The N-chloro amines are protonated in 30% H<sub>2</sub>SO<sub>4</sub> and are confined to the aqueous acid, whereas the alkane reactants are slightly soluble in the acid. It is not known whether reaction occurs at the interface or on the small amount of dissolved alkane. Despite this hindrance, the reactions proceed readily with both alkanes and chloroalkanes, as already shown by Minisci and coworkers.<sup>3,6</sup>

Steric effects have already been invoked by Minisci and coworkers to explain the increase in ratio of 2chloro- to 3-chloroheptane (56:29 to 64:23) as R is increased in size from methyl to isobutyl in the  $R_2NCl.^4$ Ratios of p:s:t were not studied.

Di-tert-butylamine was made by conversion of 2methyl-2-nitropropane<sup>7</sup> to di-tert-butyl nitroxyl<sup>8</sup> and reduction of the nitroxyl by a general method.<sup>8,9</sup> Dineopentylamine was prepared as described.<sup>10</sup> tert-Butyltert-amylamine was prepared from tert-butylamine and 3-chloro-3-methyl-1-butyne.<sup>11</sup> The remaining amines were commercially available. The N-chloro amines were prepared from N-chlorosuccinimide and the amine in diethyl ether. Some had been used before.<sup>3-6</sup> N-Chlorodi-tert-butylamine had been made by a similar method.<sup>12</sup> The N-chlorodineopentylamine, -dicyclohexylamine, -tetramethylpiperidine, and -tert-butyl-tertamylamine do not appear to have been described.

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## Remarkably Facile Pseudorotation of Four-Membered-Ring Phosphoranes<sup>1</sup>

Sir:

Compounds 1 and 2 have been prepared by allowing the appropriate phosphine to react with diethyl peroxide.<sup>2</sup> The <sup>1</sup>H nmr spectrum (100 MHz) of 1 at 78° in o-dichlorobenzene shows a doublet centered at  $\delta$  1.19 ( $J_{\rm PH} = 16$  Hz, ring methyl hydrogens), a doublet at 1.32 ( $J_{\rm PH} = 32$  Hz, ring methylene hydrogens), a quintet at 3.47 ( $J_{\rm PH} = J_{\rm HH} = 7$  Hz, methylene hydrogens of the ethoxy groups), and a triplet at 1.10 ppm ( $J_{\rm HH} = 7$  Hz, methyl group hydrogens of the ethoxy group). At 30° all of the absorptions are the same except for those of the methylene hydrogens of



the ethoxy group, which have coalesced into a broad, ill-defined absorption. At  $-20^{\circ}$  in toluene- $d_8$  the rest of the spectrum is still unchanged, but now the methylene hydrogens of the ethoxy groups absorb as a many-line pattern which is analyzable as an ABM<sub>3</sub>X spectrum, assuming  $J_{AB} = 10$  Hz,  $J_{HCCH} = 7$  Hz,  $J_{AX} = 7$  Hz, and  $J_{BX} = 7$  Hz; the difference in chemical shift between A and B is found to be ca. 31 Hz. At  $-51^{\circ}$  coalescence is observed for the absorptions due to the hydrogens of the ring methyl groups, and at  $-68^{\circ}$  these are now found as two doublets at  $\delta$  1.32  $(J_{\rm PH} = 14 \text{ Hz})$  and 1.06 ppm  $(J_{\rm PH} = 18 \text{ Hz})$ . On the basis of the "Muetterties rules"<sup>3</sup> and assuming trigonal-bipyramidal structures, such a spectrum arises when pseudorotation<sup>4,5</sup> is limited to apical-equatorial switching of the ring and the ethoxy groups, *i.e.*, the phenyl group is locked in an equatorial position, 3. Between -51 and  $30^{\circ}$  the spectra are explainable



if structure 4 is now allowed. Above 30° the diastereotopic hydrogens of the methylene groups of the ethoxy groups apparently become isochronous. Equivalency can occur by pseudorotation only if the molecule passes through a structure with a diequatorial ring, such as 5. Apparent equivalency can occur if on heating the population of rotational conformers of the ethoxy groups changes such that the methylene nonequivalency is reduced below the level of detection. Loss of nonequivalency by this latter mechanism does not proceed with coalescence, whereas loss of nonequivalency via pseudorotations which render the diastereotopic hydrogens equivalent does proceed with coalescence. The results therefore strongly suggest that a diequatorial ring such as is found in 5 is responsible for the equivalency.<sup>3</sup>

Similar results were found with 2. The <sup>1</sup>H nmr spectrum in toluene- $d_8$  at 100° has a doublet centered at  $\delta$  1.38 ( $J_{PH} = 19$  Hz,  $R_5$  and  $R_6$  methyl group hydrogens), another doublet at 0.76 ( $J_{PH} = 1$  Hz,  $R_3$  and  $R_4$  methyl group hydrogens), two quartets at *ca*.

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<sup>(2)</sup> The assignment of structure rests on their method of preparation and their <sup>1</sup>H and <sup>3</sup>P nmr spectra. The materials as prepared in solution are quite pure and only slightly contaminated with the corresponding oxide.

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The apparent equivalence of the methylene hydrogens of the ethoxy groups of 2 at 100° can arise if structures containing a diequatorial ring are permitted. If the Berry mechanism for pseudorotation is assumed,<sup>4a</sup> then a minimum of five pseudorotations in which each group bonded to phosphorus is used as a pivot leads to isochronous hydrogens of the methylene groups. Apparent equivalency can arise as discussed above; however, coalescence is not predicted.

Previous work with four-membered-ring phosphoranes in which an oxygen is bonded to phosphorus in the ring has shown that these substances do not pseudorotate rapidly on the nmr time scale.<sup>6</sup> On the other hand, pseudorotation has been implicated in various reactions of four-membered-ring phosphorus-containing compounds.<sup>4e</sup> No experimental evidence has been presented for a diequatorial ring, although it has been suggested.<sup>7</sup> Later work has shown that a diequatorial ring is not required to explain the results.8 Calculations have attested to the possibility of such a geometry.4e

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## **Reversal of a Substituent Effect on Cation** Stabilities between the Gas and Liquid Phases

## Sir:

In spite of the enormous amount of work done on substituent effects in organic chemistry, studies in which gas-phase and solution data can be compared are rare.<sup>1-5</sup> We wish to report such a comparison for the formation of substituted oxocarbonium ions (R-C+=O) in the gas phase and in "magic acid" solution. A normal inductive order is observed in the gas phase while a Baker-Nathan order is observed in solution.

Using the techniques developed by Arnett and Larsen<sup>6</sup> the relative heats of formation of several oxo-

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carbonium ions from the corresponding acid chlorides were measured calorimetrically in 11.5 mol % antimony pentafluoride in fluorosulfonic acid at 25°. The reaction is shown in eq 1 and the data are given in

$$\begin{array}{c} O \\ \parallel \\ R - C - Cl \xrightarrow{\text{SbF}_{5} - FSO_{4}H} \\ \end{array} R - C^{+} = O + \text{anion}^{-}$$
 (1)

Table I. The oxocarbonium ions are well known in

**Table I.** Relative Heats of Formation  $(\Delta H_R +)$  of Acylium Ions in 11.5 mol % SbF5-FSO3H at 25°

R	$\Delta \overline{H}_{S,CC1_4},$ kcal/mol	$\Delta H_{\mathbf{R}}$ +, kcal/mol	$\Delta ar{H}_{\mathbf{S}, \mathbf{CH}_3 \mathbf{NO}_2}$
Me Et <i>i</i> -Pr	$\begin{array}{r} +0.96 \pm 0.01 \\ +0.83 \pm 0.03 \\ +0.47 \pm 0.01 \end{array}$	$\begin{array}{r} -21.2 \pm 0.2 \\ -19.4 \pm 0.3 \\ -19.0 \pm 0.3 \end{array}$	$\begin{array}{r} +0.25 \pm 0.02 \\ +0.58 \pm 0.01 \\ +1.01 \pm 0.05 \end{array}$
<i>tert</i> -Bu	$+0.46 \pm 0.02$	$-16.1 \pm 1.2$	$+1.25 \pm 0.02$

strong acids<sup>7</sup> and, except for the ion from pivoyl chloride, are stable in this solvent at 25° as verified by nmr studies. The tert-butyloxocarbonium ion decarbonylates at room temperature.<sup>8</sup> It is stable at  $-60^{\circ}$ , however, and the value reported in Table I was measured at this temperature. The heats of formation of the methyl- and cyclopropyloxocarbonium ions were the same at 25 and  $-60^\circ$ , so the errors introduced by this extrapolation are small.<sup>9</sup> It is obvious from the data in Table I that a large Baker-Nathan order exists. Also shown in Table I are the heats of solution of the acid chlorides in nitromethane. It has recently been shown<sup>10</sup> that Baker-Nathan orders can be generated by cavity effects on transferring a series of solutes from one solvent to a second solvent of higher cohesive energy density. This effect is indeed observed here, but it is too small to explain the observed Baker-Nathan order.

The heats of formation for the methyl-, ethyl-, and isopropyloxocarbonium ions in the series are known in the gas phase.<sup>11</sup> We have selected the data of Murad and Inghram<sup>12</sup> to give a very reliable set of data from the same source. These are presented in column 1 of Table II. To obtain the heat of formation for the *tert*-butyloxocarbonium ion, semiempirical calculations using the MINDO approximation<sup>13,14</sup> were

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