Table I

Acid:Cu	% H_2 in H_2–HD mixture[13a]	Mol of gas/ equiv of Cu	Active H^-/Cu[13b]
1.45:1	45.6	0.718	1.045
1.26:1	32.9	0.788	1.047
1.35:1	44.3	0.729	1.052

of 1.05 ± 0.05 indicates a molecular stoichiometry of $H_6Cu_6(PPh_3)_6$.[14]

Although the hydride ligands were not detected directly from the X-ray diffraction study, the following observations can be made. (i) The arrangement of phosphine ligands precludes the possibility of terminal hydride ligands; slight variations of phosphine ligands from truly apical positions [$<(\text{P—Cu}\cdots\text{Cu}_{\text{trans}}) =$ 168.3–177.3°] appear to result from intramolecular phenyl···phenyl repulsions. (ii) There are three symmetric possibilities for hydride ligand locations: (a) bridging hydrides on each edge of the two large triangular faces, (b) bridging hydrides on the six shortest Cu–Cu vectors, or (c) triply bridging hydrides on the six small octahedral faces. Previously it was demonstrated that both bridging hydride ligands (in $[H_2Re_3(CO)_{12}^-]$)[15] and triply bridging hydride ligands (in $H_2Ru_6(CO)_{18}$)[16] cause *expansion* of the metal–metal bond, which would favor structural possibility a. However, there is insufficient evidence to determine positively the correct alternative.

Finally, if one assumes that each phosphine and hydride ligand contributes two electrons to the copper cluster, a noble gas configuration is achieved if each copper atom is linked by a bond of unit bond order to each of its nearest neighbors. It may be noted that the mean *bonding* Cu–Cu distance of ~2.60 Å in the present molecule and ~2.83 Å in $[Cu_8(\text{i-MNT})_6{}^{4-}]$[17] are comparable to values of ~2.60 Å in $[AsEt_3CuI]_4$ and $Cu_4(S_2CNEt_2)_4$, where copper–copper interactions are claimed to be absent.[18]

Acknowledgments. We thank Dr. G. O. Dudek for assisting with the mass spectral studies and Professor R. H. Holm for the use of his Faraday balance for magnetic measurements.

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(14) This formulation is also consistent with the apparent diamagnetism of the compound.

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(19) National Science Foundation Predoctoral Fellow, 1968–1971.

(20) Alfred P. Sloan Fellow, 1968–1970.

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Cation Radicals. III. Sterically Hindered Chlorinating Agents

Sir:

It is the ultimate goal of this effort to develop sterically hindered chlorinating agents that will selectively chlorinate (or oxidize) the terminal methyl of a long alkane chain. Such a reagent would mimic the enzymatic selectivity found in the conversion of stearic acid to 18-hydroxystearric acid[1] and in the terminal oxidation of linear alkanes.[2] Although this goal is still distant, results of sufficient significance have been obtained to warrant a preliminary report.

Table I summarizes the results of chlorination of isopentane and 2,2- and 2,3-dimethylbutanes with agents of increasing steric hindrance. The most unusual result is the chlorination of isopentane with *N*-chloro-di-*tert*-butylamine and *tert*-butyl-*tert*-amylamine (last two entries). In these two cases, the primary hydrogens are attacked 1.7 times faster than the tertiary hydrogen (after correcting for statistical effects). Other examples in the table show secondary hydrogens being attacked faster than tertiary.

Table I. Photochemical Chlorinations with R_2NCl in 30% H_2SO_4 at 15°

	Relative hydrogen reactivities						
	Isopentane[a]			2,2-Dimethylbutane[b]		2,3-Dimethylbutane[c]	
N-Chloro amine	p	s	t	p	s	p	t
Dimethyl	0.32	0.93	1	0.28	1	0.26	1
2,2,6,6-Tetramethylpiperidine	0.26	0.79	1	0.31	1		
Dicyclohexyl	0.40	1.12	1	0.36	1		
Diisopropyl	0.25	0.70	1	0.33	1	0.33	1
Dineopentyl	0.71	2.70	1	0.42	1	0.67	1
Di-*tert*-butyl	1.70	6.00	1	0.48	1		
tert-Butyl-*tert*-amyl	1.72	5.98	1				

[a] The products from primary attack were 1-chloro-2-methylbutane and 1-chloro-3-methylbutane in the statistical ratio 6:3. The products from secondary and tertiary attack were 2-chloro-3-methylbutane and 2-chloro-2-methylbutane, respectively. [b] The products from primary attack were 1-chloro-2,2-dimethylbutane and 1-chloro-3,3-dimethylbutane in the statistical ratio 9:3. The product from secondary attack was 2-chloro-3,3-dimethylbutane. [c] The products from primary and tertiary attack were 1-chloro-2,3-dimethylbutane and 2-chloro-2,3-dimethylbutane, respectively.

These are the first examples in which the normal order of tertiary > secondary > primary is reversed. This reversal is ascribed entirely to steric hindrance in the attacking radicals ($R_2NH\cdot^+$).

The products were analyzed by gas chromatography using a 6-ft 20% SE-30 column. Authentic samples were used for reference in every case.

The reactions were conducted at 15° using a 3% solution of R_2NCl in 30% H_2SO_4, a 5:1 ratio of alkane: R_2NCl, irradiation with a 300-W tungsten lamp, and vigorous stirring. The R_2NCl disappeared (KI test negative) after 1–4 hr. The conditions are similar to those used before with R_2NCl chlorinating agents.[3–5]

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The N-chloro amines are protonated in 30% H_2SO_4 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 R_2NCl.[6] Ratios of p:s:t were not studied.

Di-*tert*-butylamine was made by conversion of 2-methyl-2-nitropropane[7] to di-*tert*-butyl nitroxyl[8] 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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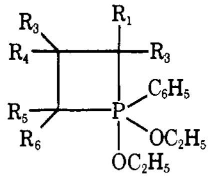
Remarkably Facile Pseudorotation of Four-Membered-Ring Phosphoranes[1]

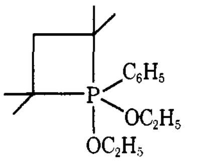
Sir:

Compounds **1** and **2** have been prepared by allowing the appropriate phosphine 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 the ethoxy group, which have coalesced into a broad, ill-defined absorption. At −20° 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_3X 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]

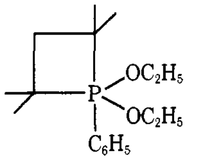


1, $R_1 = R_2 = R_5 = R_6 = CH_3$; $R_3 = R_4 = H$; $\delta(^{31}P)$ +22

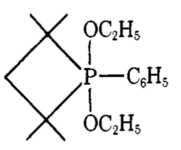
2, $R_1 = R_2 = H$; $R_3 = R_4 = R_5 = R_6 = CH_3$; $\delta(^{31}P)$ +36



3



4



5

Similar results were found with **2**. The ^1H nmr spectrum in toluene-d_8 at 100° has a doublet centered at δ 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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[1] This investigation was supported by Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

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

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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.