$P(RNCH_2CH_2)_3N$: An Efficient Promoter for the Nitroaldol (Henry) Reaction

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The use of catalytic amounts of the proazaphosphatranes $P(MeNCH_2CH_2)_3N$, $P(i\text{-}PrNCH_2CH_2)_3N$ and $P(HNCH_2CH_2)(i\text{-}PrNCH_2CH_2)_2N$ as nonionic bases in the reaction of nitroalkanes with carbonyl compounds is reported. The reaction proceeds at room temperature in the presence of 2.2 equiv of magnesium sulfate to produce the corresponding β-nitroalkanols in generally superior yields. Aldehydes react quantitatively in 5−60 min, whereas ketones require up to 3 h to react with nitromethane and up to 7 h for the reaction of ketones with higher nitroalkanes.

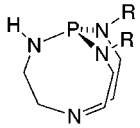
Introduction

β-Nitroalkanols are important and versatile intermediates in the synthesis of nitroalkenes, 2-amino alcohols, and α-nitro ketones.[1] 2-Amino alcohols are of particular significance in the synthesis of biologically important compounds such as epinephrine[2] and anthracycline antibiotics,[3] while α-nitroketones are valuable intermediates in the synthesis of several natural products.[4] β-Nitroalkanols are also important because of their properties as fungicides[5] and because of their utility as intermediates in the synthesis of amino sugars,[6] antibiotics such as ezomycins[7a] and tunicamycin,[7b] and alkaloids.[8]

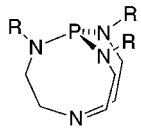
Classical methods for preparing β-nitroalkanols include the condensation of the carbonyl substrates and a nitroalkane in the presence of an ionic base such as alkali metal hydroxides, alkaline earth oxides, carbonates, bicarbonates, alkoxides, alkaline earth hydroxides, or magnesium and aluminum alkoxides.[1] While this approach is quite simple and inexpensive, its limitations often render it unattractive. For example, base-catalyzed elimination of water can occur to form nitroolefins which unfortunately polymerize readily. Moreover, it is not easy to remove the base before workup because acidification of the reaction mixture may lead to the Nef[9] reaction if it is not done with extreme care. The use of primary amines and triethylamine as condensing agents has also been reported.[1] Although this methodology leads to high yields of the β-nitroalkanol, the production of unsaturated nitro compounds through base-catalyzed elimination of water has been observed as well as formation of 1,3-dinitro compounds. The latter substances are also the predominant products when diethylamine is used as a base.[1]

Several variations of the nitroaldol reaction have recently been developed which include the use of tetramethylguanidine,[10] dendritic catalysts,[11] Amberlyst A-21,[12] and a sodium hydroxide-catalyzed process in the presence of cetyltrimethylammonium chloride (CTACl).[13] Although these methods afford high yields of the nitroaldol with aldehydes, they suffer from their inability to produce high product yields with alicylic or aliphatic ketones when such reactions are even observed. Self-condensation[10] of aliphatic ketones has been cited as a possible reason for the inability of this class of compounds to form the nitroaldol product in appreciable amounts.

The proazaphosphatranes **1a**,[14] **1b**,[15] and **1c**[16,17] have recently been shown to be strong nonionic bases. Thus



1a
R = *i*-Pr



1b: R = *i*-Pr
1c: R = Me

they are able to deprotonate acetonitrile,[18,19] benzyl nitrile,[18] and other activated methylene compounds,[20]

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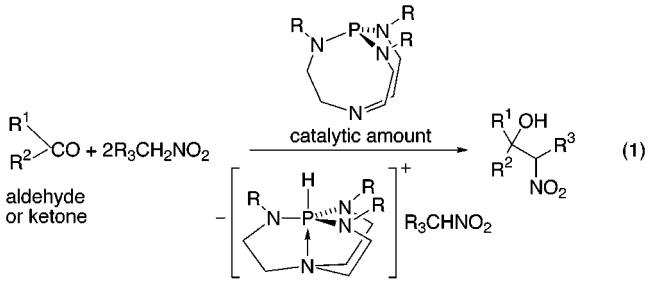
thereby providing access to carbanions that can in turn participate in interesting and useful transformations. In our continued search for reactions in which these proazaphosphatranes provide improved synthetic methodology over conventional approaches, we have found that bases of type **1** also catalyze the Henry reaction in a superior manner.

Results and Discussion

The simplicity of reaction 1 stems from the fact that the catalytic amount of the base used is protonated



(1)

during the reaction to form the salt shown that is easily separated chromatographically; a process that requires neither acidic nor aqueous workup. Self-condensation of ketones is not possible under the reaction conditions since none of the promoter (**1**) is present in unprotonated form at the concentrations employed. Because the basicity order of **1a**−**c** is **1c** < **1b** < **1a**,[15] we focus our attention here mainly on **1a** and **1b**. It is worth mentioning that the pK_a of **1c** has been estimated to have a lower limit of 25[15] and an upper limit of 26.8[16b,19] in DMSO based on competetitive deprotonation.

A. The Reaction of Carbonyl Compounds with Nitromethane in the Presence of 1a. The reaction of aldehydes with nitromethane in the presence of **1a** is fast and virtually quantitative. Thus, for example, aldehyde **2k** forms **3k** (via the plausible pathway shown in Scheme 1) in less than 5 min in the presence of 2.2 equiv of $MgSO_4$ and 20 mol % of **1a**. (See Chart 1 for structures.) The decision to use $MgSO_4$ as a Lewis acid was based on another study[18b] in which we observed that $MgBr_2$ and $MgSO_4$ were the only Lewis acids found to activate carbonyl groups in the synthesis of β-hydroxy nitriles catalyzed by bases of type **1**. Since $MgSO_4$ is less expensive and more convenient to handle and its insolubility allows it to be easily filtered by column filtration, we have thus far preferred to use it over $MgBr_2$. Moreover, $MgBr_2$ in the present study did not appear to be effective. The reaction of cyclohexanone **2a** (employed as a model ketone) with nitromethane in the presence of 10 mol % of **1a** is rather sluggish, requiring 18 h at room temperature to achieve a yield of **3a** (48%) that is comparable to literature values (48−74%[10,21]). Although the yield of **3a** increased to 64% when the amount of **1a** was increased to 20 mol %, 8% of the corresponding dinitro derivative **4a** was also formed. When this reaction was repeated in the presence of 30% mol % of **1a**, the yield of the nitroaldol product increased to 68% while the

Scheme 1

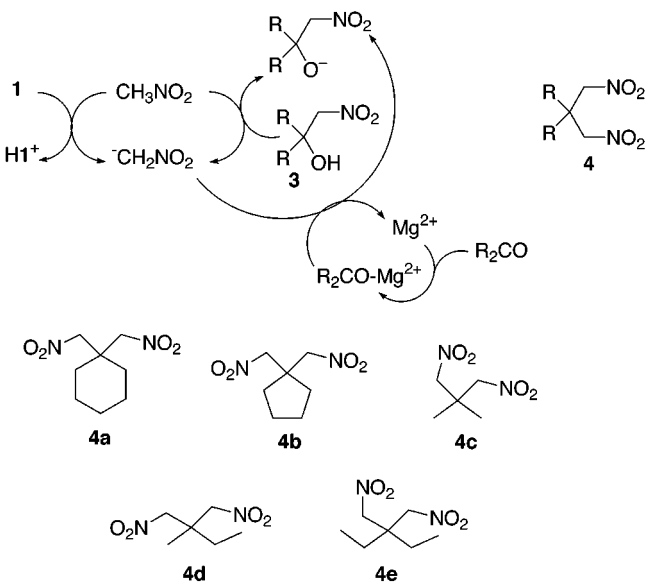


Table 1. Reactions of Ketones with Nitromethane in the Presence of 10 mol % of 1a and 2.2 equiv of Magnesium Sulfate for 3 h

substrate	product (% yield)	substrate	product (% yield)
2a	**3a** (95)	**2d**	**3d** (88)
2b	**3b** (93)	**2e**	**3e** (60)
2c	**3c** (94)	**2f**[a]	

[a] Only the starting material was recovered at the end of the reaction time.

production of the dinitro product **4a** increased to 20%. In the presence of 2.2 equiv of anhydrous magnesium sulfate (in which the Mg^{2+} presumably acts as a carbonyl group activator) and 30 mol % of **1a**, the conversion was quantitative and a 96% isolated yield of the nitroaldol product **3a** was obtained in about 3 h. Reducing the amount of **1a** to 10 mol % did not materially affect the yield (95%) of **3a**. At concentrations lower than 10 mol % of **1a**, some of the starting material was still observed after 3 h. The reactions of cyclopentanone, acetone, 2-butanone, and 3-pentanone with nitromethane in the presence of 10 mol % of **1a** and 2.2 equiv of Mg^{2+} were equally successful. Pertinent data for these reactions are shown in Table 1.

Since the formation of the dinitro compounds of type **4** has been reported in several syntheses of β-nitroalkanols,[1] we decided to investigate the limitations such reactions might have on our methodology. At a higher concentration of **1a** (30 mol %), the formation of dinitro compounds was observed to begin at reaction times greater than 5 h. When the reaction was allowed to proceed for 18 h in the presence of 30 mol % of **1a** and 2.2 equiv of magnesium sulfate, an 84% yield of the nitroaldol **3a** and a 14% yield of the dinitro derivative **4a** was realized. The reactions of cyclopentanone, acetone, and 2-butanone with nitromethane in the presence of 30 mol % of **1a** and 2.2 equiv of Mg^{2+} were equally successful. With 3-pentanone (**2e**), only 43% of the nitroaldol product **3e** was isolated in addition to 23% of the corresponding dinitro product **4e**, with the rest being unidentified material. Therefore, even with longer reaction times, the formation of the nitroaldol products still predominates. The sterically hindered ketones **2f** and **2h** (as a mixture of diastereomers) have so far failed to form

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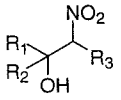
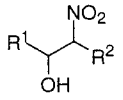
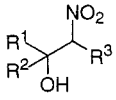
Chart 1



	R^1	R^2		R^1	R^2	R^3
2a:	$(CH_2)_5$		**3a**:	$(CH_2)_5$		H
2b:	$(CH_2)_4$		**3b**:	$(CH_2)_4$		H
2c:	Me	Me	**3c**:	Me	Me	H
2d:	Me	Et	**3d**:	Me	Et	H
2e:	Et	Et	**3e**:	Et	Et	H
2f:	*i*-Pr	*i*-Pr	**3f**:	*i*-Pr	*i*-Pr	H
2g:	$(CH_2)_4CH(Me)$		**3g**:	$(CH_2)_4CH(Me)$		H
2h:	$CH(Me)(CH_2)_3CH(Me)$		**3h**:	$CH(Me)(CH_2)_3CH(Me)$		H
2i:	Ph	Me	**3i**:	Me	Me	H

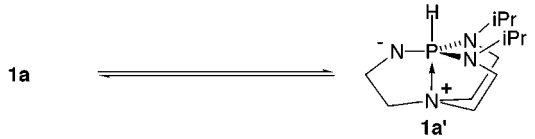




	R		R^1	R^2		R^1	R^2	R^3
2j:	*p*-$MeOC_6H_4$	**3j**:	*p*-$MeOC_6H_4$	H	**3r**:	$(CH_2)_5$		Me
2k:	*p*-$O_2NC_6H_4$	**3k**:	*p*-$O_2NC_6H_4$	H	**3s**:	H	*i*-Pr	Me
2l:	*n*-Pr	**3l**:	*n*-Pr	H	**3t**:	$(CH_2)_5$		Et
2m:	*i*-Pr	**3m**:	*i*-Pr	H	**3u**:	H	Ph	Et
2n:	Ph	**3n**:	Ph	H	**3v**:	H	$CH_3(CH_2)_5$	Et
2o:	2,5-$Me_2C_6H_3$	**3o**:	2,5-$Me_2C_6H_3$	H				
2p:	PhCH(Me)	**3p**:	PhCH(Me)	H	**3w**:	$Me(CH_2)_5CH(OH)C(NO_2)Me_2$		
2q:	$CH_3(CH_2)_5$	**3q**:	$CH_3(CH_2)_5$	H	**3x**:	$PhCH(OH)C(NO_2)Me_2$		

the corresponding nitroaldol products when reacted with nitromethane in the presence of **1a** and 2.2 equiv of magnesium sulfate. Starting materials were recovered quantitatively.

The formation of the dinitro products (via the plausible pathway shown in Scheme 2) in the reaction of ketones with nitromethane in the presence of catalytic amounts of **1a** can be rationalized in terms of the relative basicities and steric features of **1a**−**c**.[15] In addition to the superior base strength of **1a**, which is attributed to its ability to exist as an amide base in tautomeric form (eq 2),[14] this base is also less sterically hindered because of the more open amide site in **1a′**. At higher concentrations (30 mol %) the free base present induces a base-assisted dehydration. At longer reaction times, the alkoxide **3′**$^-$ produced can tautomerize to **3″**$^-$, leading to the elimination of OH^- and subsequent formation of the dinitro system **4**, as shown in Scheme 2. The results of reactions of nitromethane with some of the ketones involved in this study with 30 mol % of **1a** in the presence of 2.2 mol equiv of magnesium sulfate for 18 h at room temperature are shown in Table 2.



(2)

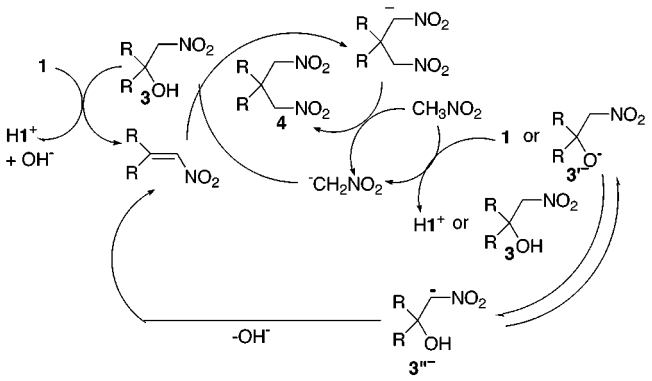
B. The Reaction of Carbonyl Compounds with Nitroalkanes in the Presence of 1b. The reaction of aldehydes is fast and quantitative in the presence of **1b**.

Table 2. Reactions of Ketones with Nitromethane in the Presence of 30 mol % of 1a and 2.2 equiv of magnesium sulfate for 18 h

substrate	product (% yield)	product (% yield)	substrate	product (% yield)	product (% yield)
2a	**3a** (75)	**4a** (21)	**2e**	**3e** (43)	**4e** (23)
2b	**3b** (59)	**4b** (15)	**2f**[a]		
2c	**3c** (83)	**4c** (13)	**2g**	**3g** (38)	**4g** (0)
2d	**3d** (61)	**4d** (27)	**2h**[a]		

[a] Only starting material was recovered at the end of the reaction time.

Scheme 2



Thus **2k** reacts with nitromethane in the presence of 20 mol % of **1b** and 2.2 equiv of magnesium sulfate in less than 5 min at room temperature to form **3k** as the only product. When **2a** was reacted with nitromethane in the presence of 10 mol % of **1b** and 2.2 equiv of magnesium sulfate for 3 h, a 95% yield of **3a** was isolated and no dinitro derivative **4a** was observed. Scheme 1 suggests that the reaction requires catalytic amounts of magnesium ions. In the presence of 1 mol % of $MgSO_4$, **2a** reacted with nitromethane in the presence of 10 mol % of **1b** to form **3a** (ca 70% conversion as estimated by ^{1}H NMR integration) in 3 h at room temperature. When the temperature was raised to 40 °C, the conversion in 2 h was 73%. Increasing the reaction time beyond 2 h led to no significant change in the conversion. On the other hand, increasing the amount of magnesium sulfate to 1 mole equivalent increased the conversion to 83% in 2 h at the same temperature. At mole ratios greater than 2.0 equiv of magnesium sulfate and 10 mol % of **1b**, the conversion in 2 h at 40 °C was estimated by ^{1}H NMR integration to be 96%. This dependence of the nitroaldol reaction of ketones on Mg^{2+} concentration is attributable to its activation of the carbonyl group via oxygen coordination and its subsequent stabilization of the alkoxide produced upon C−C bond formation. This dual role of $MgSO_4$ is again demonstrated in the reaction of **2m** with $MeNO_2$ in the presence of 1 mol % of magnesium sulfate and 10 mol % of **1b**. Although this reaction is complete in about 1 h at 40 °C, several spots were observed on TLC. In the presence of 2.2 mol equiv of magnesium ions, however, the conversion is complete in less than 1 h at room temperature with **3m** as the only product. Results of the reactions of **2a**−**q** with nitromethane in the presence of **1b** and 2.2 mol equiv of magnesium sulfate are summarized in Table 3.

The nitroaldol **3p** was obtained as a 7:4 (syn:anti) mixture of diastereomers (determined by ^{1}H NMR integration of the methinyl protons). The syn preference is due to attack from the less hindered side of the carbonyl group.

That high concentrations of **1** deprotonate the methylene group in products of type **3** (leading to the formation of the corresponding dinitro compound **4** as shown in Scheme 2) is demonstrated by our observation of the reactions of nitromethane with some of the ketones used in this study. The results of these reactions in the presence of 40 mol % of **1b** and 2.2 equiv of magnesium sulfate for 18 h at room temperature are given in Table 4. No corresponding dinitro products were observed at reaction times of less than 5 h.

Table 3. The Reaction of Carbonyl Compounds with Nitroalkanes in the Presence of 1b and 2.2 equiv of Magnesium Sulfate[a]

substrate	product (% yield)	substrate	product (% yield)
2a	**3a** (70)[b]	**2m**	**3m** (98)[c]
2a	**3a** (96)	**2n**	**3n** (96)[c]
2b	**3b** (93)	**2o**	**3o** (92)[c]
2c	**3c** (91)	**2p**	**3p** (88)[c]
2d	**3d** (85)	**2q**	**3q** (99)[c]
2e	**3e** (67)	**2a**	**3r** (82)[e]
2f	**3f** (0)	**2m**	**3s** (98)[c,e]
2g	**3g** (40)	**2a**	**3t** (93)[f,g]
2h	**3h** (0)	**2n**	**3u** (97)[f,h]
2i	**3i** (0)	**2q**	**3v** (99)[f,i]
2j	**3j** (94)[c]	**2q**	**3w** (99)[j,k]
2k	**3k** (99)[d]	**2n**	**3x** (95)[j,l]
2l	**3l** (98)[c]		

[a] The amount of **1b** used was 10 mol % and the reaction time was 3 h, unless stated otherwise. [b] The reaction was performed at 40 °C for 2 h in the presence of 1% $MgSO_4$ and 30 mol % of **1b**. [c] The reaction time was 40 min and the amount of **1b** used was 10 mol %. [d] The reaction time was 5 min. [e] The nitroalkane used was nitroethane. [f] The nitroalkane used was 1-nitropropane. [g] The amount of **1b** used was 0.3 equiv and the reaction time was 7 h. [h] The amount of **1b** used was 0.2 equiv and the reaction time was 2.25 h. [i] The reaction time was 1.25 h. [j] The nitroalkane used was 2-nitropropane. [k] The reaction time was 1.5 h. [l] The reaction time was 4 h.

In a similar way to that described above, nitroethane reacts with cyclohexanone (**2a**) and isobutyraldehyde (**2m**) in the presence of 10% of **1b** and 2.2 equiv of magnesium sulfate to form the corresponding nitroaldols **3r** and **3s** (1:1 mixture of diastereomers) in 82% and 98%, respectively. However, we found that 1-nitropropane requires 1.25 h to undergo a quantitative reaction with *n*-heptanal (**2q**) to form **3v** as a 3:2 mixture of the syn and anti diastereomers, respectively. The diastereomeric ratio was determined by ^{1}H NMR integration based on a comparison of both the ^{1}H NMR and ^{13}C NMR spectral data for the diastereomeric mixture with those reported by Seebach et al.[22] for the nitroaldol diastereomeric product obtained from the reaction of *n*-hexanal with 1-nitropropane. The reaction of benzaldehyde under similar conditions afforded only 85% conversion to the desired β-alkanol, as estimated by ^{1}H NMR integration of the reaction mixture. Upon increasing the amount of the base to 0.2 equiv, this substrate also reacted quantitatively in 2.25 h to afford a 3:1 (syn:anti) diastereomeric mixture of **3u** in 97% yield. The observed prefer-

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Table 4. The Reaction of Ketones with Nitromethane in the Presence of 40 mol % of 1b and 2.2 equiv of Magnesium Sulfate[a]

substrate	product (% yield)	product (% yield)	substrate	product (% yield)	product (% yield)
2a	**3a** (79)	**4a** (15)	**2d**	**3d** (64)	**4d** (21)
2b	**3b** (59)	**4b** (9)	**2e**	**3e** (40)	**4e** (20)
2c	**3c** (85)	**4c** (13)	**2f**[b]		

[a] The reaction time was 3 h. [b] Only starting material was recovered.

ence for the syn diastereomer is probably due to the favorable intramolecular hydrogen bonding in this diastereomer. The reaction of cyclohexanone as a model ketone under similar conditions proceeded with 43% conversion but afforded the nitroaldol **3t** in 93% yield upon increasing the ratio of **1b** to 0.3 equiv and carrying out the reaction for 7 h (Table 3). However, nitrocyclohexane did not afford the corresponding nitroaldols when reacted with benzaldehyde, *n*-heptanal, 2-butanone, or cyclohexanone. Thus a quantitative mixture of reactants was isolated when benzaldehyde or cyclohexanone was reacted with nitrocyclohexane for 6 and 72 h, respectively. Unreacted 2-butanone was lost on workup and evaporation of the volatiles, and therefore only nitrocyclohexane was recovered quantitatively. *n*-Heptanal, however, afforded the corresponding aldol product in 91% yield. The formation of the aldol product from primary aldehydes has been observed in our laboratories in previous studies.[18] The lack of reactivity of nitrocyclohexane in these reactions is assumed to be the result of steric hindrance. Although protonation of **1b** is observed by ^{31}P NMR analysis, the nitronate anion thus produced, which is associated with the azaphosphatrane countercation (eq 1), forms a bulky ion pair that is too sterically hindered to approach a carbonyl group. The use of magnesium bromide (the only other Lewis acid we have so far found to be compatible with our system[18b]) was also fruitless. The reaction of 2-nitropropane with *n*-heptanal on the other hand afforded the corresponding nitroaldol **3w** in 99% yield in 1.5 h, while the reaction with benzaldehyde required 4 h to give a 95% yield of the desired product **3x**. The reaction of 2-nitropropane with 2-butanone afforded only the starting nitroalkane after workup and removal of the volatiles, while the reaction of cyclohexanone afforded a mixture of the starting materials after workup. The inability of the 2-nitropropane to produce 2-nitroalkanols in reactions with ketones is again rationalized in terms of the steric hindrance of the ion pair formed after deprotonation. However, since aldehydes are more reactive and less sterically hindered than ketones, they are able to react with 2-nitropropane, which is less hindered than nitrocyclohexane. An attempt at employing magnesium bromide as the carbonyl activator for this substrate was also fruitless.

C. The Reaction of Carbonyl Compounds with Nitromethane in the Presence of 1c. The yields of β-nitroalkanols using **1c** as a base are equal, within experimental error, to those obtained with **1b**. For example, **2a** or **2b** reacted with nitromethane in the presence of 10 mol % of **1c** and 2.2 mol equiv of magnesium sulfate to afford a 95% and 91% yield of the nitroaldol products **3a** and **3b**, respectively. The yields of the same two products in the presence of 10 mol % of **1b** were 96% and 93% respectively (Table 3). However, in contrast to our observation with **1b**, increasing the concentration of **1c** from 10 up to 40 mol % did not lead to the formation of the corresponding dinitro product. Thus when the ratio of **1c** was increased from 10 up to 40 mol % in the reaction of ketones in the presence of 2.2 equiv of magnesium sulfate, the yield of the nitroaldol product did not appear to change appreciably. For example, **2a** gave a 97% yield of **3a** in 18 h while **2b** produced a 92% yield of the corresponding nitroaldol in the presence of 40 mol % of **1c**. The yields of the same two products with 10 mol % of **1c** (vide supra) were 95% and 91%, respectively. This result is consistent with the relatively weaker basicity of **1c** relative to **1b** and **1a**.

We have so far been unable to induce the nitroaldol reaction with aromatic ketones. Only starting materials were recovered upon reacting acetophenone (**2i**) with nitromethane in the presence of 30 mol % of either **1a** or **1b** and 2.2 mol equiv of magnesium sulfate. Warming the reaction mixture to 40 °C also did not lead to the production of the expected β-nitroalkanol. This result can be attributed to resonance stabilization of the carbonyl group by the benzene ring in the substrate.

Conclusions. We have shown here that the proazaphosphatranes **1a**−**c** are highly efficient promoters at room temperature for the Henry reaction in the presence of 2.2 equiv of magnesium sulfate. While the reaction of primary nitroalkanes and 2-nitropropane proceed with excellent yields, the reaction of nitrocyclohexane fails under similar conditions.

The high yields observed in the nitroaldol reaction of ketones promoted by bases of type **1** are due to the virtual lack of free base present at the concentrations used in these reactions. Since the corresponding nitronates are much weaker bases than the alkoxide, they are unable to deprotonate the ketones (a process that would lead to self-condensation). Once the nitronate adds to the ketone, the alkoxide thus produced preferentially deprotonates the more acidic nitroalkane that is present in large excess. Thus ketone self-condensation is less likely to be observed under these reaction conditions.

Experimental Section

All reactions were carried out under nitrogen. The carbonyl compounds were purchased from Aldrich Chemical Co. and were used as received. Nitroethane and nitromethane were dried over anhydrous magnesium sulfate, distilled under nitrogen, and then stored over 4 Å molecular sieves.

General Procedure for the Preparation of the Nitroalkanols. In a typical experiment, a small test tube containing a microstirbar and 0.53 g (4.4 mmol) of magnesium sulfate was sealed with a septum and then evacuated to 200 milliTorr. The tube was then filled with nitrogen gas followed by 1.0 mL of the nitroalkane, and then the mixture was stirred vigorously until all the magnesium sulfate was incorporated into the suspension. To this suspension was added 2.0 mmol of the carbonyl compound. The mixture was stirred for 5 min, after which a solution of 60 mg of **1b** (or 43 mg of **1a** or 52 mg of **1c**, 0.20 mmol) dissolved in 1.0 mL of the nitroalkane was added. After the time periods specified in Tables 1−5 had elapsed, the reaction mixture was then loaded onto a small silica gel column and eluted with 100% diethyl ether. The solvent and any remaining unreacted nitroalkane were removed under reduced pressure. Nitroalkanols **3e**, **3k**, **3l**, **3m**,

Table 5. Comparison of the Reaction of Ketones with 1b and 1c in the Presence of 2.2 equiv of Magnesium Sulfate

	yield with **1b**[a]		yield with **1c**		
substrate	10 mol %	30 mol %	10 mol %[a]	30 mol %[a]	40 mol %[b]
2a	95	97	95	96	97
2b	91	93	91	92	92

[a] The reaction time was 3 h. [b] The reaction time was 18 h.

3n, **3q**, **3s** (as a 1:1 mixture of diastereomers), **3t**, and **3u** were obtained as pure products in excellent yields, while the remaining nitroalkanols were separated and purified as detailed below.

Separation of the Dinitro/Nitroalkanol Product. The product mixture of the nitroalkanol and the dinitro derivative was loaded onto a silica gel column using a small amount of ether. The separation of the two compounds was then achieved by eluting with diethyl ether in pentane. The ratio of ether was increased in 5% portions from 0% to 80% in 50 mL volumes, and 20 mL fractions were collected. The nitroalkanol eluted first while the dinitro compounds followed at about 50% diethyl ether in pentane.

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Supporting Information Available: ^{1}H and ^{13}C NMR data, mass spectral molecular weights, and elemental analyses are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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