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Reactions of Triphenylphosphine- and Trialkyl Phosphite-Silver Nitrate Complexes with Positive Halogen Compounds. Synthesis of α-Nitro Nitriles

Rachid Ketari and André Foucaud*

Groupe de Physicochimie Structurale associé au CNRS, Université de Rennes, Campus de Beaulieu, 35042 Rennes, France

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The reaction of α-bromo-α-cyano esters, α-bromo-α-cyano nitriles, and α-bromo-α-cyano imides with triphenylphosphine- or trialkyl phosphite-silver nitrate complexes leads to replacement of the positive bromine atom by a nitro group under mild conditions. In the case of the α-bromo-α-cyano esters, α-keto esters are also formed. The thermolysis of α-nitro nitriles gives keto compounds or coupled products via a radical pair.

The nitration of compounds containing active methylene groups has been carried out with nitrating agent such as nitric acid, alkyl nitrates with acid catalysts, nitrite anion, or nitrogen dioxide.[1,2] The use of nitronium salts, which are convenient for the nitration of aromatic compounds[3-5] and alcohols,[6] has not been well developed for the nitration of compounds with an acidic hydrogen attached to carbon.[7] We report here a method for the selective substitution of an acidic hydrogen by a nitro group, proceeding via the intermediate bromide and using a nitratophosphonium ion.

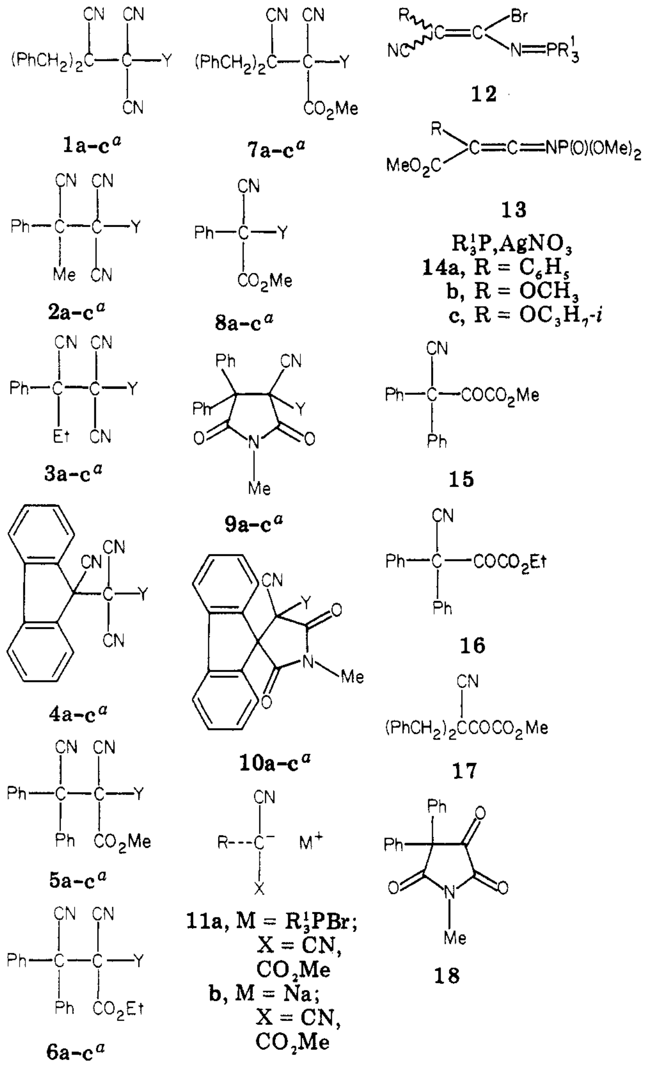
Treatment of the acidic hydrogen compounds **1a**-**10a** with bromine in a basic medium converts them into the corresponding bromo compounds **1b**-**10b** (Chart I). Reaction of these α-bromo nitriles with phosphines or phosphites in an inert solvent gives ion pairs such as **11a** that rearrange into either iminophosphoranes (**12**)[8,9] or N-phosphorylketenimines (**13**).[10,11] We show here that reaction of the α-bromo nitriles with phosphine- or phosphite-silver nitrate complexes (**14**) takes a different course.[12]

Results and Discussion

Reaction of the α-bromo nitriles **1b**-**10b** with the silver nitrate complexes **14** in dry acetonitrile gave predominantly the α-nitro nitriles **1c**-**10c** (Table I). The esters **5b**-**7b** also gave minor amounts of the α-keto esters **15**-**17**, respectively, and the imide **9b** gave a small amount of the α-keto imide **18** (Table II).

Structural assignments are based on spectral data. The IR spectra of **1c**-**10c** show ν_{NO_2} at 1580-1598 cm^{-1}. The ^{15}N NMR spectrum of **5c** exhibits three signals (MeNO$_2$, δ 0): the nitrogen of CN at -109.2 and -115.7 ppm and the nitrogen of NO$_2$ at -21.4 ppm.[13] The mass spectra of the nitro compounds (supplementary material) correspond to the parent ion with a principal fragment (M - NO$_2$ - CN)$^+$ for **1c**-**8c** and (M - MeNCO - NO$_2$)$^+$ for **9c** and **10c**. The structures of **15**-**17** were assigned on the basis of their ^{1}H NMR and mass spectra.

Chart I



[a] a, Y = H; b, Y = Br; c, Y = NO$_2$.

The α-nitromalononitriles **1c**-**4c** are not very stable. Thermolysis of **2c** in toluene under nitrogen at 100 °C for

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Table I. Properties of Nitro Compounds 1c–10c

compd	mp, °C[a]	yield, %[b]	IR (Nujol), cm^{-1}	^{1}H NMR (CDCl$_3$), δ
1c	134	78	2252, 1598	3.23–3.06 (AB, J = 15 Hz, 4 H), 7.3 (m, 10 H)
2c	104	80	2258, 1597	2.40 (s, 3 H), 7.4 (m, 5 H)
3c	oil[c]	67	1580	1.10 (t, 3 H), 2.6 (m, 2 H), 7.4 (m, 5 H)
4c	126[d]	84	2257, 1596	7.5 (m)
5c	124	67	1764, 1587	3.92 (s, 3 H), 7.4 (m, 10 H)
6c	84[e]	66	1760, 1588, 1578	1.29 (t, 3 H), 4.26 (q, 2 H), 7.4 (m, 10 H)
7c	128	75	1775, 1586	3.20–3.58 (AB, J = 15 Hz, 4 H), 3.81 (s, 3 H), 7.32 (s, 10 H)
8c	oil[c]	90[f]	1763, 1584	
9c	138	85	1795, 1729, 1584	3.18 (s, 3 H), 7.2 (m, 10 H)
10c	150–152	78	1799, 1726, 1575, 1569	3.38 (s, 3 H), 7.4 (m, 8 H)

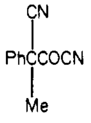
[a] Recrystallized from ether except as noted. [b] Isolated product from reaction of 1b–10b with silver nitrate complex 14b. [c] Not isolated as a pure product. [d] Recrystallized from benzene. [e] Recrystallized from petroleum ether. [f] Yield determined from ^{1}H NMR spectrum; the other product was 23.

Table II. Properties of α-Keto Esters and Keto Imide

compd	mp, °C	recryst solvent	yield, %[a]	IR (Nujol), cm^{-1}	^{1}H NMR (CDCl$_3$), δ
15	153	benzene	33	2245, 1757, 1752	3.82 (s, 3 H), 7.3 (m, 10 H)
16	128	benzene–ether	25	2240, 1761	1.02 (t, 3 H), 2.99 (q, 2 H), 7.3 (m, 10 H)
17	85	benzene–ether	20	2236, 1749, 1726	2.30–3.58 (AB, J = 15 Hz, 4 H), 3.81 (s, 3 H), 7.3 (s, 10 H)
18	138	ethanol	10	1794, 1726, 1773, 1715	3.28 (s, 3 H), 7.3 (s, 10 H)

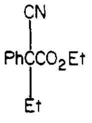
[a] Yield of isolated product from reaction of α-bromo ester with silver nitrate complex 14b.

15 min gave the acyl cyanide **19**. Treatment of **3c** with ethanol at 30 °C yield the α-cyano ester **20**. Hydrolysis of **1c** gave the α-cyano acid **21**.



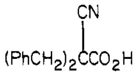
$\mathrm{PhC(CN)(Me)COCN}$

19



$\mathrm{PhC(CN)(Et)CO_2Et}$

20

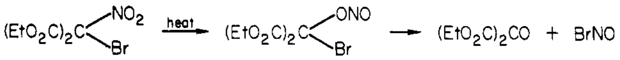


$\mathrm{(PhCH_2)_2C(CN)CO_2H}$

21

The α-nitro esters **5c**-**7c** are quite stable at room temperature. Thermolysis of **5c** in toluene at 80 °C led to the keto ester **15** (35%) and the related dimer **22a** (65%). When the thermolysis was carried out at 110 °C, only **22a** was formed.

The mechanism previously suggested for the rearrangement of a nitroalkane into an alkyl nitrite, which involves homolytic cleavage–recombination via a radical pair,[14] can explain our results (Scheme I). These reactions are analogous to the decomposition of diethyl bromonitromalonate (**24**) to diethyl oxomalonate (**25**) and nitrosyl bromide.[18]

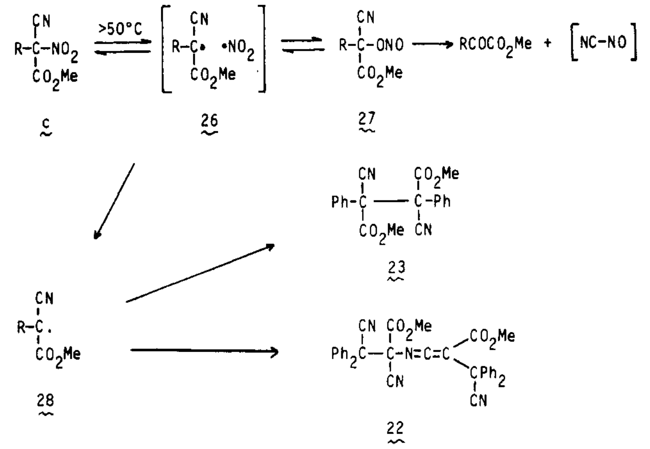


24 **25**

The α-nitro ester **8c**, which can give a relatively stable radical, decomposes at room temperature into the diester **23**.[15,16]

The nitro ester **5c** decompose at 80 °C into radical pair **26**, which produces unstable nitrite **27**. At 110 °C the radical pair is destroyed, leading to the dimers **22**.[17] These results suggest that α-nitro esters are not the intermediates in the formation of α-keto esters from the reaction of α-bromo esters with the silver nitrate complexes **14** at low temperature.

Scheme I



Scheme II

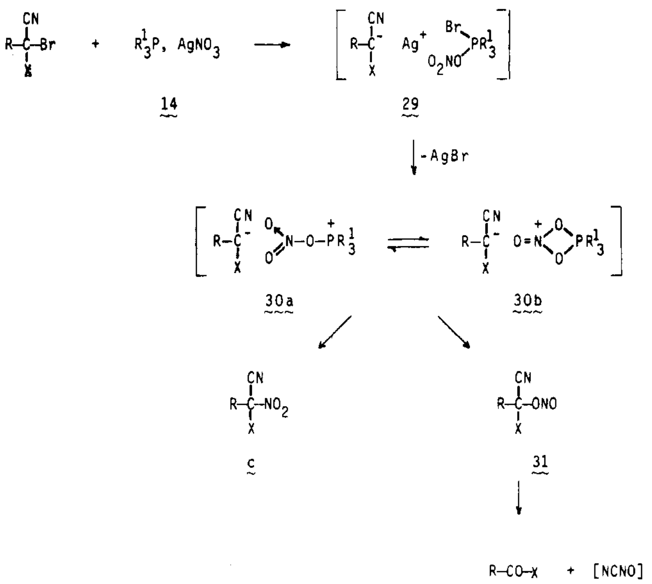


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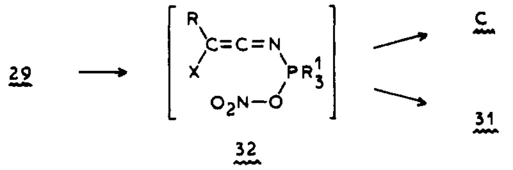
Table III. Ratios of α-Nitro Esters c to α-Keto Esters 15-17 from Various Reactants[a]

α-bromo nitrile	$AgNO_3$ complex	temp, °C	α-nitro ester/ α-keto ester ratio
5b	14b	-15	52:48
5b	14b	0	52:48
5b	14b	20	67:33
5b	14a	20	70:30
5b	14c	0	50:50
6b	14a	20	70:30
7b	14b	20	79:21
9b	14b	20	86:14

[a] Determined by ^1H NMR.

Scheme III

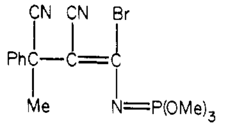


The first step in the reaction of a silver nitrate complex **14** with an α-bromo nitrile probably involves attack of the phosphorus atom on the positive bromine to give an ion pair, **29**, which eliminates silver bromide to give the intermediate **30** (Scheme II). A nitrogen-containing phosphorane, analogous to **30**, has been postulated as an intermediate in deoxygenation reactions of nitro compounds.[19,20] The rearrangement of the ion pair **30** gives an α-nitro nitrile (c, Scheme II) by attack on nitrogen or an α-nitrito nitrile (**31**) by attack on oxygen. The nitrite **31** is not stable and decomposes to an α-keto ester and presumably nitrosylcyanide; the latter can account for the deep blue color that appears in the reactions of the α-bromo esters **5b**–**8b** and the imide **9b** with the silver nitrate complexes and diseappears in 30–35 min. This color is not observed in similar reactions of the dinitriles **1b**–**4b**. The formation of nitric oxide follows from the formation of an α-keto ester or **18**. As the temperature is lowered, the amount of α-keto ester increases (Table III).

There is no reaction when the bromide **5b** is treated with silver nitrate in acetonitrile. However, when **5b** is treated with triphenylphosphine–silver nitrate (**14a**) in acetonitrile–water (95:5), the products are silver bromide, triphenylphosphine oxide, and the ester **5a**: these products result from hydrolysis of the ion pair **29**. The nitronium ion NO_2^+, which can arise from **29**, is probably not the nitrating agent. Indeed, reaction of nitropyridinium tetrafluoroborate with **5a** in pyridine gave a small amount of the nitro ester **5c** and the keto ester **15**.

As an alternative mechanism, the rearrangement of **29** with elimination of silver bromide might give an intermediate **32** with nitrile nitrogen–phosphorus bond formation.[8] The decomposition of **32** occurs with elimination of phosphine oxide or phosphate and leads to α-nitro nitrile c or α-nitrito nitrile **31** (Scheme III). To determine if this mechanism is right, the phosphorane **34** was treated with a solution of silver nitrate in acetonitrile. Silver bromide, α-nitro nitrile **2c** in less than 5% yield, and a polymeric residue were obtained.

The first mechanism, with the intermediate **30**, therefore appears to be the most likely.



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Although the positive bromine atom in the imide **9b** was not attacked by dimethyl sulfide alone, reaction of **9b** with dimethyl sulfide in the presence of excess silver nitrate gave the nitro imide **9c** and dimethyl sulfoxide.

When a mixture of phosphite or phosphine and silver nitrate was used instead of complex **14**, lower yields of nitro compounds were obtained. Apparently, with the mixtures, the ion pair **11a**, which is formed in part in the first step of the reaction, cannot react quantitatively with silver nitrate to give intermediate **30** before its rearrangement into **13**, and the ketenimine **13** is hydrolyzed into an α-cyano ester (**5a**–**8a**).

It appears that nitro compounds are formed with the silver nitrate complex reagent only from halides that contain a positive halogen. Thus, reaction of benzyl chloride with the complex **14b** gave benzyl nitrate, and a similar reaction of phenacyl bromide gave α-nitroacetophenone.

The complex **14b** is a more convenient reagent than its triphenylphosphine analogue **14a** because the byproduct from the former, trimethyl phosphate, is water soluble and easily removed from the reaction mixture in contrast to the triphenylphosphine oxide formed from **14a**.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 225 spectrometer. Proton magnetic resonance spectra were obtained with a JEOL MH 100 spectrometer. Mass spectra were recorded on a Varian MAT 311 mass spectrometer at an ionization voltage of 70 eV with sample temperatures between 130 and 145 °C. α-Bromo nitriles **1b**–**10b**[8,10,21] were prepared as reported in the literature earlier. Acetonitrile was distilled from P_2O_5. All reactions were conducted in the dark under dry nitrogen.

Silver Nitrate Complex of Triphenylphosphine 14a. The procedure was the same that for the preparation of the other silver nitrate complexes of phosphines.[22,23] To a solution of 4.25 g (0.025 mol) of silver nitrate in 25 mL of MeCN was added 6.25 g (0.025 mol) of triphenylphosphine in 25 mL of MeCN. After 15 min, the solution was concentrated and gave the complex: mp 222 °C (MeCN); 82% yield. Anal. Calcd for $C_{18}H_{15}PNO_3Ag$: C, 50.00; H, 3.47; N, 3.24; P, 7.17. Found: C, 50.26; H, 3.68; N, 3.23; P, 7.08.

Silver Nitrate Complex of Trimethyl Phosphite 14b. The procedure described for the preparation of **14a** was used. Evaporation of the solvent gave the complex as a viscous colorless liquid: ^1H NMR ($CDCl_3$) δ 3.61, 3.75 (J_{PH} = 14 Hz).

Silver Nitrate Complex of Triisopropyl Phosphite 14c. The previous procedure was used. The complex was a viscous colorless liquid, which should be prepared just prior to use (silver ion was slowly reduced into silver): ^1H NMR ($CDCl_3$) δ 1.32 (d, 6 H), 4.59 (m, 1 H, J = 7 Hz).

General Procedure for the Preparation of Nitro Compounds 1c/10c. A solution of 0.01 mol of α-bromo nitrile **1b**–**10b** in 25 mL of acetonitrile was stirred under nitrogen while a solution of 3.9 g (0.013 mol) of **14b** in 25 mL of acetonitrile was added dropwise during the course of 10 min. Stirring was continued for 30 min. From the beginning, silver bromide precipitated, and, in the case of the reaction with the α-bromo esters **5b**–**9b**, a blue color appeared and disappeared after 30 min at room temperature. The nitric oxide which was formed was expelled with a stream

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of nitrogen. The solution was filtered to remove silver bromide. The solvent was removed in vacuo, and the residue was dissolved in ether. The ether solution was washed with water, dried, and concentrated. The residue was analyzed by NMR (Table III). The α-keto esters **15**–**17** were separated by dissolving the product mixtures in 10 mL of ether. The nitro imide **9c** was recrystallized from ethanol; after filtration and concentration, the ethanol solution was cooled to give **18**.

Nitro ester **8c** decomposed slowly at room temperature to give the diester **23** (mp 150–155 °C (MeOH), mixture of two diastereoisomers) which was identified by comparison with samples obtained by independent synthesis.[17]

The mass spectral data of nitro compounds **1c**–**10c** are presented in a table as supplementary material.

Methyl 3-cyano-3,3-diphenyl-2-oxopropanoate (**15**): high-resolution mass spectrum calcd for $C_{17}H_{13}NO_3$ *m/e* 279.089 536, found 279.0902.

Methyl 3-benzyl-3-cyano-4-phenyl-2-oxobutanoate (**17**): high-resolution mass spectrum calcd for $C_{19}H_{17}NO_3$ *m/e* 307.120 834 3, found 307.120 35.

Methyl 2,3-dicyano-2-nitro-3,3-diphenylpropanoate (**5c**). Anal. Calcd for $C_{18}H_{13}N_3O_4$: C, 64.48; H, 3.88; N, 12.54. Found: C, 64.55; H, 3.68; N, 12.24.

1-Methyl-3-cyano-3-nitro-4,4-diphenylpyrrolidine-2,5-dione (**9c**). Anal. Calcd for $C_{18}H_{13}N_3O_4$: C, 64.48; H, 3.88; N, 12.54. Found: C, 64.76; H, 3.69; N, 12.36.

1-Methyl-3-cyano-3-nitro-4,4-*o*-diphenylenepyrrolidine-2,5-dione (**10c**). Anal. Calcd for $C_{18}H_{11}N_3O_4$: C, 64.22; H, 3.36; N, 12.84. Found: C, 64.32; H, 3.70; N, 12.37.

Reaction of 14b with Bromo Ester 5b in MeCN–H$_2$O. The general procedure was used, but 0.5 mL of water was added to the solvent. The cyano ester **5a** was isolated in quantitative yield.

Reaction of Bromo Ester 7b with a Mixture of Silver Nitrate and Trimethyl Phosphite. A 1.36-g (0.011 mol) sample of trimethyl phosphite in 20 mL of acetonitrile was added to a solution of 3.97 g (0.01 mol) of **7b** and 1.85 g (0.011 mol) of silver nitrate in 40 mL of acetonitrile. The mixture was stirred for 30 min at room temperature. Silver bromide was filtered off. The acetonitrile was removed, the residue was dissolved in ether, and the ether solution was washed with water and concentrated. The residue was a mixture of the corresponding ester **7a** (20%) with nitro ester **7c** and keto ester **17** (80%, analyzed by NMR). Ester **7a** was not detected when trimethyl phosphite–silver nitrate complex **14b** was used as the reagent.

Thermolysis of α-Nitro Ester 5c. A 0.5-g sample of nitro ester **5c** in 10 mL of dry solvent was heated at 80 °C under nitrogen for 20 min. The solvent was evaporated and the mixture analyzed by NMR. When the solvent was acetonitrile, pure nitro ester **5c** was recovered. When the solvent was toluene, the residue was a mixture of nitro ester **5c** (50%) and keto ester **15** (50%).

A solution of 0.78 g of nitro ester **5c** in 20 mL of dry toluene was heated at 110 °C during 10 min. Nitrogen peroxide was evolved. The solvent was evaporated and the residue crystallized from ethanol to give ketenimine **22a**: mp 190 °C (lit. mp 191 °C); 40% yield; NMR ($CDCl_3$) δ 3.47, 3.58.

Thermolysis of 3-Phenyl-2,3-dicyano-2-nitrobutanenitrile (2c). A solution of 0.5 g of nitrile **2c** in toluene was heated to 110 °C for 15 min. Nitric oxide was evolved. The solvent was evaporated and the residue crystallized from ether to give 2-phenyl-2-cyanopropionyl cyanide: mp 115 °C (hexane–ether); 90% yield; IR 2252, 2238 (C$\equiv$N) cm^{-1}; NMR ($CDCl_3$) δ 2.10 (s, 3 H), 7.4 (m, 5 H); mass spectrum, calcd for $C_{11}H_8N_2O$ *m/e* 184.06366, found *m/e* 184.0647, *m/e* (relative intensity) 184 (6, M$^+$), 130 [100, (Ph(Me)(CN)C)$^+$], 116 (7) 103 (44) 77 (17).

2-Benzyl-2-cyano-3-phenylpropanoic Acid (21). Treatment of 0.55 g of nitrile **1c** in wet chloroform gave slowly 2-benzyl-2-cyano-3-phenylpropanoic acid: mp 190–192 °C (benzene) (lit.[24] mp 189 °C); IR (hexachlorobutadiene) 2960 (OH), 2236 (C$\equiv$N), 1709 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 3.22, 3.42 (AB, J = 14 Hz, 4 H), 7.4 (m, 10 H). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.98; H, 5.66; N, 5.28. Found: C, 76.68; H, 5.59; N, 4.67.

Ethyl 2-Cyano-2-phenylbutanoate (20). The treatment of 0.5 g of nitrile **3c** with EtOH at 50 °C for 30 min gave ethyl 2-cyano-2-phenylbutanoate: bp 150 °C (10 min) [lit.[25] bp 147 °C (11 mm)]; IR (neat) 2232 (C$\equiv$N) 1735 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.08 (t, 3 H J = 7 Hz), 1.24 (t, 3 H, J = 7 Hz), 2.31 (m, 2 H), 4.24 (q, 2 H, J = 7 Hz), 7.5 (m, 5 H). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.88; H, 6.91; N, 6.45. Found: C, 71.43; H, 6.70; N, 7.61.

Reaction of *N*-Nitropyridinium Tetrafluoroborate with Ester 5a. To a well-stirred suspension of nitronium tetrafluoroborate (1.33 g, 0.01 mol) in acetonitrile (30 mL) at 0 °C was added 0.8 g (0.01 mol) of pyridine in acetonitrile (20 mL). The solution was stirred for 30 min, and then 2.9 g (0.01 mol) of **5a** and 0.8 g of pyridine in acetonitrile (40 mL) were added. After the mixture was stirred for 1 h at room temperature, the solvent was removed in vacuo, and the residue was dissolved in ether, washed with 1 M HCl, dried, and evaporated. The residue, analyzed directly by NMR and IR spectroscopy, was a mixture of **5a** (90%) and **5c** plus **15** (10%).

Reaction of Phosphorane 34 with Silver Nitrate. A solution of 0.68 g (0.004 mol) of silver nitrate in 20 mL of acetonitrile was added to a solution of 1.59 g (0.004 mol) of **34**[8] in 20 mL of acetonitrile. The mixture was stirred for 40 min at 0 °C. Silver bromide (0.75 g, 0.004 mol) was filtered. The solvent was removed in vacuo, and the residue was dissolved in ether, washed with water, dried, and evaporated. The NMR spectrum shows a small quantity of **2c**, measured by the peak ratios of the protons of the C–Me groups.

Reaction of Bromo Imide 9b with Dimethyl Sulfide and Silver Nitrate. A solution of 3.7 g (0.01 mol) of **9b**, 0.6 g (0.01 mol) of dimethyl sulfide, and 1.7 g (0.01 mol) of silver nitrate in acetonitrile was stirred for 15 h at room temperature. Silver bromide and dimethyl sulfide–silver ion complex were filtered off, and the acetonitrile was removed in vacuo to give an oil which contained dimethyl sulfoxide, **9b**, and **9c**. The ratio of **9b** to **9c**, as determined by ^{1}H NMR, was 9:16.

Reaction of Benzyl Chloride with 14b. A solution of 2.5 g (0.02 mol) of benzyl chloride in 25 mL of acetonitrile was added to a solution of 5.88 g (0.02 mol) of **14b** in 25 mL of acetonitrile. The mixture was stirred for 12 h at room temperature. Silver bromide was filtered off, and the solvent was removed to give benzyl nitrate: bp 110 °C (20 mm) [lit.[6] bp 107–110 °C (22 mm)]; IR (neat) 1632 cm^{-1} (lit.[6] 1635 cm^{-1}); NMR ($CDCl_3$) δ 5.34 (s, 2 H), 7.32 (s, 5 H).

Reaction of Phenacyl Bromide with 14b. Phenacyl was obtained in a manner similar to that described for the preparation of benzylnitrate: bp 170 °C (1 mm); NMR ($CDCl_3$) δ 5.62 (s, 2 H), 7.56 (m, 3 H), 7.95 (m, 2 H); IR (neat) 1591, 1640, 1690 cm^{-1}.

The IR and NMR spectra were superimposable with spectra of authentic phenacyl nitrate prepared by the reaction of silver nitrate with phenacyl bromide in acetonitrile.

Registry No. 1b, 38351-92-7; **1c**, 75436-15-6; **2b**, 38351-93-8; **2c**, 75436-16-7; **3b**, 38351-94-9; **3c**, 78515-67-0; **4b**, 78515-68-1; **4c**, 78515-69-2; **5a**, 57519-79-6; **5b**, 39950-39-5; **5c**, 75436-17-8; **6b**, 37713-58-9; **6c**, 78515-70-5; **7a**, 65739-13-1; **7b**, 40296-30-8; **7c**, 75436-18-9; **8b**, 75436-12-3; **8c**, 75436-20-3; **9b**, 35789-62-9; **9c**, 75436-19-0; **10b**, 35789-66-3; **10c**, 78515-71-6; **14a**, 78514-14-4; **14b**, 78514-13-3; **14c**, 78514-12-2; **15**, 75436-13-4; **16**, 3122-22-3; **17**, 75436-14-5; **18**, 78515-72-7; **20**, 718-71-8; **21**, 1224-54-0; **22**, 65739-17-5; **23** (isomer 1), 78515-73-8; **23** (isomer 2), 30698-35-2; **34**, 23692-56-0; 2-phenyl-2-cyanopropionyl cyanide, 78515-74-9; benzyl chloride, 100-44-7; benzyl nitrate, 15285-42-4; phenacyl bromide, 70-11-1; phenacyl nitrate, 66702-75-8.

Supplementary Material Available: Table containing mass spectral data of nitro compounds **1c**–**10c** (1 page). Ordering information is given on any current masthead page.

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