Table II. Palladium-Catalyzed α-Arylation of Butyl Vinyl Ether (1) with Triflates 2b–g[a]

entry	substr	T (°C)	t (h)	3/4[b]	product (yield, %[c])	mp (°C)[d]
1	**2b**	100	3.5	99/1[e]	**5b** (54)	79–81 (80–81)
2	**2c**	80	3	98/2[f]	**5c** (94)	59–61 (60–61)
3	**2d**	80	5	100/0	**5d** (96)	110–112 (114)
4	**2e**	100	2	100/0	**5e** (92)	78–80 (80–81)
5	**2f**	100	5	100/0	**5f** (89)	*g*
6	**2g**	100	5	100/0	**5g** (90)	37–39 (38–39)

[a] The triflate (0.6 mmol), butyl vinyl ether (3.0 mmol), triethylamine (1.2 mmol), DPPP (0.0165 mmol), and $Pd(OAc)_2$ (0.015 mmol) were reacted in 2 mL of DMF. [b] Determined by GLC of the crude products before acidic treatment. [c] Isolated yields. [d] In parentheses are mp from literature.[8] [e] Compound **4b** was isolated as an 80/20 *E*/*Z* mixture by flash chromatography[9] (J_{H-H} = 12.9 Hz, *E* isomer; J_{H-H} = 7.0 Hz, *Z* isomer). [f] Compound **4c** was isolated as a 16/84 *E*/*Z* mixture by flash chromatography[9] (J_{H-H} = 12.5 Hz, *E* isomer; J_{H-H} = 6.9 Hz, *Z* isomer). [g] **5f**: bp 119–121 °C (13 mmHg), lit.[8] bp 112.5 °C (11 mmHg).

reaction between butyl vinyl ether (**1**) and aryl triflates **2a–g**[6] with very high regioselectivity toward the α position. The well-known instability of the α-arylated products **3a–g**[7] allows one to obtain, after treatment with acids, the corresponding aryl methyl ketones **5a–g** (Scheme I). When **1** and naphthyl triflate (**2a**) were reacted in the absence of any palladium ligands, decomposition of the catalyst was observed; after 24 h only a small amount of the product was found in the reaction mixture (Table I, entry 1). This result is in agreement with the data reported by Hallberg on phenyl triflate.[3d]

In the presence of PPh_3 complete conversion with low selectivity toward α/β and *E*/*Z* isomers was observed (entry 2). The use of a DPPP-containing catalyst, very active in palladium-catalyzed reduction of aryl triflates,[5] allows one to obtain a complete selectivity toward the α-arylated product. The regioselectivity observed is independent both from reaction temperature (entries 3–5) and solvent (entries 6 and 7). These results prompted us to extend the reaction to substrates **2b–g**, containing substituents of different electronegativity, in order to check the scope and limitation of the method. The data obtained are reported in Table II. In every case almost complete α-regioselectivity and high yields (with exception of entry 1) were observed.

Electronic effects, exerted by the substrate, reported to play an important role in the regiochemistry in the absence of ligands,[3b] thus turn out to be not important in the presence of DPPP. On the other hand, with the exception of *p*-NO_2, electron-withdrawing groups at the para position increase the reaction rate, the reactivity order being *p*-CN > *p*-CH_3CO > H > *p*-CH_3 ≅ *p*-CH_3O. These results suggest that the slow step in this reaction is the oxidative addition of aryl triflates on the Pd^0 complex. The study of the factors favoring the formation of the α-arylated product in the presence of different ligands and leaving group are under investigation.

Summing up, we have developed a high yield method for the synthesis of aryl methyl ketones that offers a synthetical alternative to the Friedel–Crafts acylation and related reactions.

(6) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.
(7) (a) Loudon, G. M.; Smith, C. K.; Zimmerman, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 465. (b) Loudon, G. M.; Berke, C. *J. Am. Chem. Soc.* **1974**, *96*, 4508. (c) Chiang, Y.; Kresge, A. J.; Young, C. I. *Can. J. Chem.* **1978**, *56*, 461.
(8) Buckingham, J. *Dictionary of Organic Compounds*, 5th ed.; Chapman Hall: New York, 1982.

Experimental Section

All products were identified through their ^1H NMR spectra (Bruker AM 200; $CDCl_3$ as solvent with tetramethylsilane as an internal standard), mass spectra (CHS-DF Varian MAT-GC/MS), mp (determined on a Kofler apparatus and are uncorrected), or bp (bulb-to-bulb distillation conducted with a Büchi Kugelrohr apparatus) and by comparison with an authentic sample. The GLC analyses were carried out on a Carlo Erba HRGC 5300 chromatograph equipped with a Nordibond OV-1 column (25-m length, id 0.32 mm) and a flame ionization detector. Elemental analyses were performed by the microanalytical laboratory of the Istituto G. Donegani.

1,4-Dioxane and toluene were distilled from sodium and stored over activated 4A molecular sieves under argon. DMF and Et_3N were distilled from calcium hydride and stored over activated 4-Å molecular sieves under argon.

DPPP was an Aldrich product and used as received.

Palladium-Catalyzed Reaction. General Procedure (Table I, entry 3). To a stirred solution of **2a** (1 g, 3.62 mmol) in DMF (10 mL) under an argon atmosphere at room temperature were sequentially added Et_3N (0.731 g, 1 mL, 7.24 mmol), **1** (1.81 g, 2.3 mL, 18.1 mmol), DPPP (0.044 g, 0.1 mmol), and $Pd(AcO)_2$ (0.0203 g, 0.090 mmol). The reaction flask was heated to 80 °C. After 0.5 h the conversion was complete (GLC) and the reaction mixture was cooled to room temperature, 5% HCl (15 mL) was added, and after another 0.5 h of stirring the mixture was poured into CH_2Cl_2 (40 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL), and the combined organic layers were washed with water until neutrality, dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography[9] (hexane/ethyl acetate 9/1 by volume), affording **5a** (0.604 g, 97%).

The only new product isolated was (Table I, entry 2) (***E***/***Z***)**-1-(2-butoxyethenyl)naphthalene (4a)** (32%): pale yellow oil; ^1H NMR δ 1.00 (t, *J* = 7.3 Hz, 3 H), 1.32–1.63 (m, 2 H), 1.64–1.86 (m, 2 H), 3.95 (t, *J* = 6.4 Hz, 2 H), 5.89 (d, *J* = 6.9 Hz, 0.2 H, *Z* isomer), 6.43 (d, *J* = 6.9 Hz, 0.2 H, *Z* isomer), 6.5 (d, *J* = 12.5 Hz, 0.8 H, *E* isomer), 6.95 (d, *J* = 12.5 Hz, 0.8 H, *E* isomer), 7.20–8.22 (m, 7 H); GLC-MS (*E*)-**4a** *m*/*e* 226 (M^+), 170 (100), 169, 141, (*Z*)-**4a** *m*/*e* 226 (M^+), 170 (100), 169, 141.

Anal. Calcd for $C_{16}H_{18}O$: C, 84.91, H, 8.02. Found: C, 84.89; H, 8.04.

(9) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Rotation Barrier in a Doubly Vinylogous Amide

Hugo E. Gottlieb,* Samuel Braverman, and Shlomo Levinger

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100, Israel

Received August 14, 1989

In the course of a synthesis of nicotinaldehyde, we followed the method of Arnold.[1] This involves a bis-Vilsmeier–Haack formylation of aminoenamine **1**, which is readily obtained from crotonaldehyde. The product of this reaction, an orange crystalline material with a violet luster and a sharp melting point, was described by Arnold as having structure **2**, but alternative **3** was not excluded.[1] On the basis of NMR spectroscopy, we can establish **3** as the correct structure for this substance, but in addition, we notice broad lines characteristic of an ongoing dynamic process. In this paper we determine the nature and the energy barrier of this process.

(1) Arnold, Z. *Collect. Czech. Chem. Commun.* **1960**, *25*, 1308.

0022-3263/90/1955-3655$02.50/0

Table I. NMR Data[a]

	3a		3b		3	
	$^{13}C^b$	$^1H^c$	$^{13}C^b$	$^1H^c$	$^{13}C^d$	$^1H^e$
1	168.13	8.21, d (11.6)	165.25	7.99, d (11.7)	166.14	7.77, d (11.8)
2	104.26	7.24, dd (13.9, 11.6)	101.72	7.08, dd (13.2, 11.7)	102.56	7.11, dd (13.3, 11.8)
3	151.86	7.58, dd (13.9, 2.6)	160.58	7.28, dd (13.2, 2.7)	156.55	7.38, dd (13.3, 2.4)
4	118.18		118.77		120.37	
5	190.41	9.39, s	191.56	9.30, s	190.10	9.41, s
5′	189.63	9.55, d (2.6)	187.35	9.98, d (2.7)	189.25	9.80, d (2.4)
Me	46.80	3.54, s	46.21	3.47, s	46.32	3.40, s
Me′	38.50	3.32, s	38.00	3.23, s	38.53	3.18, s

[a] In acetone-d_6; δ's in ppm from internal TMS; coupling constants (in parentheses) in hertz. The estimated errors are ±0.01 and ±0.02 ppm for the ^1H and ^{13}C chemical shifts, respectively, and ±0.2 Hz for the J_{HH} values. The data for **3** correspond to the averaged values at high temperature. [b] At −59 °C. [c] At −90 °C. [d] At 24 °C. [e] At 49 °C.

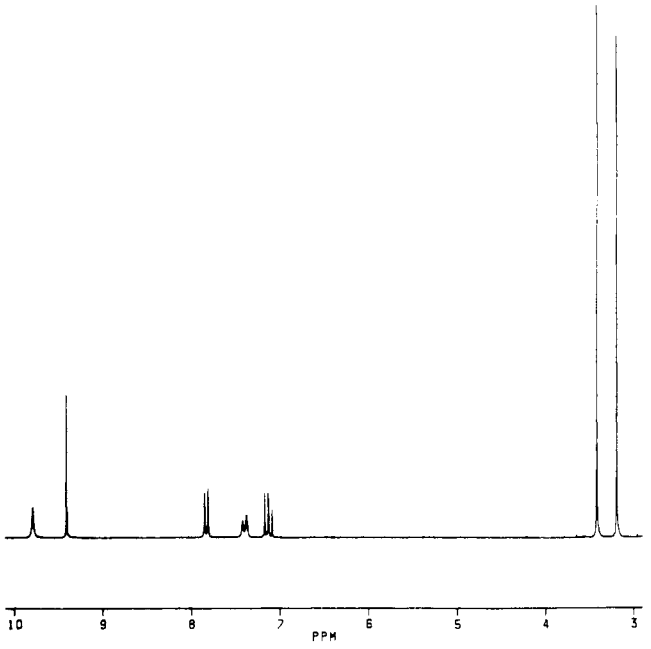
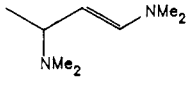


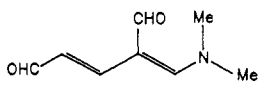
Figure 1. ^1H NMR spectrum of **3**, at 24 °C, in acetone-d_6.

Results

The ^1H NMR spectrum of **3** at room temperature in acetone-d_6 is shown in Figure 1. The olefinic region consists of two doublets and a double doublet with coupling constants > 11 Hz, indicating the presence of three protons on adjacent carbons, and therefore excluding **2** as a possible structure. An interesting feature of the spectrum is that the signals assigned to H(3) and to one of the aldehyde protons are visibly broader than the others. In part, this is due to a long-range coupling between these two hydrogens (as proved by double irradiation), but this is not enough to explain the additional linewidth. Clearly, the molecule undergoes a conformational change which is not fast enough for complete averaging at room temperature.



1



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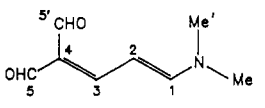


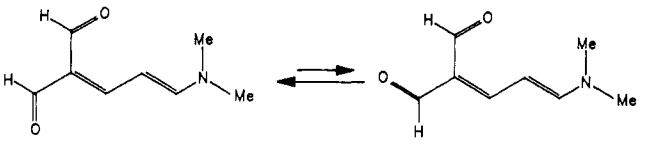
3

This was proved by lowering the temperature to below −30 °C whereas the spectrum splits into two sets of signals,

Table II. Rate Constants for the 3b → 3a Conversion

T, °C	k, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol
−52.8 ± 0.5	4 ± 1	12.2 ± 0.2
−44.3 ± 0.5	8 ± 1.5	12.3 ± 0.1
−35.8 ± 0.5	20 ± 3	12.4 ± 0.1
−27.3 ± 0.5	50 ± 8	12.4 ± 0.1
−18.8 ± 0.5	120 ± 20	12.4 ± 0.1
−10.3 ± 0.5	300 ± 50	12.3 ± 0.1
−1.8 ± 0.5	550 ± 80	12.4 ± 0.1
6.8 ± 0.5	1500 ± 200	12.3 ± 0.1
15.3 ± 0.5	3200 ± 500	12.2 ± 0.2
24.3 ± 0.5	7500 ± 1000	12.1 ± 0.2
48.5 ± 0.5	22000 ± 5000	12.4 ± 0.3

in an intensity ratio of 1.9:1. The vicinal coupling constants between the olefinic protons (see Table I) are very similar in both species and are only consistent with a trans C(1)–C(2) and s-trans C(2)–C(3) arrangement.[2] The only conceivable conformational interconversion is, therefore, rotation around the C(4)–CHO bonds, with four isomers being possible (each of the carbonyls can be either s-trans or s-cis to the adjacent double bond). We would like to suggest structures **3a** and **3b** for the major and minor species, respectively. This assignment is based first on the ca. 2.6-Hz coupling constant between one of the aldehyde hydrogens of each isomer and H(3). The most likely explanation for such a large $^4J_{HH}$ is a planar, zig-zag arrangement of the two protons involved. Only H(5′), in the conformation shown in **3a** and **3b**, can be the partner of H(3) in this interaction. Second, an NOE of 6% was observed on H(5′) of the major isomer when H(5) was irradiated; the analogous experiment on the minor isomer failed to show any measurable peak in the NOE difference spectrum.[3] This is consistent with the proximity of the two aldehyde protons in the former but not in the latter conformer, demonstrating that these are **3a** and **3b**, respectively. Third, the ^{13}C NMR spectrum taken at low temperature (Table I) shows that the biggest chemical shift difference between two equivalent nuclei in the two isomers is for C(3). This carbon is shielded by almost 9 ppm in **3a**, a result of the strong γ-effect induced by the in-plane, eclipsing carbonyl oxygen, an interaction which is absent in **3b**.



3a 3b

(2) Filleux-Blanchard, M. L.; Durand, H.; Bergeon, M. T.; Clesse, F.; Quinion, H.; Martin, G. J. *J. Mol. Struct.* **1969**, *3*, 351.

(3) Significant NOE's were also observed between the NMe protons and H(1) and between NMe′ and H(2).

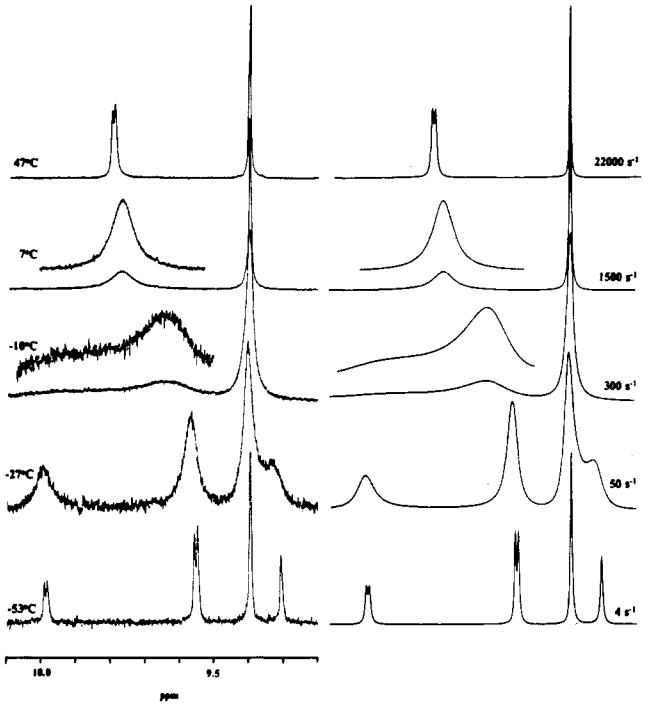


Figure 2. Experimental and calculated lineshapes for the aldehyde protons of **3**, as a function of temperature. The values of k used in the calculations are indicated on the computed traces.

In order to determine the energy barrier for the carbonyl rotation, spectra were taken at several temperatures and the rate constants for the process obtained for each by fitting to computed lineshapes (see the Experimental Section and Figure 2). The kinetic parameters for the **3b** → **3a** process are shown in Table II. the $\Delta G^{\ddagger}$ values are not significantly temperature-dependent, which indicates a small absolute value for $\Delta S^{\ddagger}$ (no more than 3 eu).

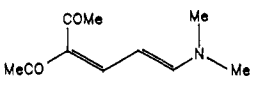
Experimental Section

NMR spectra were recorded on a Bruker AM model instrument, at 300.1 (^{1}H) or 75.5 (^{13}C) MHz, in acetone-d_6 as a solvent, with internal TMS set at 0 ppm as a reference. ^{1}H and ^{13}C signals were correlated via a series of off-resonance decoupled spectra obtained at room temperature, which is above coalescence for all the nuclei involved. The temperatures were determined with a calibrated Eurotherm 840/T digital thermometer via the following procedure: the termocouple was inserted in an NMR tube filled with an inert liquid up to the normal solution height, and this assembly lowered to the normal sample position; the temperature was read after it reached equilibrium. This operation was performed just preceding or following the spectra taken at −90, −53, 24, and 49 °C. The temperatures for the runs between −44 and 15 °C were obtained by interpolation, taking into account the nominal reading of the variable-temperature unit of the spectrometer. All temperatures are estimated to be correct to ±0.5 °C.

Rate constants for the interconversion process (Table II) were obtained by fitting the experimental spectra at different temperatures to computer-generated lineshapes, using the equations described by Sutherland;[4] the low- and high-field components of the H(5′) doublets were made to exchange with each other, respectively (the high-temperature results show that the two $J_{H(3),H(5')}$ have the same sign). Line widths used in the computation took into account spectrometer resolution (from the TMS line) and unresolved long-range couplings (from the observed line widths at −90 °C, at which temperature the broadening from the dynamic process can be calculated to be negligible). Several measurements were made below coalescence (five for H-5 and seven for H-5′); from these, $\Delta\delta$ values were extrapolated to higher temperatures. In addition, an equilibrium constant of 1.9 ± 0.1 was measured by integration of NMR signals for all spectra below coalescence; a $K = 1.9$ value was therefore assumed for the other temperatures as well. The k values determined from the computer fitting were converted to $\Delta G^{\ddagger}$ via the Eyring equation.[4] The errors quoted for $\Delta G^{\ddagger}$ values in Table II include an estimated 15% error in the fitting of k (25% for the −53 °C and 49 °C cases), the error in the temperature measurement, and also the probable errors in the extrapolation of $\Delta\delta$ and K.

Discussion

Dialdehyde **3** can be considered by vinylog of a β-amino-α,β-unsaturated carbonyl compound or, indeed, a doubly vinylogous amide. This class of substances gives rise to a number of possible interconversion processes which are well amenable to NMR study (for a recent review, see ref 5). Prokof'ev, Krasnaya, and Kucherov, for instance, measured activation energies for two degenerate processes—rotation around the =CH—NMe_2 and the C=$C(COMe)_2$ bonds—for a variety of such compounds, in different solvents.[6] For **4**, the bis(methyl ketone) analogue of **3**, the reported values are 14.5 and 22.1 kcal/mol, respectively, in $CDCl_3$ solution. A more polar solvent, like acetone, is expected to increase the former and considerably decrease the latter barrier.[5] In addition, such activation energies tend to be higher for aldehydes than for ketones, since the planar ground states are less sterically destabilized.[5] Since these two processes have been quite well studied, we did not attempt to measure their rates for compound **3**. We would only like to note that both must be in the 18.0 ± 0.5 kcal/mol range, since we saw no line broadenings due to these processes even at 49 °C, but we did observe a certain degree of saturation transfer at room temperature (a decrease in the integrated intensity of one CHO proton signal when the other is irradiated, and the same for the N-methyls).



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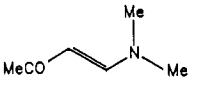

5

There is little quantitative data in the literature for s-cis/s-trans interconversions of the type we measured. In simple α,β-unsaturated carbonyl compounds, the barriers are probably too low to be determined by NMR spectroscopy.[5] A conjugated nitrogen will slow the process down, but we could find only one report on aminoenones, by Filleux-Blanchard, Mabon, and Martin.[7] A typical value is 12.2 kcal/mol for **5**, in very good agreement with our results.

It is interesting to speculate on the reasons for the preference of isomers **3a** and **3b** over the other two possible rotamers. **3a** is in fact doubly s-cis, in spite of the fact that most α,β-unsaturated aldehydes are predominantly s-trans conformers.[5] The doubly s-trans isomer would have the two carbonyls in a parallel arrangement, which is probably an unfavorable situation due to repulsion of the two dipoles. It is difficult to see, however, how other electronic and steric interactions combine to produce the experimental observations. We should add that we found no evidence for the presence of the second possible inter-

(4) Sutherland, I. O. in *Annual Reports on NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: London, 1971; Vol. 4, pp 71–235.

(5) Gottlieb, H. E. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; pp 129–150.

(6) Prokof'ev, E. P.; Krasnaya, Zh. A.; Kucherov, V. F. *Org. Magn. Reson.* **1974**, *6*, 240.

conversion process, i.e. rotation around the C(5')-C(4) bond, even down to -90 °C, which is not far from the freezing point of the acetone solvent.[8]

Registry No. 1, 126615-13-2; 3, 126615-14-3.

(7) Filleux-Blanchard, M. L.; Mabon, F.; Martin, G. J. *Tetrahedron Lett.* **1974**, 3907.

(8) The temperature dependence of the chemical shifts (Table I), which is somewhat stronger than usual, may be attributed to a gradual deviation from planarity in the ground states and concomitant change in solvation; see the small but significant decrease of $J_{H(2),H(3)}$ and $J_{H(3),H(5')}$, and the deshielding of the aldehyde and shielding of the NMe protons, as the temperature is increased.

Chemoselective Alcohol Oxidations by the Anionic Molybdenum-Picolinate *N*-Oxidoperoxo Complex MoO_5PICO[1]

Sandro Campestrini, Fulvio Di Furia,* and Giorgio Modena*

Centro di Studio sui Meccanismi di Reazioni Organiche del CNR, Dipartimento di Chimica Organica dell'Università di Padova, Via Marzolo 1, I-35131 Padova, Italy

Olga Bortolini

Dipartimento di Chimica dell'Università, Via Borsari 46, I-44100 Ferrara, Italy

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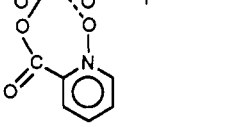
In previous papers[1-3] we reported on the synthesis and chemistry of the anionic peroxomolybdenum complex $[MoO(O_2)_2(C_5H_4N(O)COO)]^-Bu_4N^+$ (MoO_5PICO):



Both peroxogroups of MoO_5PICO react with primary and secondary alcohols in nonpolar solvents under mild conditions to give high yields of aldehydes and ketones, respectively.[2] Although there are several procedures for alcohol oxidations,[4] including recent ones,[6-9] MoO_5PICO may be considered to be of particular synthetic interest because it allows for the oxidation of a primary alcoholic function to aldehyde without overoxidation to the carboxylic acid.[4,7,9] Taking into account its ease of preparation from commercially available reagents as well as its remarkably stability, MoO_5PICO could be proposed as a substitute for classical alcohol oxidation reagents, such as the Cr(VI) derivatives. With a view to enlarging the synthetic scope of this reagent, we have further investigated its chemoselectivity. Previously, we showed that double-bond epoxidation does not compete with alcohol oxidation even in the case of homoallylic and allylic alcohols.[2] In this paper we present results indicating that the oxidation of the alcoholic function by MoO_5PICO also proceeds smoothly in the presence of other functional groups. Table I presents the data obtained in the oxidations of a series of model substrates. As a general comment, it is noteworthy that in all cases the oxidation of a primary alcoholic function leads to the corresponding aldehydic group without further oxidation to the carboxylic acid. In addition, it may be noted that for most of the examples reported, equimolar amounts of active oxygen ($[O]_{act}$ = 2[MoO_5PICO]) and of substrate are used. In the series of the three epoxy alcohols examined, a high yield of the epoxy aldehyde is found for compound **3a**; for **1a** and **2a**, epoxides of homoallylic and allylic alcohols respectively, the yields of the corresponding aldehydes are only moderate, ranging from 60 to 67% (not far, however, from the values obtained for classical oxidation reagents).[4,5] The iodometric and gas chromatographic analyses of the reaction mixtures reveal that appreciable amounts of the oxidant are still present when all the substrate has been consumed. At the same time, higher molecular weight products are detected. Although this behavior has not been investigated in detail, it appears that under the reaction conditions compounds **1a** and **2a** may undergo a parallel condensation reaction, likely Lewis acid catalyzed, for which there is precedent in the literature.[10] At any rate, the yield of epoxy aldehyde may be increased up to 95% for compound **2a** simply by using a 5-fold excess of the substrate thus, presumably, enhancing the rate of oxidation compared with that of the condensation process.

As might have been expected based on previous results concerning double bond vs alcohol oxidations,[2] the pyridine nitrogen (**4a**) and the triple bond (**5a**) do not compete with the oxidation of the OH group. By contrast, the presence of a basic group (**6a**) greatly diminishes the yields of the carbonyl product, probably due to the ability of the substrate to displace the picolinate-*N*-oxido ligand of the reagent.[1] In fact, analysis of the reaction mixture of compound **6a** reveals that ca 80% of the substrate is recovered unreacted. Based on these results, the synthetically significant oxidation of amino alcohols by MoO_5PICO requires the preliminary protection of the amino group. Compounds **7a**, **8a**, **9a** show that the oxidation of the alcoholic function of carbamates or amides is efficiently carried out by this reagent such that, following deprotection by standard methods, amino aldehydes or amino ketones are obtained. Finally, the oxidation of diols has been briefly examined. Both primary alcoholic groups of 1,6-hexanediol are oxidized (**10a**), providing adipaldehyde in good yield. It is interesting to note that the oxidation of meso-hydrobenzoin (**11a**) provides only minor amounts of benzaldehyde, at variance with the behavior of other oxidizing agents[11] and in spite of the ease of carbon-carbon bond cleavage in such model substrates. Instead, a fairly good yield of the more synthetically attractive α-diketone, benzil, is obtained.

Many of the model oxidations examined herein represent a key step in the route to complex molecules containing several functional groups. The scope of MoO_5PICO

(1) Part 33 of the series Metal Catalysis in Oxidation by Peroxides. Part 32: Bonchio, M.; Conte, V.; Di Furia, F.; Modena, G.; Padovani, C.; Sivak, M. *Res. Chem. Interm.* **1989**, *12*, 111.

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