Alkaline Hydrolysis of 5-Methyl-3-phenyl-4-nitroisoxazole (3a). A suspension of 2.04 g (10 mmol) of 5-methyl-3-phenyl-4-nitroisoxazole (**3a**) in 100 mL of 0.5 N sodium hydroxide was refluxed for 1 h. The resulting solution was cooled, acidified with 2 N hydrochloric acid, and extracted with diethyl ether. The organic phase was washed with sodium bicarbonate solution and with water, dried over anhydrous sodium sulfate, then filtered, and evaporated. The residual oil was chromatographed on a silica gel column; elution with benzene–chloroform (9:1) and crystallization from dichloromethane gave 1.26 g (70% yield) of ω-nitroacetophenone oxime (**5**); mp 95 °C (lit.[4] mp 96 °C).

3,5-Disubstituted 4-Nitroisoxazoles (3a–f). General Procedure. To an ice-cold solution of the α-bromoalkyne **1a–f** (10 mmol) in 10 mL of ethanol was added, with stirring, a solution of sodium nitrite (6.9 g, 100 mmol) in 10 mL of water. Stirring was continued at room temperature until the starting compound disappeared on a TLC control. Then 10 mL of water was added, most of the ethanol was removed under vacuum, and the mixture was extracted with ether; the organic phase was washed with water and dried over sodium sulfate. The solvent was evaporated, and the crude residue was fractionated by flash chromatography on a silica gel column (1:50) packed in hexane. 4-Nitroisoxazoles **3a–f** were collected from hexane–benzene (1:1) or benzene fractions and further purified by bulb to bulb distillation or by crystallization. Alkynols **4a–f** were collected from benzene–ethyl acetate (8:2) fractions.

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Registry No. **1a**, 27975-80-0; **1b**, 61783-71-9; **1c**, 72343-39-6; **1d**, 114395-58-3; **1e**, 114395-59-4; **1f**, 29795-81-1; **2**, 75079-84-4; **3a**, 57354-90-2; **3b**, 114395-54-9; **3c**, 114395-55-0; **3d**, 114395-56-1; **3e**, 53215-16-0; **3f**, 114395-57-2; **4a**, 5876-76-6; **4b**, 41746-22-9; **4c**, 17475-10-4; **4d**, 114395-60-7; **4e**, 1817-49-8; **4f**, 27975-78-6; **5**, 21205-24-3; $NaNO_2$, 7632-00-0.

(11) Prepared from corresponding alcohol and PBr_3 in ether: bp 110–112 °C/1 Torr; molecular formula $C_{11}H_{11}BrO$; ^1H NMR (CCl_4) δ 1.91 (d, 3 H, CH_3), 3.6 (d, 2 H, CH_2), 4.6 (m, 1 H, CH), 7.35 (s, 5 H, arom). The starting alcohol 1-phenyl-3-hydroxy-2-pentyne was obtained from benzylacetylene according to Bartlett and Rosen: Bartlett, P.; Rosen, L. *J. Am. Chem. Soc.* **1942**, *64*, 543. Yield 56%; bp 110 °C/0.4 Torr.

(12) Crude halide obtained from 1,3-diphenyl-3-hydroxypropyne[14] with PBr_3 (Py, −30 °C, ether, 7 h) was used.

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A Convenient Preparation of Ring-Methoxylated Phenylnitromethanes

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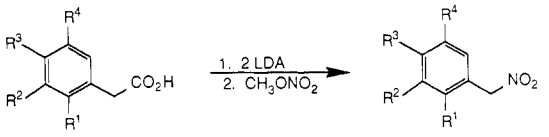
The reaction of benzyl halides with silver nitrite[2-5] and the base-induced alkylation of phenylacetonitriles with alkyl nitrates[6,7] are the only two methods that have been reported for the preparation of phenylnitromethanes, and neither has been demonstrated to be of general synthetic utility for the preparation of analogues in which the aromatic ring is methoxylated. Kornblum and co-workers[4] observed that while benzyl bromide reacts with silver nitrite to give phenylnitromethane, corresponding reaction of *p*-methoxybenzyl bromide gives predominantly the nitrite ester (55%). The alkylation of phenylacetonitriles with alkyl nitrates, a two-step procedure in which the α-nitrophenylacetonitrile from the initial condensation is first isolated and then hydrolyzed and decarboxylated, also has not been used for the preparation of (methoxyphenyl)nitromethanes.

In conjunction with other work, we needed phenylnitromethanes with a methoxylated aromatic ring. The lack of precedent and apparent synthetic limitations of the previously reported methods led us to explore the one-step preparation of phenylnitromethanes through alkylation of the dianions of phenylacetic acids with methyl nitrate.[8] Although it has been shown that dianions of aliphatic acids react with alkyl nitrates to give nitro paraffins,[9] the preparation of phenylnitromethanes was not investigated.

Initially, the phenylacetic acids **1** were reacted with 3 equiv of lithium diisopropylamide (LDA) at −78 °C, quenched with 3 equiv of methyl nitrate, and acidified.



1 2

	R1	R2	R3	R4
a.	H	H	H	H
b.	CH_3O	H	H	H
c.	H	CH_3O	H	H
d.	H	H	CH_3O	H
e.	H	CH_3O	CH_3O	H
f.	CH_3O	H	H	CH_3O

The product mixture was separated by chromatography, furnishing the desired phenylnitromethane **2** and diisopropylnitramine. The latter material was shown to arise from reaction of the excess LDA and methyl nitrate. Decreasing the relative stoichiometry of LDA to 2.2 equiv minimized formation of the nitramine byproduct and permitted, in most instances, direct isolation of product phenylnitromethanes through crystallization and/or distillation.

In initial work on the reaction, we observed that while 2-methoxy- and 2,5-dimethoxyphenylacetic acids gave clear solutions of the dianions, the remaining acids gave suspensions. It has been noted previously[9] that addition of HMPA to dianion suspensions effects their solution and gives improved yields on subsequent reaction with electrophiles. Generation of phenylacetic acid dianions in the presence of added HMPA gave homogeneous solutions, which on reaction with methyl nitrate and subsequent acidification resulted in the best yields of phenylnitromethanes. Irrespective of the presence of HMPA, nearly identical yields of phenylnitromethanes were obtained from dianions of acids that initially gave clear solutions.

In summary, condensation of the dianions of ring-methoxylated phenylacetic acids with methyl nitrates provides a general, one-step procedure to the corresponding phenylnitromethanes in good yields.

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Table I. Yields of Phenylnitromethanes (2) from Phenylacetic Acids (1)

product no.	yield, %	mp (°C)[a] or bp (°C)/p (mm)	lit. mp (°C) or bp (°C)/p (mm) or mol formula[b]	IR (film)[c] ν, cm⁻¹	¹H NMR (CDCl₃/TMS)[d] δ, ppm	¹³C NMR (CDCl₃/TMS) δ, ppm	MS (70 eV)[e] m/e (%)
2a	72[f]	80–83/2.7	90–92/3[6]	1554, 1375	5.42 (s, 2 H), 7.42 (s, 5 H)	79.7, 128.8, 129.7	136 ($M-1^+$, 1.4), 91 (100)
2b	83[g]	64–65 (167.2)[b]	$C_8H_9NO_3$	1559, 1373	3.83 (s, 3 H), 5.46 (s, 2 H), 6.9–7.5 (m, 4 H)	55.4, 74.4, 110.8, 118.5, 120.6, 131.5, 131.9, 158.0	167 (M^+, 8), 131 (32), 121 (100)
2c	56,[f] 72[h]	82–85/0.15 (167.2)[b]	$C_8H_9NO_3$	1555, 1374	3.82 (s, 3 H), 5.40 (s, 2 H), 6.9–7.5 (m, 4 H)	55.1, 79.8, 115.2, 115.4, 122.0, 129.9, 130.9, 159.8	167 (M^+, 7), 151 (14), 121 (100)
2d	66,[f] 77[h]	90–95/0.15	102–103/0.5[4]	1553, 1373	3.82 (s, 3 H), 5.36 (s, 2 H), 6.93 (bd, 2 H), 7.40 (bd, 2 H)	55.1, 79.3, 114.2, 121.8, 131.3, 160.6	167 (M^+, 0.4), 166 (2.2), 121 (100)
2e	57,[f] 63[h]	91–92 (197.2)[b]	$C_9H_{11}NO_4$	1555, 1373	3.90 (s, 6 H), 5.37 (s, 2 H), 6.8–7.1 (m, 3 H)	54.4, 74.1, 109.7, 111.1, 120.7, 121.5, 147.7, 148.9	197 (M^+, 1), 151 (100)
2f	70[h]	105–107/0.15 (197.2)[b]	$C_9H_{11}NO_4$	1559, 1372	3.74–3.75 (s, 6 H combined), 5.40 (s, 2 H), 6.8–7.0 (m, 3 H)	55.5, 55.8, 74.3, 111.8, 116.0, 117.6, 119.0 152.1, 153.3	197 (M^+, 10), 151 (100), 121 (77)

[a] Uncorrected, measured on a Kofler hot-stage microscope. [b] Satisfactory microanalysis obtained: C, ±0.21; H, ±0.11; N, ±0.14. [c] Recorded on a Perkin-Elmer 1800 FT-infrared spectrophotometer. [d] Obtained on JEOL FX-90Q spectrometer. [e] Recorded on a VG 7070E spectrometer. [f] Purified by distillation. [g] Purified by recrystallization from methylene chloride–hexanes. [h] Purified by silica gel chromatography (25 g); methylene chloride.

Experimental Section

(Methoxyphenyl)nitromethanes. General Procedure. A solution of the methoxyphenylacetic acid (10.2 mmol) in THF (8 mL) was added to a magnetically stirred, chilled (0 °C) solution of LDA (23.5 mmol of *n*-butyllithium and 24.5 mmol of diisopropylamine) and HMPA (10.2 mmol) in THF (20 mL) under nitrogen. The yellow solution was stirred at room temperature for 1.5 h and then chilled to −60 °C. Addition of methyl nitrate (1.9 mL, 30.6 mmol) to the dianion solution produced a brownish yellow solution, which faded to the original yellow color. The reaction was stirred for 1 h, and then acetic acid (1.4 mL) was added. The mixture was allowed to warm to 0 °C, at which point hydrochloric acid (12 mL, 4 N) was added and evolution of carbon dioxide occurred. Water (20 mL) and ether (20 mL) were added and the layers separated. The water layer was extracted again with ether (20 mL), and the combined organic phases were successively washed with water (20 mL), aqueous bicarbonate (2 × 25 mL), hydrochloric acid (2 × 20 mL of 0.01 N), water (2 × 20 mL), and brine. The organic solution was dried ($MgSO_4$), filtered, and evaporated at reduced pressure. Final purification of the product was performed as indicated in Table I. All products were homogeneous by TLC, ¹H NMR, and ¹³C NMR.

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Registry No. **1a**, 103-82-2; **1b**, 93-25-4; **1c**, 1798-09-0; **1d**, 104-01-8; **1e**, 93-40-3; **1f**, 1758-25-4; **2a**, 622-42-4; **2b**, 33241-80-4; **2c**, 53016-47-0; **2d**, 29559-26-0; **2e**, 114131-33-8; **2f**, 79101-76-1; CH_3ONO_2, 598-58-3.

Communications

Effect of Phosphine Substitution on Nucleophilic Addition to α,β-Unsaturated Acyliron Complexes

Summary: Michael addition reactions of α,β-unsaturated acyliron complexes, where the iron atom is chiral, have been examined. Iron complexes containing various phosphine ligands were examined to determine if the steric bulk of phosphine ligands affects the diastereoselectivity in the reaction.

Sir: Chiral-at-iron acyl complexes of the type Cp(CO)(PPh₃)FeCOR have been used extensively as chiral enolate equivalents.[2] Alkylation of enolate anions derived from these complexes, and Michael addition and Diels–Alder[3] reactions with α,β-unsaturated complexes all proceed with a high degree of diastereoselectivity. It has been proposed that this selectivity arises from the ability of the triphenylphosphine ligand to lock the acyl ligand in a conformation where the acyl C=O is anti with respect to the carbonyl ligand (Figure 1, complex 4), and from the bulky triphenylphosphine ligand blocking one face of the molecule. On the basis of extended Hückel and ab initio SCF MO calculations,[4] the conformational locking of the acetyl ligand in 4 was attributed to a steric interaction between the acyl oxygen and a phenyl ring of the triphenylphosphine ligand, which was twisted out of plane. Alternatively, it has been proposed that a "metalloanomeric effect"[5] is inducing the acyl oxygen atom to go anti to the carbonyl ligand.

Reactions involving chiral-at-iron complexes of the type Cp(CO)(L)FeCOR, where L ≠ PPh_3, have not been ex-

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