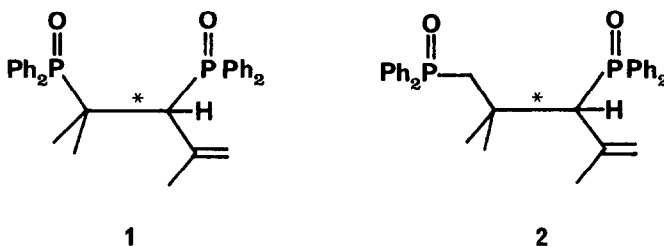# RESTRICTED ROTATION ABOUT CARBON-CARBON

SINGLE BONDS AT ROOM TEMPERATURE

D. Howells and Stuart Warren

University Chemical Laboratory, Lensfield Road,

Cambridge CB2 1EW.

The n.m.r. spectrum of a substituted ethane is normally a weighted average of the three staggered rotamers at room temperature. At lower temperatures, near -100°, equilibration between the rotamers can become slow on the n.m.r. time scale if the substituents are large. Polyhalogenated ethanes are well-known examples[1] and restricted rotation of t-butyl groups attached to crowded atoms has been observed[2].

We have synthesised two phosphine oxides[3] (1,2) each having one carbon-carbon single bond (* in 1,2) bearing five substituents, some very large. These compounds show restricted rotation about that bond: at room temperature their n.m.r. spectra show two sets of signals for each proton in the ratio of roughly 2:1. At higher temperatures the signals coalesce until above 120° the spectrum of (2) is that expected for free rotation (table). The more crowded compound (1) does not show complete coalescence even at 160°. Cooling to 40° restores

the original spectra.

100 mHz n. m. r. spectrum of compound (2)
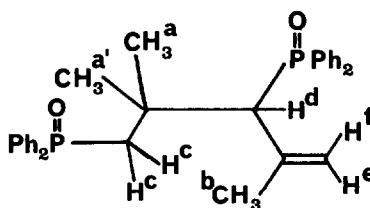
| Protons	Spectrum at 120°, δ	Δδ Hz 25°	Coalescence Temperature T_c
a*	1.10	18	90
a'*	1.17	14	80
b	1.64	13	80
c	2.60	74	120
d*	3.92	96	120+
e*	4.88	5	40
f	5.30	32	100

* These two methyl groups are diastereotopic

♦ Not used to determine ΔG*

A plot of $\log \Delta\delta / T_c$ against $1/T_c$ for (2) gives an unusually reliable value
for the barrier to rotation[4] as we can use five different types of proton
(table). Our value of ΔG* = 19 kcals/mol (80 kJ/mol) made up of ΔH* = 11±2
Kcals/mol (46 kJ/mol) and ΔS* = -21.5±5 e.u. (90 J/deg./mol) is nevertheless
approximate. The enthalpy is similar to that observed for many other compounds
(e.g. 3) and the large barrier to rotation is a result of the entropy term.
This suggests that the chance of the molecule rotating is small, but that when
it does rotate the barrier is about the same as that for other crowded compounds
We take this to mean that rotation is possible only when the CH_2POPh_2, $CMe.=CH_2$,
and $POPh_2$ groups are arranged, perhaps as in (4) to reduce vicinal interactions.

3

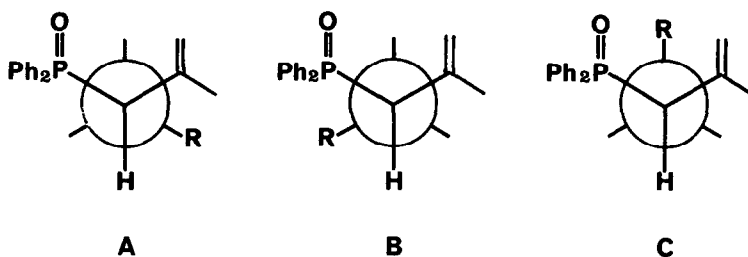$\Delta H^* = 8.4$ kcal/mol

$\Delta S^* = -8.8$ e.u.

4
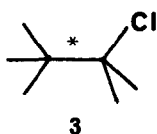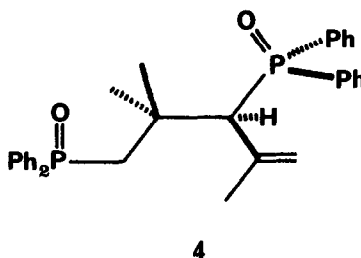
The room temperature spectra of (1) and (2) show that two rotamers are present in a ratio of about 2:1 in each case. We suggest that A is the more populated rotamer, B the less, and that C, in which R is gauche to both the large $POPh_2$ and $CMe=CH_2$ groups, is absent.

A   B   C

Staggered conformations of (1, R=POPh₂ and 2, R=CH₂POPh₂)

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