

The *N*-chloro amines are protonated in 30% H₂SO₄ 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.^{3,6}

Steric effects have already been invoked by Minisci and coworkers to explain the increase in ratio of 2-chloro- to 3-chloroheptane (56:29 to 64:23) as R is increased in size from methyl to isobutyl in the R₂NCl.⁶ Ratios of p:s:t were not studied.

Di-*tert*-butylamine was made by conversion of 2-methyl-2-nitropropane⁷ to di-*tert*-butyl nitroxyl¹⁸ and reduction of the nitroxyl by a general method.^{8,9} Dineopentylamine was prepared as described.¹⁰ *tert*-Butyl-*tert*-amylamine was prepared from *tert*-butylamine and 3-chloro-3-methyl-1-butyne.¹¹ 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.³⁻⁶ *N*-Chlorodi-*tert*-butylamine had been made by a similar method.¹² The *N*-chlorodineopentylamine, -dicyclohexylamine, -tetramethylpiperidine, and -*tert*-butyl-*tert*-amylamine do not appear to have been described.

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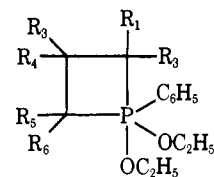
Remarkably Facile Pseudorotation of Four-Membered-Ring Phosphoranes¹

Sir:

Compounds **1** and **2** have been prepared by allowing the appropriate amine to react with diethyl peroxide.² The ¹H nmr spectrum (100 MHz) of **1** at 78° in *o*-dichlorobenzene shows a doublet centered at δ 1.19 (*J*_{PH} = 16 Hz, ring methyl hydrogens), a doublet at 1.32 (*J*_{PH} = 32 Hz, ring methylene hydrogens), a quintet at 3.47 (*J*_{PH} = *J*_{HH} = 7 Hz, methylene hydrogens of the ethoxy groups), and a triplet at 1.10 ppm (*J*_{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

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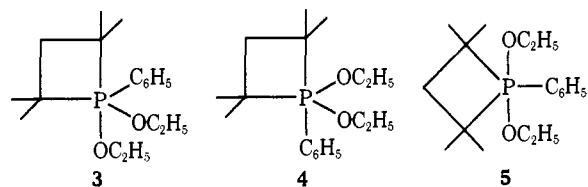
(2) The assignment of structure rests on their method of preparation and their ¹H and ³¹P nmr spectra. The materials as prepared in solution are quite pure and only slightly contaminated with the corresponding oxide.



$$1, R_1 = R_2 = R_5 = R_6 = \text{CH}_3; R_3 = R_4 = \text{H}; \delta(^{31}\text{P}) +22$$

$$2, R_1 = R_2 = \text{H}; R_3 = R_4 = R_5 = R_6 = \text{CH}_3; \delta(^{31}\text{P}) +36$$

the ethoxy group, which have coalesced into a broad, ill-defined absorption. At -20° in toluene-*d*₆ 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 ABM₃X 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° coalescence is observed for the absorptions due to the hydrogens of the ring methyl groups, and at -68° these are now found as two doublets at δ 1.32 (*J*_{PH} = 14 Hz) and 1.06 ppm (*J*_{PH} = 18 Hz). On the basis of the "Muetterties rules"³ and assuming trigonal-bipyramidal structures, such a spectrum arises when pseudorotation^{4,5} 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° 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.³

Similar results were found with **2**. The ¹H nmr spectrum in toluene-*d*₆ at 100° has a doublet centered at δ 1.38 (*J*_{PH} = 19 Hz, R₅ and R₆ methyl group hydrogens), another doublet at 0.76 (*J*_{PH} = 1 Hz, R₃ and R₄ methyl group hydrogens), two quartets at *ca.*

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(5) These results do not provide information on the mechanism of pseudorotation, nor do they exclude highly distorted geometries for the transition states in which there is considerable strain. Reference 4 contains discussions of possible mechanisms for pseudorotation.

3.50 ($J_{\text{PH}} = 8.5$; $J_{\text{HH}} = 7$ Hz, methylene hydrogens of the ethoxy group), and a triplet at 1.12 ppm ($J_{\text{HH}} = 7$ Hz, methyl hydrogens of the ethoxy group). The ring methylene hydrogens are found at δ 2.68 ($J_{\text{PH}} = 11$ Hz). At 75° the spectrum is unchanged except that the absorption due to the methylene hydrogens of the ethoxy groups is now broad and ill defined; at 50° it has sharpened into a many-line pattern. The low-temperature spectra are readily understandable in terms of the pseudorotation processes discussed for 1.

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,^{4a} 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.⁶ On the other hand, pseudorotation has been implicated in various reactions of four-membered-ring phosphorus-containing compounds.^{4e} No experimental evidence has been presented for a diequatorial ring, although it has been suggested.⁷ 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.^{1–5} We wish to report such a comparison for the formation of substituted oxocarbenium ions ($\text{R}-\text{C}^+=\text{O}$) 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 Larsen⁶ the relative heats of formation of several oxo-

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(5) W. M. Schubert, R. B. Murphy, and J. Robins, *J. Org. Chem.*, **35**, 951 (1970), and references therein.

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

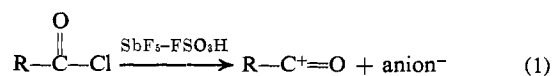


Table I. The oxocarbenium ions are well known in

Table I. Relative Heats of Formation (ΔH_{R^+}) of Acylium Ions in 11.5 mol % $\text{SbF}_5-\text{FSO}_3\text{H}$ at 25°

R	$\Delta \bar{H}_{\text{S}, \text{CCl}_4}$, kcal/mol	ΔH_{R^+} , kcal/mol	$\Delta \bar{H}_{\text{S}, \text{C}_2\text{H}_5\text{NO}_2}$
Me	+0.96 ± 0.01	-21.2 ± 0.2	+0.25 ± 0.02
Et	+0.83 ± 0.03	-19.4 ± 0.3	+0.58 ± 0.01
<i>i</i> -Pr	+0.47 ± 0.01	-19.0 ± 0.3	+1.01 ± 0.05
<i>tert</i> -Bu	+0.46 ± 0.02	-16.1 ± 1.2	+1.25 ± 0.02

strong acids⁷ and, except for the ion from pivoyl chloride, are stable in this solvent at 25° as verified by nmr studies. The *tert*-butyloxocarbenium ion decarbonylates at room temperature.⁸ It is stable at -60°, however, and the value reported in Table I was measured at this temperature. The heats of formation of the methyl- and cyclopropyloxocarbenium ions were the same at 25 and -60°, so the errors introduced by this extrapolation are small.⁹ 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 shown¹⁰ 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 isopropyloxocarbenium ions in the series are known in the gas phase.¹¹ We have selected the data of Murad and Inghram¹² 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*-butyloxocarbenium ion, semiempirical calculations using the MINDO approximation^{13,14} were

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(9) This technique also yields the heats of decarbonylation of the oxocarbenium ions. Studies of this process are in progress and will be the subject of a full paper.

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