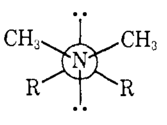
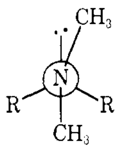
Below −120° the pmr doublet of N-deuterated I does indeed split into a pair of doublets of unequal intensity (see below). Owing to overlapping of the lines, it was not possible to measure the P–N rotational barrier exactly, but it is of similar magnitude to the barrier in the dimethylamino analog (III),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

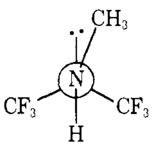
Imbery and Friebolin[4] noted that the methyl groups of symmetrically substituted aminophosphines of the type $(CH_3)_2NPR_2$(R = Cl, C_6H_5) remain equivalent down to −80° and concluded that these compounds freeze into the symmetrical conformation, **1**. However, our recent studies of symmetrically 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 $J_{\text{PNCH}'}$ = 4.9 Hz (Figure 1d). Similarly, the spectrum of III, in CF_2Cl_2 solution, exhibited anisochronous[6] methyl resonances below −120° with $J_{\text{PNCH}} \approx 14$ and $J_{\text{PNCH}'} \approx 4$ 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



2



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 $J_{\text{PNCH}'} \approx 4$ 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.

Acknowledgment. The authors are grateful to Mr. J. R. Schweiger for preparing the sample of $(CF_3)_2PCl$ used in some of the above syntheses.

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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).

(9) Robert A. Welch Postdoctoral Fellow.

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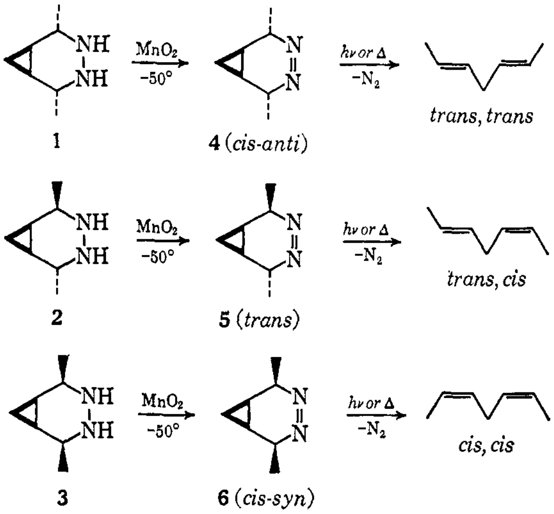
Received November 1, 1969

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.



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] ($\lambda_{\max}$ 384, 387, and 390 mμ, respectively (ε ∼100)).[6] At higher temperature the azo absorption smoothly disappears ($t_{1/2} \sim 30$ 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).

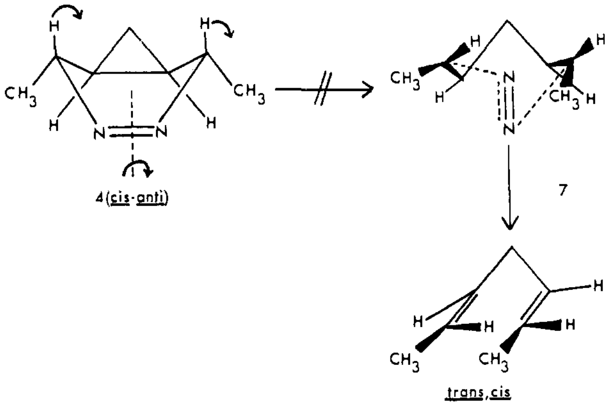
(5) *Cf.* P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968), for closely related models.

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

which incidentally fails to show any evidence of CIDNP signals[7] (under the admittedly narrow range of conditions so far examined). The products (>99.5% stereospecific) are the previously reported[4] 2,5-heptadienes: *trans,trans* from **4**, *trans,cis* from **5**, and *cis,cis* from **6**.

The course of irradiation of the azo compounds at −70° with a Pyrex-filtered 450-W Hanovia mercury lamp is followed spectrophotometrically (solution temperature monitored with internal thermocouple). After disappearance of the azo chromophore, the diene product is isolated with >99.5% stereospecificity. Again, the results are **4** → *trans,trans*, **5** → *trans,cis, and* **6** → *cis,cis*.

One strong *extrasymmetric*[8] factor that probably is at work in both the thermal and photochemical reactions is that which opposes the *trans* expulsion of nitrogen. This path has a large twisting component (*cf.* **4** → **7**) and results in *conrotation* of the methyl-bearing carbons, an odd-s process thermally "allowed" by the simple orbital symmetry rules. Presumably, this does not occur in the thermal reaction because it requires substantial disruption of the nonreacting azo N–N π bond. It may be that, in the excited state, this extrasymmetric prohibition is overcome (for example, by *cis* → *trans* isomerization of the azo link in the π,π* state). The photochemically "allowed" even-s paths from electronically excited *trans*-azo compound then would lead by *disrotation* to just those products observed. The same products would result from internal conversion of an electronically excited state to a vibrationally excited *cis*-azo ground state followed by odd-s "thermal" reaction of the latter.



Detailed correlation diagrams, which will appear in a full paper, suggest that the observations may have a more complex origin. For the present, we note that the results of such diagrams depend upon the ordering of the energy levels and upon whether the photodecomposition occurs in the n_{+},π^* or π,π^* state. Moreover, the diagrams imply two speculative but intriguing possibilities. If reaction is from n_{+},π^*, it may be facilitated by a symmetry-allowed crossing to ground state along the reaction coordinate.[9] If reaction is from π,π^* triplet (perhaps formed by internal conversion from n,π^* singlet[10]), a crude energy calculation suggests that even though photochemical promotion of azo compound to its $^1(n,\pi^*)$ state provides only about 3.2 eV of excess energy, the exothermicity of the decomposition may suffice to permit formation of the lowest triplet of nitrogen, which is 6.16 eV above ground.[11,12] The second possibility is subject to experimental test.

Although a choice among these and other possible explanations[13] must await a more complete study, the present results already illustrate the inadequacy of predictions based solely upon the symmetry properties of the reacting bond orbitals (*i.e.*, simple orbital symmetry rules). They emphasize the need for caution in the theoretical analysis of concerted reactions involving heteroatoms.

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(7) *Cf.* H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and references cited there.

(8) We suggest this term as a general one for those influences other than orbital sign relationships (*e.g.*, minimum distortion, orbital overlap, steric strain, proximity of reactive sites, etc.) which play a role in determining the course of reaction.

(9) For a similar crossing postulated on a more quantitative theoretical basis, see W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968); *J. Am. Chem. Soc.*, **91**, 6042 (1969).

(10) (a) *Cf.* I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *ibid.*, **91**, 1220 (1969). (b) Acetophenone sensitizes the photolysis of **4**, and piperylene (1.0 *M*) does not quench the direct photodecomposition of **5**. The product dienes are again *trans,trans* and *trans,cis*, respectively.

(11) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950, p 449.

(12) *Cf.* A. Ganzow, M. Z. Hoffman, N. N. Lichtin, and S. K. Wason, *J. Phys. Chem.*, **72**, 3749 (1968).

(13) (a) For example, the corresponding diazenes[13b] might be photointermediates. More detailed correlation diagrams now indicate that these could give the observed products in thermally *or* photochemically allowed processes. (b) D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1335 (1966).

(14) This investigation was supported in part by National Institutes of Health Postdoctoral Fellowship No. 2FO2CA25233-02 from the National Cancer Institute.

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Received October 27, 1969

π-Cyclobutadieneiron Ions in the Mass Spectrometer. Evidence by Labeling

Sir:

The mass spectra of C_4 compounds must be reconciled with carbon-skeleton scrambling which is nearly complete in many instances; for example, ^{13}C-labeled butene ions show a statistical loss of methyl containing each carbon atom of the chain when the $C_3H_5^+$ is produced, an observation which can be reconciled by an insertion mechanism whose rate is at least competitive with fragmentation.[1] Similarly, scrambling studies of phenylated compounds producing $C_4Ar_4\cdot^+$ have in the past always shown almost complete scrambling before this ion halves to give $C_2Ar_2\cdot^+$.[2] The latter data are consistent with the production of a tetrahedral symmetry in $C_4Ar_4\cdot^+$ before it fragments, but not with mechanisms where scrambling in the molecular ion itself occurs;[3] again, the results may be explained by some sort of insertion mechanism which produces nearly statistical scrambling before fragmentation.

Our interest in the structures of ligands originally π bonded to transition metals in organometallic mass spectra[4,5] suggested experiments to determine whether

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(1) G. G. Meisels, J. Y. Park, and B. G. Giesser, *J. Amer. Chem. Soc.*, **91**, 1555 (1969).

(2) M. M. Bursey and T. A. Elwood, *ibid.*, **91**, 3812 (1969), and references contained therein.

(3) M. K. Hoffman, *et al.*, submitted for publication.

(4) D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **90**, 973 (1968), and references contained therein.