

Hückel π systems which deviate drastically from planarity,³⁰ so this proposal deserves to be taken seriously. Nevertheless, it is intriguing to consider whether or not the racemization of helicenes might be related mechanistically to the automerization of naphthalene and other benzenoid hydrocarbons. Experimental data in this whole area remain scarce.

Overview and Outlook

Many types of thermal rearrangements of aromatic compounds have been observed. Some lead to a permanent change in the molecular skeleton, e.g., the isomerization of azulene to naphthalene and the electrocyclization of heavily substituted benzene rings to the corresponding Dewar benzenes. Others leave the carbon framework unaltered but interchange the atoms among various positions. Such "degenerate rearrangements" or "automerizations" have been revealed by ¹³C labeling in azulene, naphthalene, and pyrene and have been proposed also to account for thermal interconversions of several benzene derivatives. Stereochemical thermal rearrangements are exemplified by the racemization of optically active helicenes at high temperatures. The only major class still without representation is the uncatalyzed thermal isomerization of one fully aromatic benzenoid hydrocarbon to another (e.g., anthracene \rightarrow phenanthrene), even though such transformations should be thermodynamically favorable.

As one would expect for reactions which disrupt aromaticity, many of these thermal rearrangements are impeded by extraordinarily large energy barriers and occur only at very high temperatures, e.g., 1000-1100 °C (contact time = several seconds). Despite all the effort devoted to mechanistic study of these unusual reactions, however, not a single one can be considered fully understood at the present time. The isomerization of azulene to naphthalene appears to occur via one or more unimolecular pathways in competition with various radical processes, and similar mechanistic com-

(30) (a) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* 1981, 102, 5216-20 and references cited therein. (b) Misumi, S.; Otsubo, T. *Acc. Chem. Res.* 1978, 11, 251-6 and references cited therein.

plexities may exist in other cases as well.

Several lines of further work ought to advance our understanding of these reactions.

(1) Infrared lasers provide an alternate means of effecting rearrangement. With this form of vibrational excitation, any complications due to wall effects should be minimized. Azulene rearranges cleanly to naphthalene when irradiated with a CO₂ laser, and ¹³C-labeling experiments have been initiated.¹⁴

(2) Multiple-labeling studies will help to trace more precisely the course of movement of various atoms.

(3) It should be possible to reduce the aromaticity of the rings suffering rearrangement, and thereby lessen the temperature required for isomerization, by strategic incorporation of additional fused benzene rings.²⁵ For example, automerization in the terminal ring of anthracene might be easier than automerization in naphthalene, despite the failure of anthracene to suffer skeletal rearrangement to phenanthrene. Benz[f]-azulene rearranges to phenanthrene *much* more rapidly than azulene rearranges to naphthalene.^{10a} Under milder conditions the mechanistic morass might simplify.

(4) The shortage of good kinetic studies must be rectified.

The past decade has seen thermal rearrangements of aromatic compounds grow from an isolated curiosity in azulene chemistry to a well-established area of organized research. Much remains to be learned, and the years ahead should bring new examples of such reactions as well as greater insight into the mechanisms they follow.

It is a pleasure to express my gratitude to the students who have carried out much of the work described here, particularly G. K. Agopian, J. R. Highsmith, M. A. Kirms, and D. A. Utterback. Recent work on the laser-induced rearrangements of azulene has been conducted in collaboration with Professor B. Earl. Conversations and correspondence with R. Alder, C. Wenstrup, and F. Bickelhaupt have been most valuable, and financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the National Institutes of Health, and the University of Nevada Research Advisory Board has been indispensable.

The λ^5 -Phosphorins

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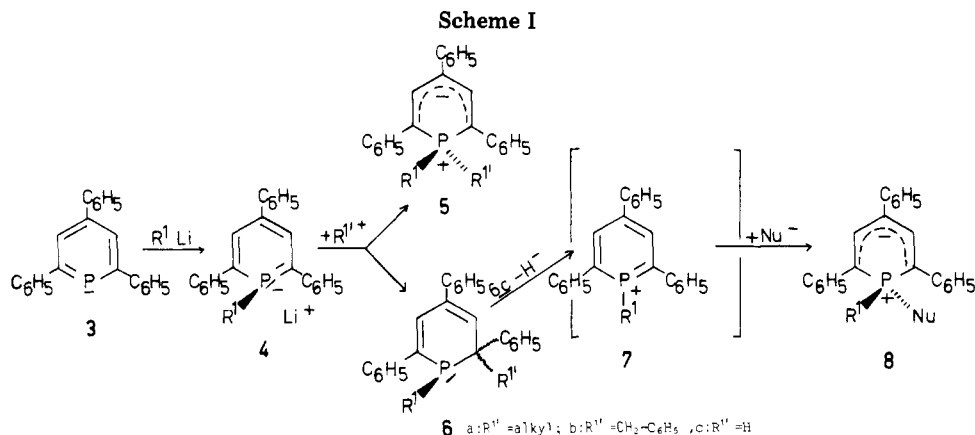
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The phenomenon of aromaticity has intrigued chemists ever since the days of Kekulé.¹ Among the many questions that have arisen is to what extent heterocyclic analogues of benzene, compounds containing one or

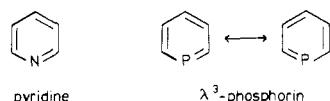
Karl Dimroth was born in Bad Tölz, Bavaria, in 1910. After university studies in München and Würzburg, he took his Ph.D. at Göttingen under A. Windaus and also did his Habilitationsarbeit at Göttingen. In 1944 he became Dozent in Marburg and in 1949 Professor Extraordinarius in Tübingen. In 1949 he returned to Marburg, first as Professor of Physiological Chemistry and since 1952 as Director of the Chemical Institute. He became Professor Emeritus in 1979.

more heteroatoms in place of the carbon atoms of benzene, are aromatic. For many such substances, structures with alternating single and double bonds around the ring can be written according to common concepts of valence. But do they actually have aromatic properties?

(1) (a) G. M. Badger, "Aromatic Character and Aromaticity", Cambridge University Press, New York, 1969; (b) P. J. Garratt, "Aromaticity", McGraw-Hill, London 1971; (c) G. Binch, *Naturwissenschaften*, 60, 369 (1973); (d) G. Maier, *Chem. Unserer Zeit*, 9, 131 (1975).

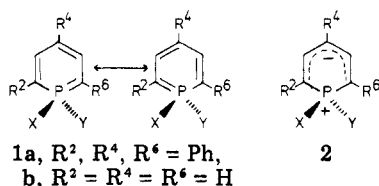


Of the group 5 heterobenzenes, pyridine, like benzene, is fully aromatic. The corresponding phosphorus



compound, λ^3 -phosphorin, is a relative newcomer to the chemical stage. The 2,4,6-triphenyl derivative was first synthesized by Märkl in 1966.² In his synthesis, he made use of a method similar to one we had used 2 years earlier in our synthesis of phosphamethincyanines. The latter were the first stable compounds containing a two-coordinated phosphorus atom and a delocalized C=P double bond.³ In 1971, Ashe developed an ingenious synthesis, not only of λ^3 -phosphorin itself, but also of its group 5 higher analogues with As, Sb, or Bi in place of P. The physical properties of λ^3 -phosphorin and its arsenic analogue, especially their NMR spectra, showed them to be truly "aromatic", with 6π delocalization around the ring just as in pyridine.⁴

Although the chemistry of organic phosphorus compounds is in some respects similar to that of their nitrogen analogues, there are major differences which arise because of the lower electronegativity and the availability of d orbitals in the valence electron shell of phosphorus. Phosphorus forms numerous compounds—the phosphoranes—with five covalent bonds to phosphorus, but all attempts at synthesizing pentavalent nitrogen compounds have failed. Knowing this, we posed to ourselves the following questions: can λ^5 -phosphorins (of generalized structure 1 or 2) be prepared from λ^3 -phosphorins, and if so,



(2) G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **5**, 846 (1966). For reviews, see (a) G. Märkl, *Lect. Heterocycl. Chem.*, **1**, 69 (1972); (b) G. Märkl, *Phosphorus Sulfur*, **3**, 77 (1977); (c) K. Dimroth, *Fortschr. Chem. Forsch.*, **38**, 1 (1973).

(3) K. Dimroth and P. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **3**, 384 (1964); *Chem. Ber.*, **99**, 1325 (1966). For reviews, see (a) P. Jutzi, *Angew. Chem., Int. Ed. Engl.*, **14**, 232 (1975); (b) N. I. Svetaov-Shilovskii, R. G. Bobkova, N. P. Ignatova, and N. N. Mol'nikov, *Usp. Khim.*, **46**, 967 (1977); *Russ. Chem. Rev.*, **46**, 514 (1977); (c) E. Fluck, *Top. Phosphorus Chem.*, **10**, 193 (1980).

(4) (a) A. J. Ashe III, *J. Am. Chem. Soc.*, **93**, 3293 (1971); (b) *Acc. Chem. Res.*, **11**, 153 (1978).

would they show "aromatic" behavior?

As described in this Account, the answers to these questions are, briefly, *yes* and *no*. In the process of answering these questions, we experienced both the fun of discovery and the satisfaction of answering significant questions definitively.

Syntheses of λ^5 -Phosphorins from λ^3 -Phosphorins

Addition of carbanions to the phosphorus of 2,4,6-triphenyl- λ^3 -phosphorin (3) leads to a λ^4 -phosphorin anion, 4^{5a} which can be isolated as a stable 1,2,4,6-tetraphenyl- λ^4 -phosphorin tetra-*n*-butylammonium salt.^{5b} The λ^4 -phosphorin anions 4 are ambident and easily add electrophiles. The outcome of the reaction depends on the nature of the electrophile, the substituents on the λ^3 -phosphorin, and the reaction conditions: addition to phosphorus affords λ^5 -phosphorins 5, whereas addition at C-2 gives 1,2-dihydrophosphorin derivatives 6a,b. Some of these, e.g., the benzyl derivative 6b, can be thermally rearranged (180 °C) to give the thermodynamically more stable λ^5 -phosphorin 5 (R¹ = R^{1'} = CH₂-C₆H₅) which at 220 °C eliminates the two benzyl groups, giving the λ^3 -phosphorin 3.^{5c}

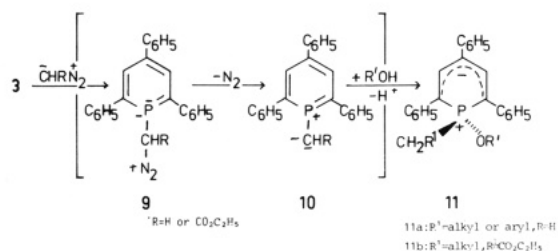
Hydrogen adds to carbon 6, affording 6c.^{6a} Hydride abstraction using triphenylcarbonium salts, mercuric acetate, or 2,4,6-triphenylphenoxy probably gives rise to an extremely reactive intermediate, the λ^4 -phosphorin cation 7. This reacts immediately with any available nucleophile (Nu), giving various substituted λ^5 -phosphorins 8^{6a,b} (Scheme I).

An interesting variation of this synthesis was realized in the addition of diazoalkanes:^{7a,b} with diazomethane and an alcohol or phenol, 3 gives a variety of mixed 1-alkoxy- or 1-phenoxy-1-methyl- λ^5 -phosphorins. As the rate is faster with the more basic diazoalkanes, it is probable that the anionic carbon first adds to the phosphorus, affording a betaine (9). This, on elimination of nitrogen, may be converted to an ylide (10). On addition of an alcohol or phenol this is immediately trapped, resulting in the formation of 11a. The same reaction with ethyl diazoacetate (R = CO₂Et), leads to

(5) (a) G. Märkl, E. Lieb, and A. Merz, *Angew. Chem., Int. Ed. Engl.*, **6**, 86 (1967); (b) G. Märkl and C. Martin, *ibid.*, **13**, 408 (1974); (c) G. Märkl and A. Merz, *Tetrahedron Lett.*, 1215 (1971).

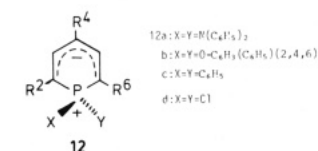
(6) (a) G. Märkl and A. Merz, *Tetrahedron Lett.*, 1231 (1969); (b) G. Märkl A. Merz, and H. Rausch, *ibid.*, 2989 (1971).

(7) (a) P. Kieselack and K. Dimroth, *Angew. Chem., Int. Ed. Engl.*, **13**, 148 (1974); (b) *Chem. Ber.*, **108**, 3671 (1975); (c) P. Kieselack, C. Helland, and K. Dimroth, *ibid.*, **108**, 3656 (1975).

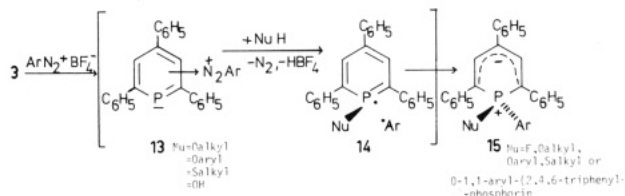


11b which on reduction with lithium aluminum hydride gives the corresponding alcohol in quantitative yield without any change in the λ^5 -phosphorin system. Phenyl azide in the presence of methanol affords 1-methoxy-1-phenylamino-2,4,6-triphenyl- λ^5 -phosphorin.^{7c}

Addition of radicals to the phosphorus atom in λ^3 -phosphorins also leads to λ^5 -phosphorins. The yields are usually excellent. Some examples are the addition of diphenylaminyl (giving 12a),⁸ of 2,4,6-triphenylphenoxy (giving 12b),⁸ of phenyl (from diphenylmercury at 240 °C) (giving 12c),⁹ and, most important, of chlorine under irradiation (giving 12d).¹⁰



When 2,4,6-trisubstituted λ^3 -phosphorins are treated in benzene with aryldiazonium tetrafluoroborates in the presence of alcohols, phenols, or water, nitrogen is evolved, and 1-aryl, 1-OR- λ^5 -phosphorins (15) are produced in yields of 30–85%. In contrast, in dimethoxyethane as solvent, 1-aryl-1-fluoro- λ^5 -phosphorins are formed; the fluoride ion from BF_4^- adds to the phosphorus atom.¹¹ The mechanism of this reaction is not fully understood. It could be that a donor-acceptor complex (13) is first formed in which the phosphorus

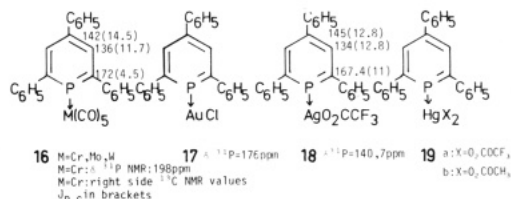


atom is so positive that in the rate-determining step it adds the strongest nucleophile available. In the following step, nitrogen, the λ^4 -phosphorin radical (14) and the aryl radical are probably formed, the latter combining to give the 1-arylated λ^5 -phosphorin derivative (15). There is some evidence in support of the above mechanism. In the presence of thiols, 1-fluoro-1-mercapto- λ^5 -phosphorins or 1,1-dimercapto-phosphorins are formed at the expense of 1-aryl- λ^5 -phosphorins. This probably occurs via a hydrogen transfer between the aryl radical and the thiol, giving rise to a thiyl radical which then combines with the λ^4 -phosphorin radical. The possibility that a λ^4 -

- (8) K. Dimroth, A. Hettche, W. Städe, and F. W. Steuber, *Angew. Chem., Int. Ed. Engl.*, **8**, 770 (1969).
 (9) G. Märkl and A. Merz, *Tetrahedron Lett.*, 1231 (1969).
 (10) H. Kanter and K. Dimroth, *Angew. Chem., Int. Ed. Engl.*, **11**, 1090 (1972), and references therein.
 (11) O. Schaffer and K. Dimroth, *Angew. Chem., Int. Ed. Engl.*, **11**, 1091 (1972).

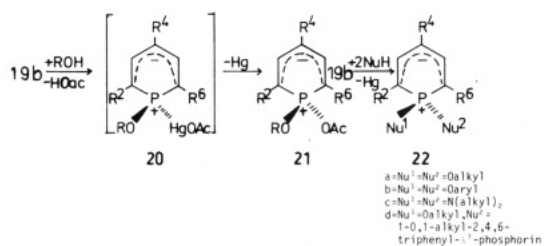
phosphorin cation (7) is an intermediate has been excluded because in the presence of methanol and thiols no 1,1-dimethoxyphosphorins, but only 1-methoxy-1-mercapto- λ^5 -phosphorins, were observed.¹²

Sequential Addition of Electrophiles and Nucleophiles. Contrary to pyridine and its derivatives, λ^3 -phosphorins do not add protons or alkyl cations. According to Schweig¹³ the unpaired electron pair at phosphorus is very diffuse and does not, therefore, bind "hard" electrophiles. In contrast, "soft" Lewis acids react with the P atom, giving λ^4 -phosphorin complexes with a P-metal bond. Nöth¹⁴ isolated the first crystalline Cr(Mo,W)-pentacarbonyl-2,4,6-triphenyl- λ^4 -phosphorins, 16a–c. The presence of a P–Cr bond was



established by X-ray crystallography (P–Cr bond length 237 pm; angle of 8° between ring plane and Cr).¹⁵ The ³¹P, ¹H, and ¹³C NMR data for 16–19 are not very different from those of λ^3 -phosphorins, except for the much smaller values of ¹J_{P–C} in the former.¹⁶ Many such addition products have been reported,^{17a–c} some of which were not subjected to further examination.¹⁸

When mercuric diacetate reacts with λ^3 -phosphorin derivatives, the complexes 19b exist only in equilibrium with λ^3 -phosphorins. But they easily add nucleophiles such as alcohols, phenols,¹⁹ and primary or secondary amines²⁰ at room temperature to give 1,1-disubstituted λ^5 -phosphorins 22 in nearly quantitative yields. Mercury(II) and silver(I) are reduced to the free metals, in the latter case with concomitant disproportionation to the λ^5 - and λ^3 -phosphorin derivatives. Reaction with mercuric diacetate may take place according to the path shown between 19 and 22. With 1 mol of alcohol the

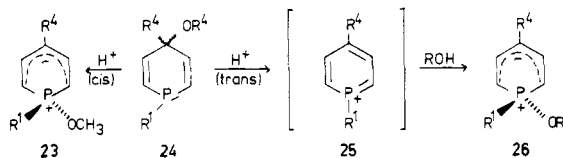


mixed compound 20 is probably first produced; it then rearranges to 21. An excess of nucleophile gives 22a–c whereas aqueous alcohols give the mixed P–O–P products of 22d.

- (12) O. Schaffer and K. Dimroth, *Chem. Ber.*, **108**, 3271, 3281 (1975).
 (13) H. Oehling and A. Schweig, *Phosphorus*, **1**, 203 (1972).
 (14) J. Deberitz and H. Nöth, *J. Organomet. Chem.*, **49**, 453 (1973).
 (15) H. Vahrenkamp and H. Nöth, *Chem. Ber.*, **106**, 2227 (1973).
 (16) K. Dimroth and S. Berger, unpublished results.
 (17) (a) 21: K. C. Dash, J. Eberlein, and H. Schmidbaur, *Synth. Inorg. Metallorg. Chem.*, 375 (1973); (b) 22 and 23: H. Kanter and K. Dimroth, *Tetrahedron Lett.*, 541 (1975); (c) K. C. Nainan and C. T. Sears, *J. Organomet. Chem.*, **148**, C31 (1978).
 (18) M. Frazer, D. G. Holah, A. N. Hughes, and B. C. Hui, *J. Heterocycl. Chem.*, **9**, 1457 (1972).
 (19) K. Dimroth and W. Städe, *Angew. Chem., Int. Ed. Engl.*, **7**, 881 (1968), and ref 4.
 (20) A. Hettche and K. Dimroth, *Tetrahedron Lett.*, 829 (1972).

Different types of λ^5 -phosphorins, including compounds with a 5-7-membered spiro ring at phosphorus, can be prepared using 1,2-, 1,3- or 1,4-diols, dithiols, diamines, or amino alcohols.

Rearrangement of 1,4-Dihydrophosphorins. Another synthesis of 1- R^1 -1-alkoxy-4- R^4 - λ^5 -phosphorins, by an acid rearrangement of 1- R^1 -4- R^4 -ethoxy-1,4-dihydrophosphorins **24**, was recently reported by Märkl.²¹

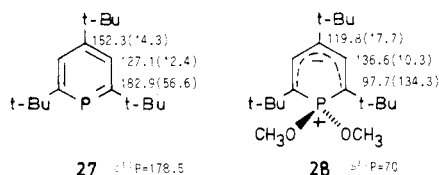


Whereas the compound **24**, where OR^4 and the non-bonding electron pair at the phosphorus are at the same side of the ring, leads to **23** via an intramolecular rearrangement, the other stereoisomer gives **26**. The latter probably arises via an intermediate of the type **25**.

Physical Properties of λ^5 -Phosphorins

X-ray analysis^{22a-c} of λ^3 - and λ^5 -phosphorins with various substituents at the phosphorus shows structures that are, strangely enough, very similar: in both types the phosphorin ring is essentially planar with P-C(2 or 6) distances (172–176 pm) which are almost equal although significantly shorter than those of phosphorus-carbon single bonds (~181 pm). In λ^5 -phosphorins containing a tetrahedral phosphorus, the C-2-P-C-6 angle is somewhat larger (105–108°) than in the λ^3 -phosphorins (102–103°). However, since shortening of the P-C bond can be caused not only by orbital overlap but also by ionic attraction,²³ information concerning the nature of the P-C bonding cannot be obtained in this way.

NMR Spectra. The best insight into the electronic structure of λ^5 -phosphorins is given by the NMR data. Jakobsen et al.²⁴ first compared the ¹³C NMR spectra of 2,4,6-tri-*tert*-butyl- λ^3 -phosphorin (**27**) with its 1,1-dimethoxy- λ^5 -phosphorin derivative (**28**). The large



¹³C NMR chemical shift values for the ring carbon atoms, J_{P-C} in brackets

high-field shifts, particularly of carbons 2 and 6 as well as carbon 4, and the large difference in the J_{P-C} coupling constants of the λ^5 -phosphorin derivative **28** indicate clearly the ylide character of the latter.²⁵

(21) G. Märkl, H. Baier, R. Liebl, and D. S. Stephenson, *Liebigs Ann. Chem.*, 870 (1981).

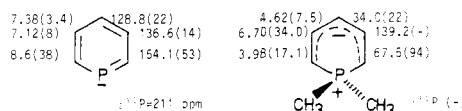
(22) (a) J. C. Bart and J. J. Daly, *Angew. Chem., Int. Ed. Engl.*, 7, 811 (1968); (b) W. Fischer, E. Hellner, A. Chatzidakis, and K. Dimroth, *Tetrahedron Lett.*, 6627 (1968); (c) J. J. Daly, *J. Chem. Soc. A*, 1832 (1970); (d) U. Thewalt, *Angew. Chem., Int. Ed. Engl.*, 8, 769 (1969); (e) U. Thewalt, Ch. Bugg, and A. Hettche, *Angew. Chem., Int. Ed. Engl.*, 9, 898 (1970).

(23) M.-W. Whangbo, S. Wolfe, and F. Bernardi, *Can. J. Chem.*, 53, 3040 (1975).

(24) T. Bundgaard, H. J. Jakobsen, K. Dimroth, and H. H. Pohl, *Tetrahedron Lett.*, 3179 (1974).

(25) See, e.g., (a) G. A. Gray, *J. Am. Chem. Soc.*, 95, 7736 (1973); (b) H. Schmidbauer, W. Buchner, and D. Scheutzow, *Chem. Ber.*, 106, 1251 (1973); (c) K. O. A. Starzewski and H. T. Dieck, *Phosphorus*, 6, 177 (1976).

Similar results were found by Ashe,²⁶ who compared the parent λ^3 -phosphorin with the otherwise unsubstituted 1,1-dimethyl- λ^5 -phosphorin. Since in these two



¹³C-NMR chemical shift values for the ring carbon atoms and J_{P-C} in brackets (right side of the formula) and ¹H NMR chemical shift values for the ring hydrogen atoms and J_{P-H} in brackets (left side of the formula)

compounds all ring protons were observable using ¹H NMR, the large differences in the electronic structures of the two classes of phosphorins were well established. In contrast to the λ^3 -phosphorin, the protons of the 1,1-dimethyl- λ^5 -phosphorin at carbons 2, 6, and 4 are shifted to a higher field, thus excluding the possibility of an aromatic ring current.

The ³¹P NMR shifts of λ^3 - and λ^5 -phosphorins are also very different. The former absorb at low field (178–211 ppm from H_3PO_4)²⁷ whereas the ³¹P shifts of λ^5 -phosphorin derivatives with aryl or alkyl substituents at the phosphorus are in the range of triphenyl- or trimethylphosphonium methylides (-5.3–2.1 ppm).^{25c}

Different substituents at the phosphorus atom strongly influence the ³¹P shifts and the J_{P-C} coupling constants. The values of some 2,4,6-triphenyl- λ^5 -phosphorins with the same two substituents at the phosphorus atoms are found (J_{P-C} in parentheses):²⁸ CH_3 +8 ppm (84.0 Hz); Cl +17 ppm (110.2 Hz); N(C_6H_5)₂ +42.5 ppm (121.2 Hz); OCH_3 +65 ppm (135.5 Hz); F^{80} +73.3 ppm (157.0 Hz), but SCH_3 +42 ppm (83.9 Hz).

The low-field ³¹P shifts and the higher J_{P-C} coupling constants appear to be a rough measure of the degree of the positive character at the phosphorus atom. The presence of electron-attracting 1,1-substituents will increase its positive charge. The correlation between δ ³¹P and $J_{P-C-2/6}$ is even better when the phosphorus atom charge is calculated from the ESCA spectra of the λ^5 -phosphorin derivatives.³¹

Photoelectron Spectra. The photoelectron spectra of seven 2,4,6-triphenyl- λ^5 -phosphorins with different substituents at the phosphorus atom are in full agreement with an ylide structure as well as the existence of some back-bonding from the cyclopentadienyl anion unit to the positively charged phosphorus atom. The calculations, using different models, show that the important features of the λ^5 -phosphorins can be predicted even if the phosphorus atom d orbitals are completely neglected.³²

Reactions of λ^5 -Phosphorins

Phosphorus Substituent Exchange. In the presence of acids, 1,1-bis(dimethylamino)- λ^5 -phosphorins (e.g., **29**) easily exchange the dimethylamino groups for

(26) (a) A. J. Ashe III and T. W. Smith, *J. Am. Chem. Soc.*, 98, 7861 (1976); (b) *Tetrahedron Lett.*, 407 (1977).

(27) A. J. Ashe III, R. R. Sharp, and J. W. Tolan, *J. Am. Chem. Soc.*, 98, 5451 (1976).

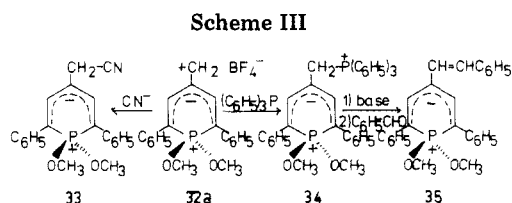
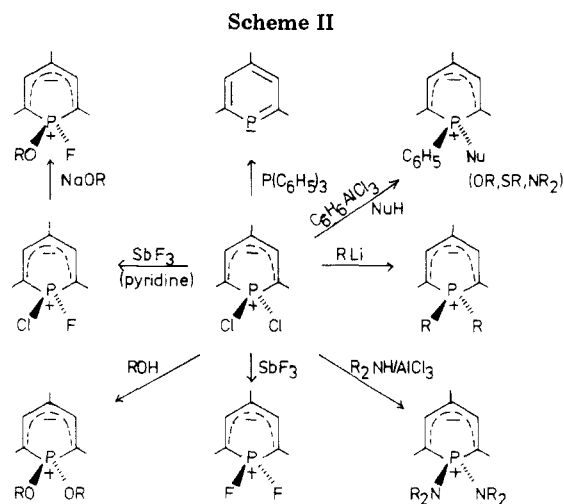
(28) K. Dimroth, S. Berger, and J. Kaletsch, *Phosphorus Sulfur*, 10, 305 (1981).

(29) A. Hettche and K. Dimroth, *Tetrahedron Lett.*, 829 (1972).

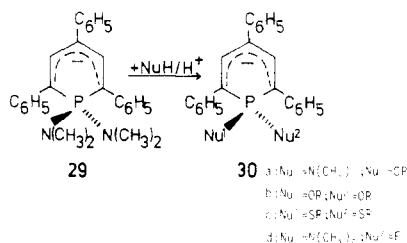
(30) H. Kanter, W. Mach, and K. Dimroth, *Chem. Ber.*, 110, 395 (1977).

(31) J. Knecht, in preparation.

(32) W. Schäfer, A. Schweig, K. Dimroth, and H. Kanter, *J. Am. Chem. Soc.*, 98, 4410 (1976).



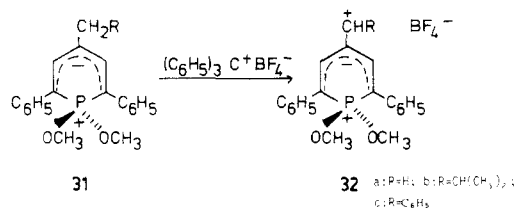
other nucleophiles. Depending upon the reaction conditions, reaction products such as 30a or 30b can be prepared. Trifluoroacetic acid and thiols afford 1,1-



dithioalkyl- λ^5 -phosphorins 30c. SbF_3 or BF_3 give 1-fluoro- λ^5 -phosphorin derivatives 30d.³³

The easily accessible 1,1-dichloro- λ^5 -phosphorins can be transformed into many different P-substituted λ^5 -phosphorins. Reduction to λ^3 -phosphorins on treatment with triphenylphosphine is also possible. Scheme II gives some of the most important reactions. These are not restricted to the 2,4,6-triphenyl- λ^5 -phosphorin derivatives.³⁴

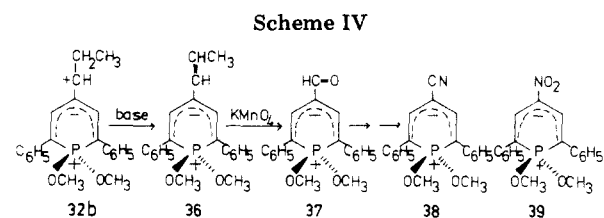
Hydride Abstraction from 1,1-Dimethoxy-4-methyl- λ^5 -phosphorin Derivatives. 2,6-Diphenyl (or di-*tert*-butyl)-1,1-dimethoxy- λ^5 -phosphorins 31 possessing a methylene group in position 4 are converted into crystalline carbenium tetrafluoroborates 32a-c on



treatment with triphenylcarbonium tetrafluoro-

(33) K. Dimroth, A. Hettche, H. Kanter, and W. Städe, *Tetrahedron Lett.*, 835 (1972).

(34) H. Kanter, W. Mach, and K. Dimroth, *Chem. Ber.*, 110, 397 (1977).



borate.^{35a,b} Starting from 32, many new transformations are possible.

Nucleophilic Addition. Nucleophiles such as CN^- add to position 4' to give the 4'-cyano derivative 33^{35a,b} (Scheme III). Triphenylphosphine affords 34, the conjugate base of which undergoes Wittig reaction with benzaldehyde to give olefin 35.³⁶

Formation and Reactions of the 4-Aldehyde. Deprotonation of 32b to 36 and subsequent KMnO_4 oxidation give the 4-aldehyde 37.³⁷ The latter is converted to the carboxylic acid by further oxidation, to the 4-cyano- λ^5 -phosphorin 38 via the oxime, or to the 4-nitro compound 39 by nitrocarbonylation³⁸ (Scheme IV).

Electrophilic Substitution. With electrophiles in aqueous acetonitrile solution, the cation 32a reacts to install an electrophilic moiety at position 4 (Scheme V). Thus, arenediazonium salts give rise to 4-aryloxy- λ^5 -phosphorins 40³⁸ and protonated formaldehyde, a reaction similar to the electrophilic substitution reaction with 4-hydroxymethyl-*N,N*-dimethylaniline.³⁹ The 4-azo or -nitro compounds 40 and 39, respectively, can be reduced to 4-acetamino- λ^5 -phosphorins 41.⁴⁰ When no electrophile is present, 32a will dimerize to the intermediate 42 which eliminates 1 mol of protonated formaldehyde to give the interesting methane bis- λ^5 -phosphorine 43 in nearly quantitative yield. This compound can readily be dehydrogenated with triphenylcarbonium tetrafluoroborate, producing the very stable phosphacyanide derivative 44.⁴¹

Halide Ion Dealkylation. Halide ions X^- , contrary to other nucleophiles, attack compounds such as 31 at the OCH_3 group, causing elimination of CH_3X and the formation of a $\text{P} \rightarrow \text{O}$ bond (Scheme VI). In the presence of H_2O_2 , OH^+ adds to position 4, giving 4-hydroxy-1-methoxy-2,4,6-triphenyl-1,4-dihydrophosphorin oxide 45a (a mixture of separable *E* and *Z* isomers). Acid treatment of 45a or 45b affords the stable, delocalized orange-red cation 46 from which 45a can be regenerated by the addition of water, or 45b by the addition of methanol. NaBH_4 reduces 46 to the 1-methoxy-2,4,6-triphenyl-1,2-dihydrophosphorin oxide 47^{42a,b} which can also be prepared by the hydrolysis of 31 with hydrochloric acid.⁴³ Alkylation of 47 using alkylating agents such as tertiary oxonium salts in the

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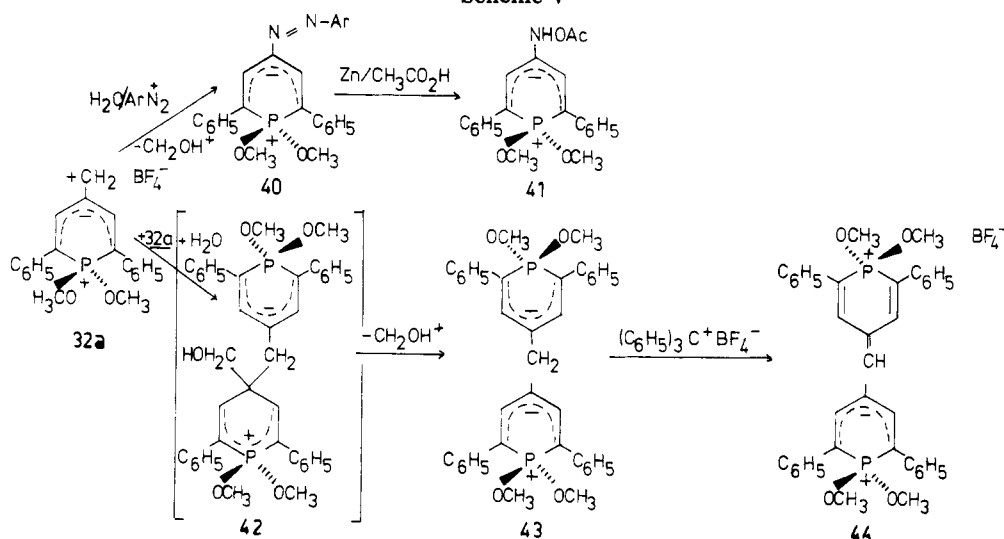
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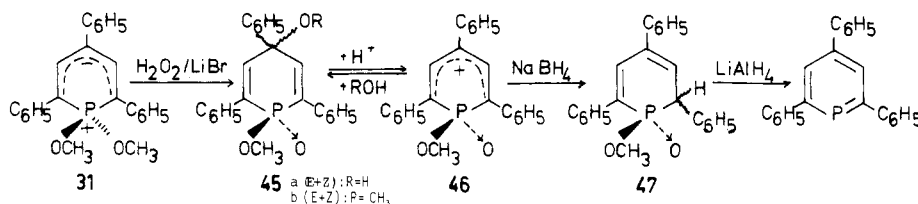
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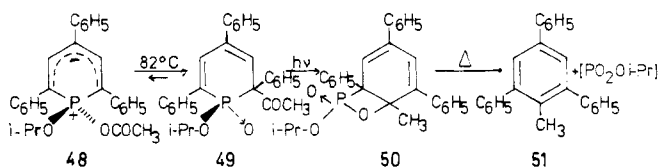
Scheme V



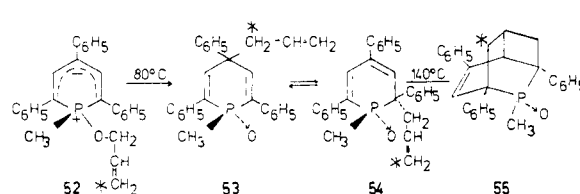
Scheme VI



Scheme VII



Scheme VIII



presence of ethyldiisopropylamine⁴³ gives 31 or 1-ethoxy-1-methoxy-2,4,6-triphenyl- λ^5 -phosphorin.

Alkoxy Group Removal. The removal of the two OR groups of λ^5 -phosphorins (31) to afford the corresponding λ^3 -phosphorins in 50% yield is possible. 1,1-Dimethoxy-2,4,6-triphenyl λ^5 -phosphorin (31) is first treated with alcoholic hydrochloric acid, affording 47, which is then reduced with LiAlH_4 .⁴⁴ Similar results were obtained with 2,4,6-tri-*tert*-butyl-1,1-dimethoxy- λ^5 -phosphorin. Removal of the methoxy groups from 1,1-dimethoxy- λ^5 derivatives with functional groups, in an effort to obtain functionalized λ^3 -phosphorin derivatives, remains to be carried out.

Rearrangements. Apart from the thermal rearrangement already mentioned,^{5c} we have observed two interesting rearrangements of λ^5 -phosphorin derivatives with oxygen-bonded residues at phosphorus; these are similar to the Fries and Claisen rearrangements of phenol derivatives.

When 1-acetoxy-1-isopropoxy-2,4,6-triphenyl- λ^5 -phosphorin (48) is heated in decalin to 82°C , the acetyl group migrates to position 2 (Scheme VII). The resulting compound 49 exists in equilibrium with 48 ($K = 15.7$ in favor of 49). Other 1-alkoxy-1-acyloxy-substituted λ^5 -phosphorins behave similarly. The same rearrangement is observed when 48 is exposed to daylight.

(44) K. Dimroth and H. Kaletsch, unpublished results.

Irradiation of 49 (λ 300 nm) in cyclohexane solution gives carbocyclic 50 (50–55%) and 2,4,6-triphenyl-toluene (51) (15–20%).^{45a,b}

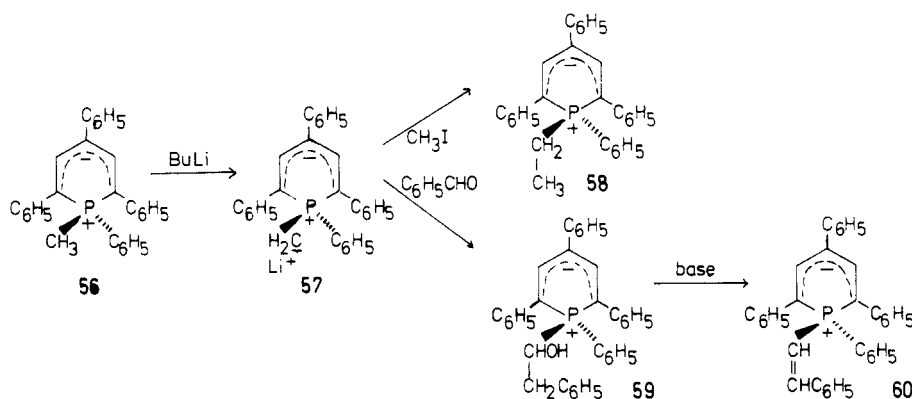
Thermal rearrangement of 1-allyloxy-1-methoxy-2,4,6-triphenyl- λ^5 -phosphorin (52) in inert solvents at 80°C produces 53 with inversion in the allyl group. A Cope rearrangement equilibrates 53 and 54 (Scheme VIII). Heating to 140°C in xylene solution affords the tricyclic compound 55 by an irreversible intramolecular Diels–Alder addition.^{46a} X-ray analysis of 55^{46b} established that all rearrangements take place exclusively in a suprafacial manner. These transformations are strictly intramolecular. The reaction $52 \rightarrow 53$ cannot be considered an electrocyclic [3.5] rearrangement since the ylide system interrupts the two parts of the electron structure. The migration of the allyl residue is favored by the high energy of the $\text{P} \rightarrow \text{O}$ bond, the stereochemistry of 52, and the electron-donating substituents in position 4 of the phenyl group.^{46c}

Deprotonation of Exocyclic Alkyl Groups at the Phosphorus Atom. The ylide structure of a com-

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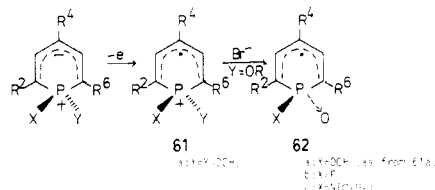
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Scheme IX



pound such as 1-methyl-1,2,4,6-tetraphenyl- λ^5 -phosphorin (56) can be strengthened by chemical reactions. With butyllithium the carbanion 57 is formed, which then adds electrophiles such as methyl iodide, giving 1-ethyl-1,2,4,6-tetraphenyl- λ^5 -phosphorin (58) or benzaldehyde (Scheme IX). The latter then gives the aldol 59 which reacts with bases to give 60. A Wittig reaction was not observed.⁴⁷

Oxidation and Reduction to Radicals. λ^5 -Phosphorins with phenyl or *tert*-butyl substituents in positions 2, 4, and 6 and substituents such as OR, NR_2 , or F at the phosphorus atom can be oxidized electrolytically to give cation radicals such as 61. In the case



of $\text{X} = \text{Y} = \text{NR}_2$ or F, these easily react with water to give the very stable neutral radicals 62a or 62b. 1,1-Dimethoxy- λ^5 derivatives first produce the stable cation radical 61a which in the presence of LiBr is transformed into the stable neutral radical 62a. Both radicals, 61 and 62, are of cyclohexadienyl type with a relatively small ^{31}P coupling constant (2–2.7 mT) which is only due to spin polarization.⁴⁸

Concluding Remarks

The evidence presented above shows that λ^5 -phosphorins containing a variety of sometimes unusual substituents at the phosphorus atom represent a new class of cyclic 6π delocalized phosphonium ylides which

are, however, not aromatic compounds. In contrast to the two-coordinated phosphorus in λ^3 -phosphorin, the tetracoordinated phosphorus of λ^5 -phosphorin disrupts the 6π delocalization over the whole ring. On the other hand, the high stability and the strong tendency of λ^5 -phosphorins to regenerate the ylide unit in chemical reactions show that they have much in common with aromatic compounds. The dipolar ylide structure is, however, probably a too simplified picture of the true state of the carbon–phosphorus bond of both these and the open-chain phosphonium ylides. Further theoretical studies may provide better insight.

Experiments which attempt to remove the protecting OCH_3 group at phosphorus from 1,1-dimethoxy- λ^5 -phosphorins are still in an early stage. λ^5 -Phosphorins are, however, an interesting class of heterocycles per se, which show many unexpected reactions. The reactions of the Cr, Mo, and W transition metal tricarbonyl complexes of λ^3 -phosphorins and their transformation into λ^5 -phosphorin complexes have not been considered here since much work remains to be done.⁴⁹ Very little is known also about the chemistry of ring-unsubstituted λ^5 -phosphorins.

Note Added in Proof. Recent ^{13}C NMR data on 32' (an analogue of 32 with $\text{R} = \text{H}$ and 2,6-di-*t*-Bu instead of 2,6-di-Ph) show the ground state to be a resonance hybrid of 4'-methylene phosphonium and 4'-carbenium ylide canonical forms.

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