and methyl iodide (5 ml) was stirred at room temperature (nitrogen) overnight. The excess methyl iodide was removed *in vacuo* and the quaternary salt was washed twice by successive addition and pipetting-out of dry ether.[8] To the original reaction vessel containing the quaternary salt was added 10 ml of ethylmagnesium bromide (25 mmol); the slurry was stirred for 48 hr at room temperature.[9] The resulting homogeneous reaction mixture was poured into 30 ml of cold water, and the ethereal solution was combined with several ether extracts from the aqueous solution and concentrated. The crude dialkyltetrahydro-1,3-oxazine (**3**) was heated at reflux for 1 hr in 40 ml of water containing 5 g of oxalic acid, the aqueous solution was extracted with ether, and the extracts were washed with dilute (5%) sodium bicarbonate, dried (K_2CO_3), and concentrated to give 1.26 g (78%) of the desired ketone.[10]

Acknowledgments. Financial assistance from the National Science Foundation (GP-9592), the Petroleum Research Fund, administered by the American Chemical Society, CIBA, Hoffman-LaRoche, and Warner-Lambert Pharmaceutical Companies is gratefully acknowledged.

[8] Addition of 1.1 equiv of methyl sulfate to an ethereal solution of the dihydro-1,3-oxazine and stirring for 3 hr afforded a quantitative yield of the N-methyl methosulfate salt which was purified only by washing excess methyl sulfate away with ether.

[9] In some cases examined, comparable yields of ketone were realized after a reaction time of 4–18 hr.

[10] Vpc analysis of this crude product as well as the other ketones prepared showed only trace contamination.

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Concerning the P–N Rotational Barriers in Aminophosphines[1]

Sir:

There is considerable current interest in the stereochemistry of aminophosphines.[2] However, there appears to be some confusion in the literature regarding the measurement of P–N rotational barriers by the nmr method. The present communication is concerned with two papers[3,4] where erroneous conclusions have been drawn.

Greenwood, Robinson, and Straughan[3] observed that the 25° pmr spectrum of methylaminobis(trifluoromethyl)phosphine, $CH_3NH \cdot P(CF_3)_2$ (I), consists of two doublets with identical coupling constants (10.3 Hz) but unequal intensities (Figure 1a). This spectral observation was ascribed to the presence of unequal amounts of two rotational isomers. It was further noted that the pmr spectrum collapsed to a doublet at 88°. Together with the signal separation at coalescence (*ca.* 5 Hz) this would imply a P–N rotational barrier of *ca.* 20 kcal/mol in I. Since this is appreciably higher than the usual range of 10–15 kcal/mol for this barrier[2b,4] and since one would expect the two PNCH couplings in I to be different, we have reinvestigated the matter. It now appears that the doublet of doublets in the pmr spectrum of I at ambient temperature is, in fact, due to coupling of the methyl protons to both the phosphorus atom and the imino proton ($J_{PNCH} = 11.5$ Hz; $J_{HNCH} = 4.9$ Hz) and *not to restricted P–N bond rotation.* This conclusion is based on the following experimental observations: (1) the splitting of the four proton lines (in hertz) of I at 44° is the same at 60 MHz and 100 MHz, indicating that the splittings arise from spin-coupling effects; (2) the ^{19}F spectrum of I at ambient temperature consists of a single doublet ($J_{PCF} = 82$ Hz), thus providing no evidence for the presence of rotational isomers; and (3) the pmr spectrum of N-deuterated I, $CH_3ND \cdot P(CF_3)_2$, consists of a doublet at ambient temperature (Figure 1b) with $J_{PNCH} = 11.5$ Hz. The collapse of the four-line pmr spectrum of I to a doublet above 88° is therefore presumably due to exchange of the imino proton with concomitant loss of H–N–C–H coupling. The unsymmetrical appearance of the doublet of doublets, together with the temperature dependence of their relative intensities, can be ascribed to the proximity and temperature sensitivity of the broad N–H resonance.[5]

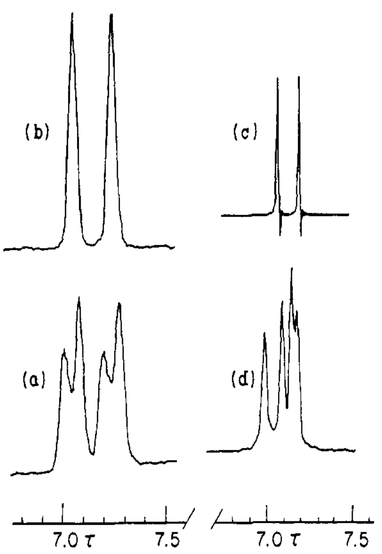


Figure 1. ^1H nmr spectra of aminophosphines: (a) 60-MHz spectrum of $CH_3NH \cdot P(CF_3)_2$ (I) at 44°; (b) 60-MHz spectrum of $CH_3ND \cdot P(CF_3)_2$ at 44°; (c) 100-MHz spectrum of $(CH_3)_2NPCl_2$ (II) in $CHFCl_2$ solution at −50°; (d) 100-MHz spectrum of II in $CHFCl_2$ solution at −120°.

[1] This work was supported by the Air Force Office of Scientific Research, Grant No. AF-AFOSR-1050-67, the National Science Foundation (Grant GP 9518), and the Robert A. Welch Foundation.

[2] (a) M. P. Simonnin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. Fr.*, 3544 (1967); (b) A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, **90**, 4185 (1968); (c) H. Goldwhite and D. G. Roswell, *Chem. Commun.*, 713 (1969); (d) W. E. Slinkard and D. W. Meek, *Inorg. Chem.*, **8**, 1811 (1969).

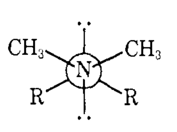
[3] N. N. Greenwood, B. H. Robinson, and B. P. Straughan, *J. Chem. Soc., A*, 230 (1968).

[4] D. Imbery and H. Friebolin, *Z. Naturforsch.*, **23b**, 759 (1968).

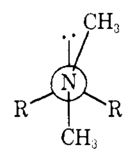
[5] The N–H resonance occurs at 0.43 ppm upfield from the methyl signals. The HNCH coupling constant is therefore of the same order of magnitude as the chemical-shift separation and leads to a relative enhancement of the high-field components of the doublet of doublets. The distortion is less evident in the spectra of I at 100 MHz owing to the increase in δ/J. The width of the NH signal can be ascribed to coupling with the methyl group and phosphorus atom together with the quadrupolar effect of the nitrogen nucleus.

Below −120° the pmr doublet of N-deuterated I does indeed split into a pair of doublets of unequal intensity (see below). Owing to overlapping of the lines, it was not possible to measure the P–N rotational barrier exactly, but it is of similar magnitude to the barrier in the dimethylamino analog (III), *i.e.*, *ca.* 8.5 kcal/mol (see below).

Imbery and Friebolin[4] noted that the methyl groups of symmetrically substituted aminophosphines of the type $(CH_3)_2NPR_2(R = Cl, C_6H_5)$ remain equivalent down to −80° and concluded that these compounds freeze into the symmetrical conformation, **1**. However, our recent studies of symmetrically substituted aminophosphines such as $(CH_3)_2NPCl_2$ (II) and $(CH_3)_2NP(CF_3)_2$ (III) at temperatures below −100° indicate that this is not the case. Thus, the ^1H spectrum of II (in $CHFCl_2$) which consists of a doublet at ambient temperature with $J_{PNCH} = 12.5$ Hz (Figure 1c) separated into a pair of doublets below −120° with $J_{PNCH} = 19.2$ and $J_{PNCH'} = 4.9$ Hz (Figure 1d). Similarly, the spectrum of III, in CF_2Cl_2 solution, exhibited anisochronous[6] methyl resonances below −120° with $J_{PNCH} \approx 14$ and $J_{PNCH'} \approx 4$ Hz. The P–N rotational barriers were determined to be $\Delta F_{-113^\circ}{}^{\ddagger} = 8.4$ and $\Delta F_{-101^\circ}{}^{\ddagger} = 9.0$ kcal/mol for II and III, respectively.[7] The observation of anisochronous methyl groups in both II and III below −120° indicates that both molecules adopt a *gauche* conformation, **2**, at low temperature. Note that the nitrogen atom in **2** is represented as planar. This would conform to the recent X-ray structure determination on $(CH_3)_2NPF_2$ which indicates that the nitrogen atom is trigonal and the CNC plane bisects the FPF angle.[8] Even if the nitrogen atoms are not completely planar in II or III, rapid nitrogen inversion would render them planar on a time-average basis.



1



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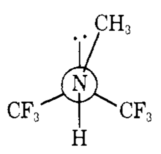

3

The problem remains of deciding how the two different P–N–C–H couplings should be assigned in relation to the two methyl environments shown in **2**. The pmr spectrum of N-deuterated I (*i.e.*, $CH_3ND \cdot P(CF_3)_2$), in CF_2Cl_2 solution, indicates the presence of two rotational isomers below −120° with $J_{PNCH} = 13.9$ Hz and $J_{PNCH'} \approx 4$ Hz. The ratio of the intensities of the doublets was *ca.* 4:1, with the more abundant rotamer having the larger coupling constant. Steric considerations suggest that the more abundant isomer would be **3**; hence the larger P–N–C–H coupling in aminophosphines may be ascribed to the methyl group *cis* to the phosphorus lone-pair electrons.

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[6] K. Mislow and M. Raban, *Topics Stereochem.*, **1**, 23 (1967).

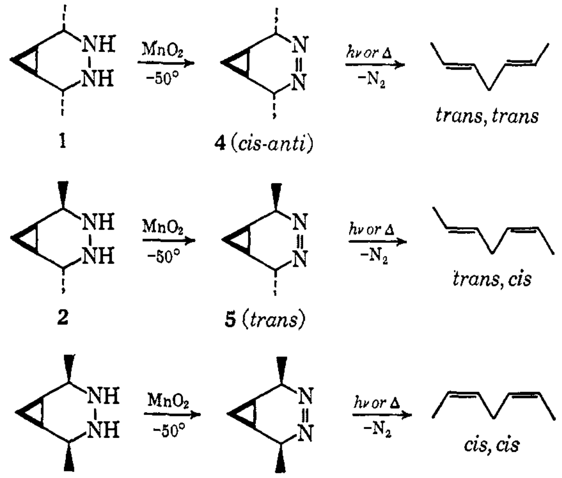
[7] In II and III the exchange rates near the coalescence temperature were obtained using a many site nmr program of the type described by Saunders [M. Saunders, *Tetrahedron Lett.*, 1699 (1963)]. The $\Delta F^{\ddagger}$ values were calculated from the Eyring equation in the usual manner. In the case of III the barrier was also determined from ^{31}P irradiated spectra to be $\Delta F_{-101^\circ}{}^{\ddagger} = 8.9$ kcal/mol, using a two-site program based on the equations of Gutowsky and Holm [H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956)].

[8] E. D. Morris, Jr., and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

Nonreversal of Stereochemistry in the Photochemical Counterpart of a Thermal Retrograde Cycloaddition[1]

Sir:

Simple orbital symmetry considerations[2] predict that the selection rule for an "allowed" thermal cycloaddition (an odd number of suprafacial (s) two-electron reaction elements) will be reversed for the photochemical counterpart (even number of s elements), and several experiments have confirmed the expected change in stereochemistry.[3] We now find a clear violation of this pattern in the series of bicyclic azo compounds **4**, **5**, and **6**, which undergo photochemical retrograde homo-Diels–Alder reactions with *disrotation* of the methyl-bearing carbons, the *same stereochemistry* previously observed[4] in the thermal decompositions.



1

4 (*cis-anti*)

trans, trans

2

5 (*trans*)

trans, cis

3

6 (*cis-syn*)

cis, cis

Ethereal solutions of these azo compounds,[4] prepared by oxidation of the hydrazo precursors **1**, **2**, and **3**, are stable for days at −70°. They show ultraviolet absorption characteristic of the n,π* transition of cyclic azo compounds[5] (λ_{max} 384, 387, and 390 mμ, respectively (ε ~100)).[6] At higher temperature the azo absorption smoothly disappears ($t_{1/2}$ ~ 30 min for compound **4** at −10°). The decomposition also can be monitored by the nuclear magnetic resonance spectrum,

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[1] The support of this work by grants from the National Science Foundation (GP-11017X) and the Petroleum Research Fund (Type C), administered by the American Chemical Society, is gratefully acknowledged.

[2] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); *Angew. Chem. Intern. Ed. Engl.*, **8**, 781 (1969).

[3] G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

[4] J. A. Berson and S. S. Olin, *J. Am. Chem. Soc.*, **91**, 777 (1969).

[5] *Cf.* P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968), for closely related models.

[6] We are indebted to Professor R. C. West and his research group for making their low-temperature spectrophotometric apparatus available to us.