Additions of Trialkyl Phosphites to Nitroalkenes

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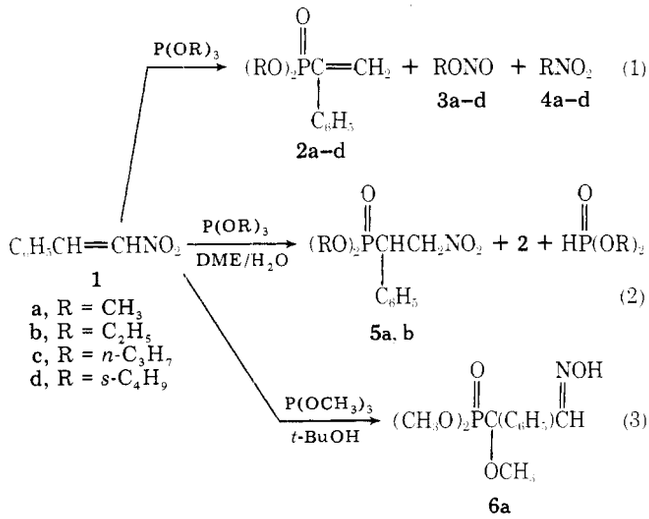
The reaction of β-nitrostyrene (1) with triethyl phosphite in DME gave diethyl α-styrylphosphonate (**2b**) in 85% yield. In DME/10% H_2O it gave a 50:50 mixture of **2b** and 1-diethoxyphosphinyl-1-phenyl-2-nitroethane (**5b**). In DME/10% D_2O with trimethyl phosphite it gave products with deuterium incorporated in the position β to the phenyl group in both **2a** and **5a**. Mechanistic implications are discussed.

Nitroalkenes may be regarded as the heteroatom analogues of α,β-unsaturated carbonyls. As such they may react by mechanisms involving attack at either nitro oxygen or at the β carbon. Attack at oxygen leads to deoxygenation and the products of a nitrene intermediate.[1] While there have been several reports that are consistent with attack at oxygen,[2] there has been none asserting attack at carbon.

Results and Discussion

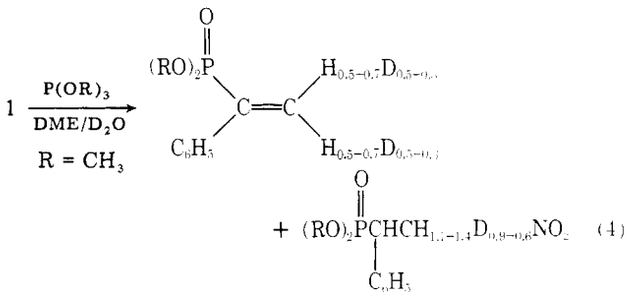
We have previously reported that the reaction of β-nitrostyrene (1) with trimethyl phosphite in *tert*-butyl alcohol gave 2-dimethoxyphosphinyl-2-methoxy-2-phenylacetaldehyde oxime (**6a**).[3] We now wish to report that by varying the trialkyl phosphite and the solvent, two additional products can be obtained from reactions with **1** (Table I). We believe that these two (eq 1 and 2) involve a common intermediate and are the first examples of attack of trialkyl phosphites on the β carbon of nitroalkenes. Formation of the aldoxime **6a** (eq 3) may, but need not, involve attack at carbon.



The reaction of **1** with triethyl phosphite in 1,2-dimethoxyethane (DME) led to a clear, nonnitrogenous liquid that was shown by IR and NMR spectroscopy and independent synthesis to be diethyl α-styrylphosphonate (**2b**). Also isolated was ethyl nitrite (**3b**) (40%), as characterized by IR and NMR spectroscopy. It is likely that 40% does not accurately reflect the yield of nitrite since once formed ethyl nitrite could react with triethyl phosphite.[4] When the reaction was run without solvent (eq 1), both nitroethane (**4b**) and ethyl nitrite (**3b**) were isolated. This is in contrast with the reaction of *o*-dinitrobenzene with triethyl phosphite and with the pyrolysis of triethoxy(ethyl)phosphonium nitrite in which only ethyl nitrite was reported.[5] However, we have found that the former does give nitroethane (less than 1%) when reacted by general method B.

The reaction of **1** with trimethyl phosphite in DME with 10% water added (eq 2) gave a white solid which was shown by IR, NMR, and mass spectrometry to be 1-dimethoxyphosphinyl-1-phenyl-2-nitroethane (**5a**). Also formed were **2a** and dimethyl phosphonate. Attempts to interconvert **2, 5,** and **6** were unsuccessful.

The reaction of **1** with trimethyl phosphite in DME with 10% D_2O gave deuterated dimethyl α-styrylphosphonate (**2a**) (eq 4). Integration of the NMR spectrum indicated that 0.95



deuterium was incorporated (calcd max = 0.91) and was randomly distributed at the β position; thus the *E* and *Z* isomers were formed in approximately equal amounts. The mass spectrum of **2a** indicated that incorporation was at least 0.6 deuterium. Also formed was **5a** with deuterium incorporated at C-2 (β to the phenyl group). Integration of the NMR spectrum indicated 0.87 deuterium (calcd max = 0.91) was incorporated. In the complex signal for the methine hydrogen at C-1, a pair of triplets (δ 4.04) for the compound without deuterium at C-2 was visible along with two sets of two doublets (four lines each) for the two diastereomeric monodeuterated species. The mass spectrum indicated that the total incorporation at C-2 was at least 0.63 deuterium. There was no mass spectral nor NMR evidence for incorporation at C-1.

These results are consistent with a mechanism involving phosphorus attack at the electrophilic carbon of **1** (eq 5). The formation of **2** may then result from a 1,2-hydrogen shift[6] in

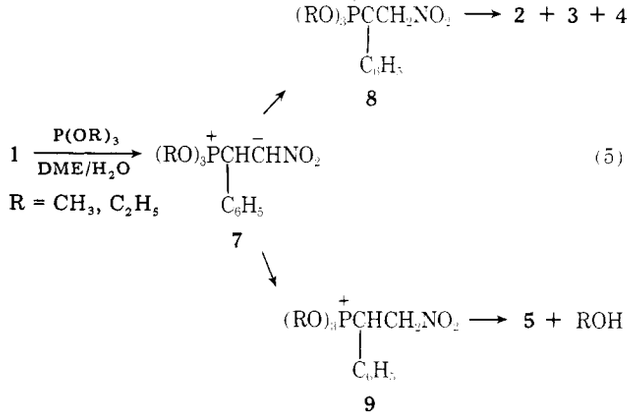


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Table I. Reactions of β-Nitrostyrene with Phosphites

R, $(RO)_3P$	Registry no.	Solvent	% yield[a] 2	Registry no.	6	Registry no.	Ratio[b] 3:4
CH_3	121-45-9	None	67	4844-39-7	7	42151-03-1	5.1
		DME	27		5[c]		
		DME/H_2O[d]	22				
		t-BuOH	Tr[c]		35		
C_2H_5	122-52-1	None	16	25944-64-3	32[c]	66324-33-2	5.6
		DME	85				
		DME/H_2O[e]	40				
		t-BuOH	25				
n-C_3H_7	923-99-9	None	60	66324-32-1	Tr[c]		4.9
s-C_4H_9	7504-61-2	None	77	66324-31-0	Tr[c]		6.5

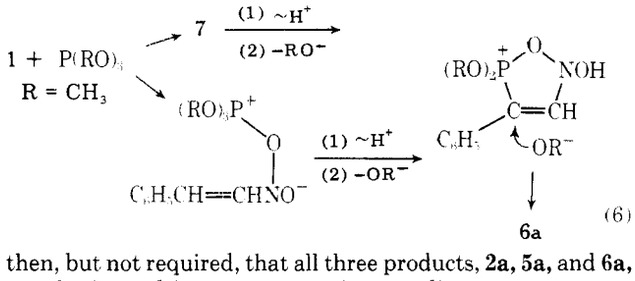
[a] Isolated yields. [b] Average of several trials. [c] Estimated by NMR. [d] Percent yield **5a** = 29. [e] Percent yield **5b** = 37.

the dipolar ion **7** to form an ylide, **8.** That this step is solvent assisted is supported by the high degree of deuterium incorporation in **2a.** Also an unassisted shift is unlikely since that would involve a cyclic four-electron antiaromatic transition state. The last step requires an Arbuzov-like dealkylation to form both alkyl nitrites and nitroalkanes. The essentially constant ratio of RONO/RNO_2 (Table I) suggests that there is little carbocation character in the alkyl group in this step.[5] And this is supported by the reaction of tri-*n*-propyl phosphite and **1** in which GC–mass spectral analysis of RONO and RNO_2 found no evidence for rearrangement of the *n*-propyl group.

The formation of **5** may result from protonation of either **7** or **8** to give a phosphonium salt **9** which is then dealkylated. The lack of deuterium incorporation at C-1 suggests, however, that **8** is not involved in the formation **5.**

The possibility that **8** and then **2** may be formed via **9** in DME/D_2O cannot be ruled out by these data since both would result in deuterium incorporation at C-2 of **2a.** But it seems unlikely to be an important pathway in dry DME in which **1** with triethyl phosphite gave 85% **2b** (Table I) to the exclusion of **5b.**

With respect to the formation of the aldoxime **6a,** it is possible to draw two relatively similar mechanisms for its formation involving either O or C attack as the first step (eq 6). Attack at carbon would lead to intermediate **7.** It is possible



(6)

then, but not required, that all three products, **2a, 5a,** and **6a,** may be formed from a common intermediate.

Experimental Section[7]

General Method A. Diethyl α-Styrylphosphonate (2b). To a solution of 14.9 g (0.1 mol) of β-nitrostyrene (**1**)[8] in 100 mL of 1,2-dimethoxyethane (Eastman) was added 49.8 g (0.3 mol) of triethyl phosphite (Eastman). The mixture was stirred for 1 h, the solvent was removed on a rotary evaporator, and the residue was distilled to give 20.4 g (85%), bp 108–112 °C (0.5 mm), of **2b:** IR (CCl_4) 1280 (P=O), 1035 (POC), 840 cm^{-1} (=CH_2); NMR (CCl_4) δ 7.40 (m, 5, C_6H_5), 6.23 (pair of doublets, 1, *c*-PC=CH, J_{HH} = 1.9 Hz, J_{HP} = 24 Hz), 6.05 (pair of doublets, 1, *t*-PC=CH, J_{HH} = 1.9 Hz, J_{HP} = 42 Hz),[9] 4.02 (m, 4, OCH_2), 1.19 (m, 6, CCH_3); mass spectrum (70 eV) *m/e* (rel intensity) 241 (3), 240 (23), 213 (5), 212 (32), 169 (3), 168 (23), 131 (46), 130 (82), 104 (73), 103 (100), 77 (57).

The reaction also produced 3.02 g (40%) of ethyl nitrite which was trapped with a dry ice–acetone cold finger distillation head placed at the top of a water jacketed condenser: NMR (CCl_4) δ 4.68 (q, 2, CH_2ONO), 132 (t, 3, CCH_3); IR (CCl_4) 1645 (s) and 1605 cm^{-1} (s) (ONO).

General Method B. Di-*n*-propyl α-Styrylphosphonate (2c). Tri-*n*-propyl phosphite[10] (23.7 g, 0.12 mol) was combined with 8.5 g (0.06 mol) of **1** in a 250-mL flask equipped with magnetic stirrer, thermometer, and distillation head. Downstream was a liquid nitrogen trap. The mixture was stirred at 0.07 mm and the temperature rose to 72 °C in 5 min, then fell to room temperature. After 2.5 h, 5.2 g of a green liquid was decanted from the N_2(l) trap. GC–mass spectral analysis showed the liquid to contain 3.6 g (40%) of *n*-propyl nitrite, 1.3 g (15%) of 1-nitropropane, and 0.7 g (11%) of 1-propanol. The presence of these compounds was confirmed by NMR spectroscopy; there was no evidence for the corresponding isopropyl compounds in either instance. The reaction mixture was then distilled to give 16.1 g (60%) of di-*n*-propyl α-styrylphosphonate (**2c**): bp 120–125 °C (0.09 mm); IR (cm^{-1}), 1280 (s, P=O), 1050 (vs, POC); mass spectrum, *m/e* (rel intensity) 268 (23.8), 226 (23.8), 184 (38.7), 103 (100), 77 (32.3); NMR (CCl_4) δ 0.93 (m, 6, CH_3), 1.57 (m, 4, CH_2), 3.85 and 3.97 (pair of triplets, 4, J_{HH} = 7.2 Hz, J_{HP} = 7.5 Hz), 5.99 (pair of doublets, 1, *t*-PC=CH, J_{HH} = 1.9 Hz, J_{HP} = 44 Hz), 6.12 (pair of doublets, 1, *c*-PC=CH, J_{HH} = 1.9 Hz, J_{HP} = 25 Hz), 7.4 (m, 5, C_6H_5).

General Method C. Dimethyl α-Styrylphosphonate (2a) and 1-Dimethoxyphosphinyl-1-phenyl-2-nitroethane (5a). To a solution of 14.9 g (0.1 mol) of **1** in 90 mL of DME and 10 mL of H_2O was added 42 g (0.34 mol) of trimethyl phosphite (Eastman). The reaction warmed to about 50 °C in 7 min before cooling to room temperature. After 2 h the solvent was removed by rotary evaporation and a 20.54-g fraction was collected by vacuum distillation and was shown by NMR spectroscopy to be dimethyl phosphonate. The residue was taken up in an equal volume of ether and slow crystallization began. Two crops were collected, combined, and recrystallized from carbon tetrachloride to give 7.51 g (29%), mp 104–106 °C, of **5a:** IR (mull) 1540 (NO_2), 1260 (P=O), 1040 cm^{-1} (POC); NMR ($CDCl_3$) δ 3.50 and 3.73 (pair of doublets, 6, $POCH_3$), 4.04 (pair of triplets, 1, CH, J_{HH} = 7.6 Hz, J_{HP} = 23.4 Hz), 4.96 (triplet, 2, CH_2, J_{HH} = J_{PH} = 7.6 Hz), 7.37 (singlet, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 260 (0.13), 259 (0.79), 213 (47), 212 (60), 181 (10), 117 (15), 116 (11), 110 (10), 109 (100), 105 (12), 104 (69), 103 (33), 93 (12), 91 (10), 77 (21).

The residue after filtration was stripped of solvent and distilled to give 4.7 g (22%) of **2a:** bp 103–107 °C (0.07 mm); IR (film) 1240 (P=O), 1045 cm^{-1} (POC); NMR (CCl_4) δ 3.66 (doublet, 6, J_{PH} = 11.2 Hz, OCH_3), 6.04 (pair of doublets, 1, J_{HH} = 1.5 Hz, J_{HP} = 45 Hz, *t*-PC=CH), 6.28 (pair of doublets, 1, J_{HH} = 1.3 Hz, J_{HP} = 24 Hz, *c*-PC=CH), 7.30 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 213 (10), 212 (64), 211 (34), 118 (12), 117 (57), 116 (48), 115 (45), 110 (31), 104 (43), 103 (100), 102 (36), 93 (38), 91 (40), 77 (68).

Method C with Deuterium Oxide. A 14.9-g (0.1 mol) sample of dried **1** was placed in a 500-mL three-neck flask equipped with condenser and pressure-equalizing dropping funnel, and the system was flushed with dry nitrogen for 0.25 h. A 90-mL sample of DME that had been refluxed over $LiAlH_4$ for 2 h was distilled directly into the flask before 10 mL of D_2O was added. Trimethyl phosphite (42 g, 0.34 mol) was then run in. The reaction mixture warmed noticeably. After 20 h the solvent was removed by rotary evaporation and the residue distilled to give a 19.4-g sample, bp 49–55 °C (0.08 mm), that was shown by NMR spectroscopy to be largely dimethyl phosphonate.[11] The remaining sample was taken up in an equal volume of ether and slow crystallization began. Two crops were collected to give 5.87 g (22%) of deuterated **5a** after recrystallization from CCl_4: mp 104–106 °C; NMR ($CDCl_3$) δ 3.50 and 3.73 (pair of doublets, 6, $POCH_3$), 4.04 (m, 1, CH), 4.96 (m, 1.13, CH_2NO_2), 7.35 (singlet, 5, C_6H_5); mass

spectrum (70 eV) *m/e* (rel intensity) 260 (0.85), 214 (48), 213 (79), 182 (10), 118 (11), 117 (14), 110 (9), 109 (100), 105 (44), 104 (39), 103 (115), 93 (10), 91 (7), 77 (10).

The residue after filtration was stripped of solvent and distilled to give a 3.48-g (16%) sample which was redistilled and a fraction of 1.27 g, bp 103–107 °C (0.07 mm), was taken: NMR ($CDCl_3$) δ 3.66 (doublet, 6, $POCH_3$), 5.75 and 6.26 (pair of doublets, 1.05, $PC{=}CH_2$), 7.30 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 214 (5), 213 (53), 212 (39), 118 (47), 117 (60), 116 (58), 115 (32), 110 (19), 109 (9), 105 (29), 104 (100), 103 (54), 102 (17), 93 (44), 91 (20), 77 (68).

Control with Diethyl α-Styrylphosphonate (2b). Triethyl phosphite (0.01 mol) and equimolar amounts of **2b** and **3b** were sealed in an NMR tube and heated at 50 °C for 2 h. The NMR spectrum was that of the individual components and remained unchanged after standing 1 month.

Control with 1-Dimethoxyphosphinyl-1-phenyl-2-nitroethane (5a). A 0.35-g sample of **5a** was mixed with 2 mL of trimethyl phosphite and 5 mL of DME and heated at 50 °C for 20 h. The solvent was removed under vacuum and the mixture solidified on standing. The solid was mixed with a small amount of ether and filtered to give 0.31 g (88%) of unchanged **5a**. There were no signals in the NMR spectrum for either **2a** or **6a**.[3]

Control with 2-Dimethoxyphosphinyl-2-methoxy-2-phenylacetaldehyde Oxime (6a). A 0.5-g sample of **6a** was mixed with 2 mL of trimethyl phosphite and 5 mL of DME and heated at 50 °C for 20 h. The low boiling materials were removed by vacuum distillation to leave a 0.55-g residue which on crystallization gave 0.35 g of unchanged **6a**. The remainder was shown by NMR to be free of **2a** and **5a**.

Synthesis of Diethyl α-Styrylphosphonate (2b). Diethyl α-styrylphosphonate (**2b**) was prepared from 3.68 g (20 mmol) of α-styrylphosphonic acid,[12] 7.15 g (43 mmol) of silver nitrate, and 2.24 g (40 mmol) of ethyl iodide according to the procedure of Werbel et al.[13] Distillation gave 3.25 g (67%) of **2b**, bp 108–112 °C (0.5 mm), whose IR and NMR spectra were identical in every respect with those of **2b** prepared from β-nitrostyrene.

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Registry No.—1, 102-96-5; **5a**, 37909-64-1; **5b**, 37909-65-2; ethyl nitrite, 109-95-5; propyl nitrite, 543-67-9; 1-nitropropane, 108-03-2; 1-propanol, 71-23-8.

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An Improved Procedure for the Addition of Dichloroketene to Unreactive Olefins[1]

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The cycloaddition of dichloroketene to hindered or unreactive olefins has, in the past, enjoyed only limited success. Not only are a large excess of the olefin or acid halide necessary, but the yields are often low. Most of these problems have now been overcome by dehalogenating trichloroacetyl chloride with activated zinc in the presence of the olefin and phosphorus oxychloride. Under these conditions, dichloroketene can even be added to tri- and tetrasubstituted olefins. An important feature of this procedure is that often only a small (5%) excess of acid chloride is necessary. The phosphorus oxychloride may function by complexing the zinc chloride produced in the reaction. Although styrene, which is normally polymerized by zinc salts, is transformed in good yield to the cyclobutanone adduct by this method, the very sensitive olefins dihydropyran and cyclopentadiene fail to yield isolable dichlorocyclobutanones.

Introduction

The cycloaddition of dichloroketene[2] to reactive olefins is a useful method for the synthesis of cyclobutanones. Certain of these dichlorocyclobutanones, for example, the adducts of indene[3] and various cyclopentadienes,[2a,4] are valuable precursors of tropolones. Many other synthetically useful transformations of cyclobutanones have been described[5] recently. Since dichloroketene is unstable and polymerizes readily, it is generated in situ in the presence of the olefin by (1) the dehydrohalogenation of a dichloroacetyl halide with an amine like triethylamine, or (2) the dehalogenation of a trichloroacetyl halide (usually trichloroacetyl bromide) with activated zinc (see eq 1 and 2). Both methods have certain

$$Cl_2CHC(=O)X \xrightarrow{Et_3N} Cl_2C{=}C{=}O + Et_3\overset{+}{N}H\,\overset{-}{X} \qquad (1)$$

$$Cl_3CC(=O)X \xrightarrow{Zn\text{-}Cu} Cl_2C{=}C{=}O + ZnCl_2 \qquad (2)$$

disadvantages. Tertiary amines and/or ammonium salts catalyze the decomposition of dichloroketene.[2b] The zinc dehalogenation method suffers from the fact that certain olefins, such as styrene, cyclopentadiene, or dihydropyran, are polymerized by zinc salts.[2b] With either method, a large excess of the olefin or acid halide is generally used.[2] Even with an excess

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