalotaxine are *N*-[2-[3,4-(methylenedioxy)phenyl]ethyl]glycine (**1a**) and *N*-[2-[3,4-(methylenedioxy)phenyl]ethyl]proline (**1b**). However,



1a



1b

under acid-catalyzed conditions these compounds failed to give Friedel–Crafts acylation products.[3,4] This is due to the basicity of the nitrogen causing decarbonylation. Use of the tosyl group has had some success in intramolecular condensation of some *N*-homopiperonylglycine derivatives.[4,5] Still, there is substantial decarbonylation. Also, the deprotection of the sulfonyl group was complicated and often unsuccessful.[4,6]

Recently, we showed a successful use of the diisopropoxyphosphinyl group as an amino protecting group in the intramolecular acylation reaction of the glycine derivatives.[7] In this paper, we report that the dimethoxy-, diethoxy-, and di-*n*-butoxyphosphinyl groups are also good amino protecting groups for the Lewis acid catalyzed

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