

The Reaction of Dipotassium Cyclooctatetraenide with Dichlorophenylphosphine. Rearrangements of 9-Phenyl-9-phosphabicyclo[6.1.0]nonatriene and 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene

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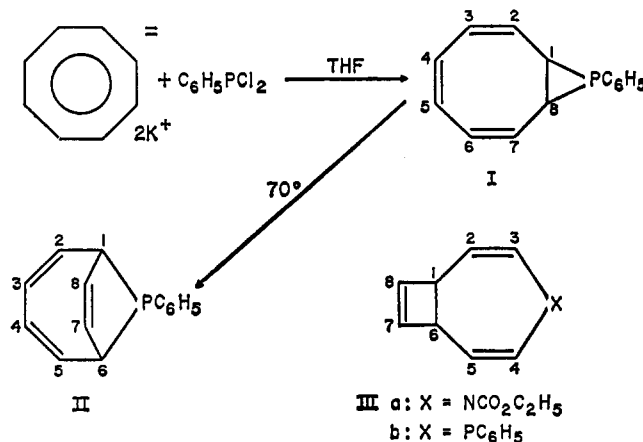
Abstract: Dipotassium cyclooctatetraenide in tetrahydrofuran reacts with dichlorophenylphosphine to give I, which upon warming isomerizes to II. Upon pyrolysis II rearranges to an isomeric substance II', shown to be epimeric with II at the phosphorus nucleus. The structures of these substances were proven by analysis of their proton nmr spectra with the aid of phosphorus and proton decoupling. The formation of I and its rearrangement to II are stereospecific reactions. The epimerization of II to II' in chloroform solution is catalyzed by HCl. (No phosphiranes, bridged phosphines, rearrangements of bicyclo[6.1.0]nonatrienes to bicyclo[4.2.1]nonatrienes, or acid-catalyzed phosphine inversions were previously known.) With methyl iodide the phosphines II and II' form methiodides, II-M and II'-M, and with hydrogen peroxide phosphine oxides, II-O and II'-O, both stereospecifically and presumably with retention of configuration. With air they both form the oxide II'-O. Palladium chloride complexes of II and II' were also prepared, and that of II' was used to purify the phosphine. Mechanisms for the acid-catalyzed inversion of configuration are discussed. Although II and II' differ only in stereochemistry, their ³¹P chemical shifts differ by 65 ppm. The ³¹P chemical shift of compound I (+181 ppm relative to 85% H₃PO₄) is higher than that of any trialkylphosphine known.

Dipotassium cyclooctatetraenide² in tetrahydrofuran (THF) reacts with a variety of *gem* dihalides to yield derivatives of bicyclo[6.1.0]nonatriene.³ Methylene chloride yields the parent hydrocarbon, while chloroform, carbon tetrachloride, dichloromethyl methyl ether, 1,1-dichloroethane, and 1,1,1-trichloroethane yield 9-substituted derivatives. Similar compounds are formed in the reaction of dilithium cyclooctatetraenide with acetyl chloride or benzoyl chloride.⁴

The reaction of dipotassium cyclooctatetraenide with *gem*-dihalo compounds of elements other than carbon was examined to determine whether heterocyclic compounds could thereby be prepared. Sulfur dichloride, however, simply oxidizes dipotassium cyclooctatetraenide to give a good yield of cyclooctatetraene,⁵ while dichloroethylphosphine⁶ reacts to yield a polymer. Dichlorophenylphosphine, in contrast, reacts effectively.⁷ The preparation of the bicyclic compounds I and II is described below.

Both compounds are unusual, for bridged phosphorus compounds are rare⁸ and the only examples of

phosphiranes are those claimed in recent patents.⁹ (The only known heteroatom-substituted cyclononatrienes are cyclooctatetraene oxide,¹⁰ N-carbethoxy-9-azabicyclo[6.1.0]nonatriene,¹¹ and the latter's rearrangement product, IIIa.¹¹ N-Cyano-9-azabicyclo[6.1.0]nonatriene was recently reported but not isolated.¹²) Compound I is obtained by the reaction of



- (1) (a) Columbia University; (b) Shell Development Co.
- (2) G. Schröder, "Cyclooctatetraen," Verlag Chemie, Weinheim/Bergstr, Germany, 1965.
- (3) (a) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963); (b) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 4876 (1964); (c) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 5194 (1964).
- (4) T. S. Cantrell and H. Shechter, *ibid.*, **85**, 3300 (1963).
- (5) (a) T. J. Katz and P. J. Garratt, unpublished results. (b) The cyclooctatetraenyl dianion reduces trimethylpyrylium cation rather than alkylating it: K. Conrow and P. C. Radlick, *J. Org. Chem.*, **26**, 2260 (1961).
- (6) M. S. Kharasch, E. V. Jensen, and S. Weinhouse, *ibid.*, **14**, 429 (1949).
- (7) Organophosphorus compounds are commonly prepared from phosphorus halides and organolithium or Grignard reagents: K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhushanan, "Topics in Phosphorus Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1964, p 17 ff; G. Märkl, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1023 (1965).
- (8) Pentaphenylphosphole and maleic anhydride form in low yield

- an adduct that has not been fully characterized: E. H. Braye, W. Hübel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961). A related approach has recently been described: D. A. Usher and F. H. Westheimer, *ibid.*, **86**, 4732 (1964). Another method, the addition of substituted phosphorus dichlorides across dienes, failed with cyclooctadiene-1,3 and PCl₃ (L. D. Quin and D. A. Mathews, *J. Org. Chem.*, **29**, 836 (1964)), but was successful with norbornadiene and CH₃PCl₂: M. Green, *J. Chem. Soc.*, 541 (1965).
- (9) (a) R. I. Wagner, U. S. Patent 3,086,053 (April 16, 1963); *Chem. Abstr.*, **59**, 10124d (1963); U. S. Patent 3,086,056 (April 16, 1963); *Chem. Abstr.*, **60**, 559d (1964).
- (10) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **80**, 5505 (1958).
- (11) S. Masamune and N. T. Castellucci, *Angew. Chem. Intern. Ed. Engl.*, **3**, 582 (1964).
- (12) A. G. Anastassiou, *J. Am. Chem. Soc.*, **87**, 5512 (1965).

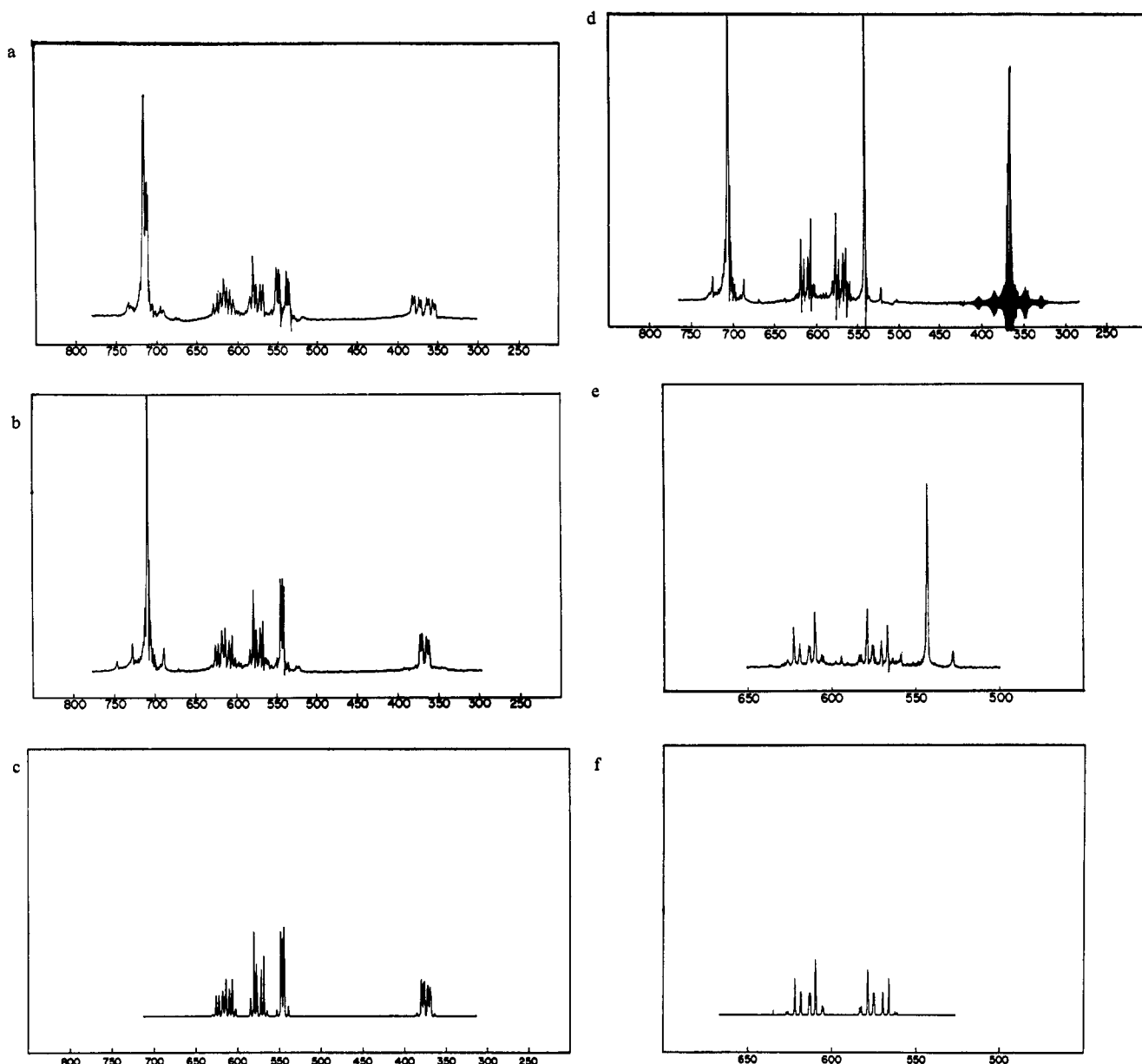


Figure 1. Proton nmr spectrum (100 Mc/sec) of phosphine II in CDCl_3 . The scale is cps from tetramethylsilane: (a) normal spectrum; (b) phosphorus spin decoupled; (c) calculated phosphorus decoupled spectrum using parameters in Table I; (d) phosphorus and allylic proton decoupled; (e) same as d on magnified scale; (f) calculated AA'BB' spectrum corresponding to e, using parameters from Table I.

dipotassium cyclooctatetraenide with dichlorophenylphosphine at low temperatures; upon warming it isomerizes to II.

Results

Addition of dipotassium cyclooctatetraenide in tetrahydrofuran to dichlorophenylphosphine at 0° gives, after addition of aqueous sodium carbonate, extraction with pentane, and distillation at $160\text{--}170^\circ$ (4 mm), a 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (II) in 46% yield. After recrystallization and sublimation, it melts at 86° . By determining the compound's proton nmr spectrum under three conditions (Figure 1)—without decoupling, with phosphorus spin decoupling, with simultaneous decoupling of the nuclear spins of the phosphorus atom and the nonolefinic protons—and by identifying the observed spectra with spectra calculated¹⁸ using the parameters listed in

Table I, the structure of the phosphine was shown to be II. The observation that the intensities of the resonances of the phenyl, olefinic, and allylic protons were in the ratio 5.16:5.93:1.92 indicated that the skeleton is bicyclic, which was confirmed by chemical evidence, the hydrogenation of the phosphine methiodide to a saturated (nmr) hexahydrophosphonium salt, isolated as the picrate. There are only six bicyclic structures with a proton on each carbon that can be drawn for the phosphine. Of these, three are eliminated because the symmetry of the nmr spectrum of II would be fortuitous if the phosphine did not possess one of the three structures with a symmetry plane, I, II, or IIIb. Of these, I is disqualified below. Structure IIIb is disqualified for four reasons: the compound should not show the large coupling J_{34} ; it should exhibit a spectrum like that of IIIa with J_{12} and $J_{18} = 0$;¹¹ it should not show a large coupling of phosphorus to the protons at 7 and

(13) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

Table I. Proton Nmr Spectral Parameters for Phosphines II and II' and Their Oxides^a

	II	II'	II-O	II-O
$\tau_1 = \tau_6$	6.37	6.59	6.58	6.86
$\tau_2 = \tau_5$	3.84	3.80	4.16	3.83
$\tau_3 = \tau_4$	4.27	4.12	4.54	4.00
$\tau_7 = \tau_8$	4.57	4.62	4.09	4.25
$J_{12} = J_{56}$	7.8	8.4	8.6	≈ 8.1
$J_{13} = J_{46}$	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5
$J_{14} = J_{36}$	≈ 0	≈ 0	≈ 0	≈ 0
$J_{15} = J_{26}$	≈ 0	≈ 0	≈ 0	≈ 0
J_{16}	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5
$J_{17} = J_{68}$	-0.5	-0.7	-0.3	+0.1
$J_{18} = J_{67}$	4.7	3.7	4.2	4.1
$J_{23} = J_{45}$	11.5 ± 0.1	11.4 ± 0.1	11.51 ± 0.08	11.5 ± 0.2
$J_{24} = J_{35}$	0.8 ± 0.1	0.7 ± 0.2	0.7 ± 0.1	0.7 ± 0.2
J_{25}	0.8 ± 0.2	0.9 ± 0.2	0.6 ± 0.1	0.5 ± 0.3
J_{34}	8.0 ± 0.1	7.9 ± 0.1	7.92 ± 0.07	7.8 ± 0.2
J_{78}	6.3	5.7	6.6	7.0
$J_{P1} = J_{P6}$	18.3	2.2	≈ 14.7	≈ 10.3
$J_{P2} = J_{P5}$	≥ 5	± 13.1	± 20.7	≤ 5
$J_{P3} = J_{P4}$	≤ 5	∓ 3.0	∓ 3.0	≥ 15
$J_{P7} = J_{P8}$	11.9	3.4	21.2	25.2
	$J_{27} = J_{58} = J_{28} = J_{57} = J_{27} = J_{48} = J_{38} = J_{47} \approx 0$			

^a Chemical shifts are given as ppm on the τ scale. Coupling constants are in cps. All spectra were determined in CDCl_3 solution.

8; it should exhibit a larger coupling of phosphorus to the protons at 2 and 3.¹⁴ Only structure II remains.

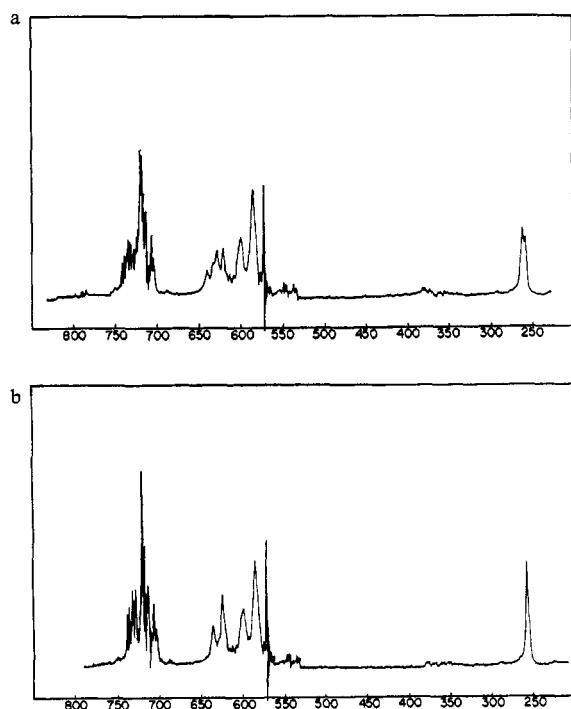


Figure 2. Proton nmr spectrum (100 Mc/sec) of phosphine I in CDCl_3 . The scale is cps from TMS (the sharp peak at 570 cps is, presumably, cyclooctatetraene present as in impurity): (a) normal spectrum; (b) phosphorus spin decoupled.

If the product of the reaction of dipotassium cyclooctatetraene with dichlorophenylphosphine is isolated

(14) W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963), analyzed the spectrum of trivinylphosphine. The coupling analogous to J_{P3} in IIIb was 11.7 cps and the one analogous to J_{P2} 30.2. They also report that in trivinylphosphine the proton nearest the phosphorus is least shielded. In structure IIIb, atom 2 has been placed next to 1 because of the large coupling J_{12} ; this puts atom 3 next to phosphorus, which may be inconsistent with the observed greater shielding of proton 2 compared to 3.

at low temperatures and purified by sublimation below 55° (10^{-6} mm), instead of II, an isomeric phosphine is obtained. The proton nmr spectrum (Figure 2) of this product appears to be consistent with structure I. The spectrum consists of three groups of multiplets of relative intensity 5.3:5.7:2.0 assigned to the phenyl protons (sharp lines centered at τ 2.86), olefinic protons (broadened bands extending from ca. 3.5 to 4.2), and allylic protons (a doublet at 7.42, whose splitting, $J = 3.5$ cps, arising from coupling with the phosphorus nucleus, disappears upon irradiation at the phosphorus resonance frequency). Irradiation at the phosphorus frequency also removes a portion of the olefinic multiplet. As among all known derivatives of bicyclo[6.1.0]nonatriene,^{3,4,10-12} the spin-spin coupling between the allylic and olefinic protons is too small to be detectable, and the allylic proton resonance lies at particularly high field (in this case 1.05 ppm above the corresponding resonance in II).^{15,16}

In chloroform at 70° (the half-life is 1.1×10^2 min), or at room temperature in the course of a few months, this phosphine is transformed into the isomer II described above. The product II is stable as a crystalline solid, but upon rapid gas phase pyrolysis at 480° , undergoes further rearrangement. The same rearrangement occurs cleanly if II is warmed to 100° overnight in chloroform containing hydrogen chloride. In unacidified chloroform the rearrangement can be effected only at higher temperatures (160° for 24 hr), but is accompanied by extensive darkening. The product of the rearrangement is in all cases a mixture mainly of an isomeric substance II', and the starting material. The purification of the phosphine II' is described below. Its melting point, 85° , is similar to that of II; its nmr spectrum shows that the two substances are epimeric. The spectrum of II' shows peaks attributable to the phenyl, olefinic, and allylic protons, and upon simultaneous irradiation at the nuclear resonance frequencies

(15) Cyclooctatetraene oxide exhibits a singlet at τ 6.64,¹⁰ 9-carboethoxy-9-azabicyclo[6.1.0]nonatriene at 6.90,¹¹ and 9-cyano-9-azabicyclo[6.1.0]nonatriene at 6.6.¹²

(16) The appearance of only one such resonance suggests that the product I consists of only one stereoisomer.

of the phosphorus and the allylic protons, the olefinic peaks collapse to a singlet and an AA'BB' pattern.¹⁷ Spectral parameters that fit the observed spectra are given in Table I.

The compounds II and II' form characteristic methiodides, II-M and II'-M, and with hydrogen peroxide, phosphine oxides, II-O and II'-O, presumably with retention of configuration.¹⁸

However, both phosphines react with air to yield the same oxide, that obtained from II' and H₂O₂. The proton nmr spectra of the oxides II-O and II'-O were determined (Figure 3), and simplified by nuclear decoupling as for II and II'.¹⁷ Spectral parameters that fit the observed spectra are given in Table I.

The phosphorus chemical shifts of I, II, II', II-O, and II'-O were determined by observing the frequencies required in double resonance experiments to eliminate phosphorus-proton coupling. This and a similar experiment performed with triethyl phosphate, whose ³¹P chemical shift is known (0.9 ppm relative to external 85% H₃PO₄),¹⁹ yielded the chemical shifts shown in Table II.

Table II. Phosphorus Chemical Shifts of the Phosphines and Their Oxides

Compd	δ _P ^a
I	+181
II	+79
II'	+14
II-O	-38
II'-O	-26

^a ³¹P-chemical shifts are given in ppm relative to 85% H₃PO₄ (see text). The more positive δ, the greater the nuclear shielding.

The ultraviolet spectra of these compounds and of the methiodides of II and II' were also determined. These are shown in Figures 4 and 5 and described, together with the spectra of known model compounds, in Table III.

Compounds II and II' form palladium chloride complexes²⁰ on reaction with bis(benzonitrile)palladium dichloride.²¹ Compound II forms two palladium chloride complexes, a yellow bisphosphine palladium dichloride and an orange, chlorine-bridged dimer of the monophosphinepalladium dichloride.²⁰ (The double bond apparently does not coordinate to the palladium in the 1:1 complex.²¹) Recrystallization of the bis(phosphine)palladium dichloride derivative of crude II' and regeneration of the phosphine from the complex (using aqueous KCN) gave the pure II'.

(17) C. R. Nicholson, Dissertation, Columbia University, 1966.

(18) (a) W. E. McEwen in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 1 ff; (b) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964); (c) D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Letters*, **30**, 2177 (1963); (d) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **86**, 2378 (1964); (e) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Letters*, 161 (1961).

(19) P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 515 ff.

(20) These experiments were initiated at Columbia by Joseph Mrowca, who prepared the PdCl₂ complexes of II.

(21) M. A. Bennett, H. W. Kowenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4570 (1964).

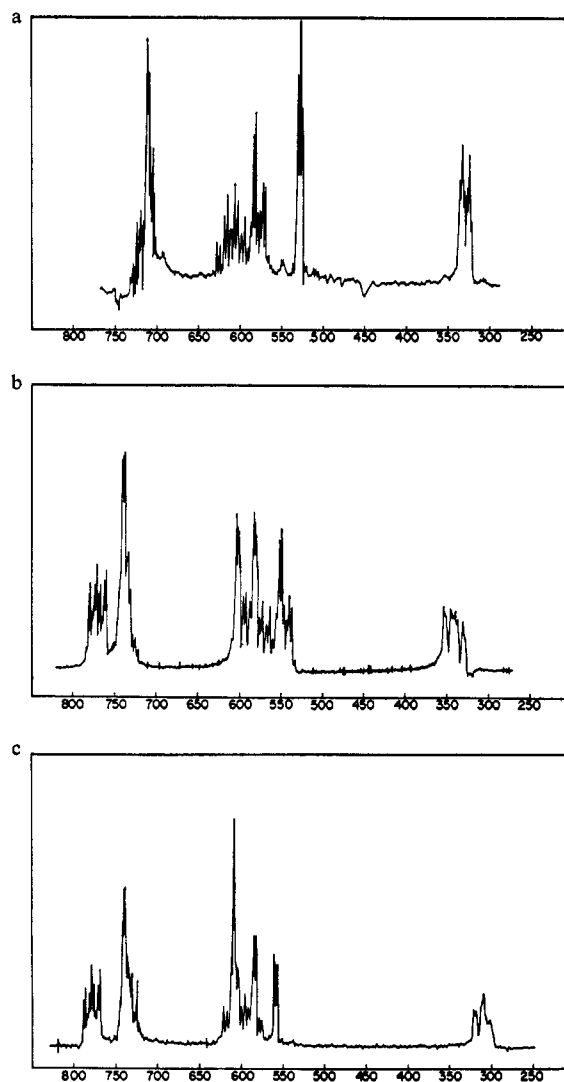
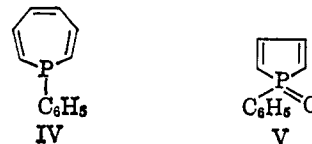


Figure 3. Proton nmr spectra (100 Mc/sec) in CDCl₃: (a) phosphine II'; (b) phosphine oxide II-O; (c) phosphine oxide II'-O. The scale is cps from TMS.

The pyrolysis of II that yielded II' was originally examined to determine whether P-phenylphosphinepin (IV)²² or phenylphosphinidene, C₆H₅P,²³ would result. Neither has yet been recognized as a product of the reaction, but this work has been only preliminary. An attempt to convert II-O into a P-phenylphosphole oxide (V) using dimethyl acetylenedicarboxylate also failed.²⁴ In fact no Diels-Alder adducts could be



(22) Cf. an azepine: K. Hafner, D. Zinser, and K.-L. Moritz, *Tetrahedron Letters*, 1733 (1964); oxepin: E. Vogel, R. Schubert, and W. A. Böll, *Angew. Chem.*, **76**, 535 (1964).

(23) (a) An unsuccessful attempt to trap C₆H₅P is described by W. A. Henderson, Jr., M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963); (b) C₆H₅P has recently been claimed to have been trapped by U. Schmidt and Oh. Osterroht, *Angew. Chem. Intern. Ed. Engl.*, **4**, 437 (1965), and to have been a reaction intermediate by M. J. Gallagher and I. D. Jenkins, *Chem. Commun.*, 587 (1965).

(24) Recently a successful use of this reaction to prepare benzocyclopropene was described: E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Letters*, **41**, 3625 (1965).

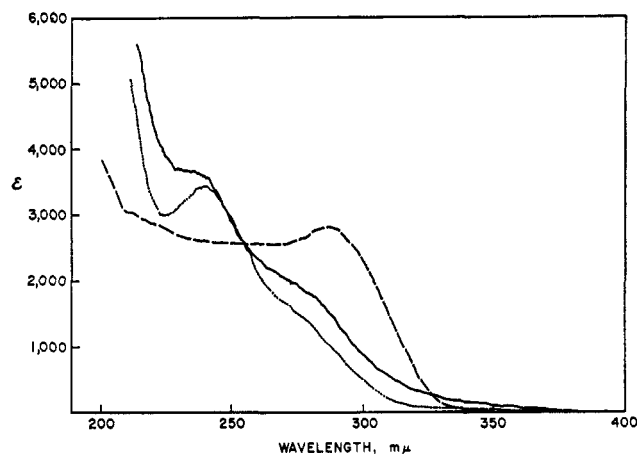


Figure 4. Ultraviolet spectra in 95% ethanol of the phosphines I (—), II (---), and II' (....).

isolated from the treatment of phosphine II and its derivatives with various dienophiles. Starting material was recovered from the attempted reaction of II-M with maleic anhydride in refluxing xylene. Similarly,

Table III. Ultraviolet Spectra^a

Compd	λ_{\max} , $m\mu^b$	Log ϵ
I	235	3.56
II	274 sh	3.30
II'	286	3.46
II-M	240	3.54
	270 sh	3.23
	267	3.61
II'-M	273 sh	3.55
	268	3.66
	273 sh	3.62
II-O	267	3.30
	275	3.35
	286	3.30
II'-O	259	3.51
	267	3.51
	273	3.50
$C_6H_5P(CH_3)_2$	251	3.54 ^c
$C_6H_5P(CH_3)_3^+I^-$	251	2.65 ^d
	260	2.78
	265	2.96
	272	2.91
9-Acetoxy-9-methylbicyclo[4.2.1]nonatriene (Xa)	265	3.56 ^e
	256	3.57
	219	3.50
9-Hydroxy-9-methylbicyclo[4.2.1]nonatriene (Xb)	260	3.80 ^e
N-Cyano-9-azabicyclo[4.2.1]nonatriene (Xc)	255	3.65 ^f
Cyclooctatetraene oxide	240	3.80 ^g
Bicyclo[6.1.0]nonatriene	247	3.69 ^h
	250	3.59

^a Spectra were determined in 95% ethanol. ^b sh = shoulder. ^c In cyclohexane: K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952). ^d In ethanol: see footnote c. ^e In methanol.⁴ ^f See ref 12: in CH_3CN . ^g S. L. Friess and V. Boekelheide, *J. Am. Chem. Soc.*, **71**, 4145 (1949). ^h See ref 3c.

the nmr spectra of the products obtained upon work-up of attempted reactions between II-O and maleic anhydride or dimethyl acetylenedicarboxylate in refluxing benzene indicated that only starting materials were present. Addition of tetracyanoethylene to II-M in

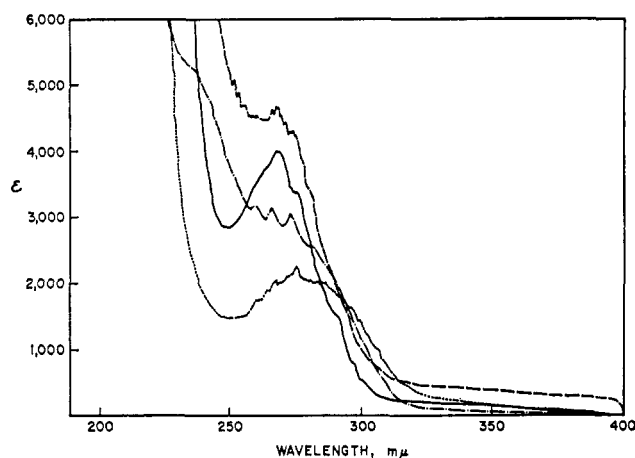


Figure 5. Ultraviolet spectra in 95% ethanol of the phosphine methiodides II-M (—) and II'-M (---), and the phosphine oxides II-O (....) and II'-O (-.-.).

methanol gave the phosphonium salt of methyl dicyanoacetate.^{25,26} An immediate reaction occurred between maleic anhydride and II, but only tar was obtained. Phosphine II reacted with tetracyanoethylene to produce a series of brightly colored compounds, but these were not characterized.

Discussion

Nmr Coupling Constants in II, II', II-O, and II'-O. That the phosphine II has the structure 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene is implied by its proton nmr spectrum. Other possible structures were eliminated above. That the phosphine II' has the same structure and that the two oxides have the related structures are implied by the remarkable similarity of the proton-proton coupling constants shown by all four of these compounds (Table I). While these coupling constants are not those expected if the skeletal structure were different, they do appear in reasonable accord with known precedents for the structure proposed. Thus the coupling $J_{78} = 6.4 \pm 0.4$ cps shown by these compounds is similar to those of cyclopentenes and bicyclo[2.2.1]heptenes, and unlike those of cycloolefins of different ring size.²⁷ The coupling $J_{23} = 11.5 \pm 0.1$ is like that of cycloheptadienes and cycloheptatrienes.²⁹ The coupling constant $J_{34} = 7.9 \pm 0.1$ cps is large compared to that of related substances. However, analogous coupling in cyclopentadiene,³¹ 1,3-cyclohexadiene,³¹ and 1,3,5-cycloheptatriene³⁰—1.94, 5.14, and 5.26 cps—indicate that these increase in magnitude with ring size,^{28c,30} and the observation that the coupling in 7,7-di(trifluoromethyl)cyclohepta-

(25) W. J. Middleton and V. A. Englehardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958).

(26) This salt exhibits the same nmr spectrum as II-M, but with an added methyl singlet at τ 6.46. Unlike II-M, whose nmr spectrum is difficult to determine because of its low solubility, that of the dicyanoacetate is easily obtained in chloroform at room temperature.

(27) Five-membered ring olefins (including bicyclo[2.2.1]heptenes) show *cis*-olefinic coupling constants of 5.1 to 7.0.²⁸

(28) (a) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); (b) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963); (c) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

(29) These are reported for a number of compounds as $J = 9.7$ to 12.5 cps^{28a} and for two cycloheptatrienes as $J = 10.67$ and 10.37 cps.³⁰

(30) G. B. Lambert, L. J. Durham, P. Loutere, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965).

(31) S. L. Manatt and D. D. Elleman, ref 30, footnote 27.

triene is much greater (6.86 cps) than in cycloheptatriene (5.26 cps) has suggested that they increase with decreasing H-C-C-H dihedral angle.³⁰ The coupling constants $J_{12} = 8.2 \pm 0.3$ and $J_{18} = 4.2 \pm 0.3$ are similar to couplings observed in simple cycloalkenes.^{28c} That the former is greater than the latter is expected, and has been attributed to the smaller H-C-C-H dihedral angle in larger rings. The couplings $J_{17} = -0.3 \pm 0.2$ and $J_{13} \leq 0.5$ are long-range allylic coupling constants,³² which are small and negative in some systems and small and positive in others.³³ The couplings $J_{24} = 0.7 \pm 0.2$ and $J_{25} = 0.7 \pm 0.1$ cps are like related couplings in cyclopentadiene, cyclohexadiene, and cycloheptatriene.³³ The homoallylic coupling³² $J_{16} < 0.5$ cps is small, like that in norbornene derivatives.³⁴

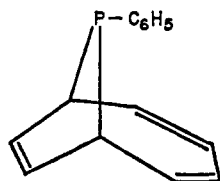
Stereochemistry. If the difference in the chemical shifts of the olefin proton resonances (Table I) in II and II' can be ascribed to shielding by the benzene ring,³⁵ the stereochemistry can tentatively be assigned to the two isomers. The differences between the chemical shifts of II and II' and their oxides are given in Table IV. In both the phosphines and the oxides, pro-

Table IV. Difference between the Proton Chemical Shifts in the Stereoisomers II, II', and II-O, II'-O^a

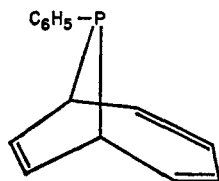
Proton	Obsd		Calcd
	II' - II	(II'-O) - (II-O)	
1	+0.22	+0.28	-0.01
2	-0.04	-0.33	-0.04
3	-0.15	-0.54	-0.38
7	+0.05	+0.16	-0.02

^a In ppm.

tons 1 and 7 are more shielded in the primed series than in the unprimed, and protons 2 and 3 are less shielded, a similarity supporting the presumption made above that the oxidations with hydrogen peroxide proceed with retention of configuration.¹⁸ If a major contribution to the differences in the chemical shifts of the olefin protons is long-range shielding owing to the magnetic anisotropy of the benzene ring, then the phosphine II has the structure VI and the phosphine II' the structure VII. The oxides have the corresponding structures.



VI



VII

The propriety of the assumption that the benzene ring current can account for the differences in chemical shift was tested by calculating the shielding at the various proton sites according to the tables of Johnson and Bovey.^{36,37} Rotation about the phosphorus-

(32) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(33) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

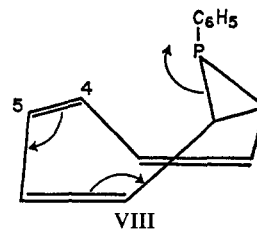
(34) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

(35) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, Chapter 7.

phenyl bond was arbitrarily assumed to be unhindered. The calculated differences in the chemical shifts of the protons 2, 3, and 7 in VI and VII, given in Table IV, are of an order of magnitude similar to those observed, but otherwise agreement is poor.

The observed differences in the chemical shifts of the bridgehead protons, 1 and 6, are not accounted for in this way, but may reflect a sensitivity to changes in the magnetic anisotropy about the phosphorus nucleus to which these protons are proximate. The other protons should be much less sensitive to such local changes because the shielding of a proton by a point dipole a distance r away is proportional to r^{-3} .³⁵ If such shielding can be attributed to an effective point dipole lying in the skeletal symmetry plane, the difference in the chemical shifts of the protons 1 and 6 in the epimers is a consequence of the C-H bond not being normal to the plane. (The bond is tilted toward the smaller ring.)

The rearrangement of the phosphine I to yield 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene is stereospecific; only II is formed, even though this isomer is less stable than its epimer II', into which it is transformed under other conditions. The facility of the transformation I \rightarrow II (it proceeds slowly at room temperature) and its stereospecificity suggest that the reaction is an internal rearrangement.⁴¹ It is likely that the reaction proceeds as pictured in structure VIII:⁴² as a bond forms between phosphorus and carbon atom 4, the phenyl moves from a position equidistant to atoms 4 and 5 toward atom 5, and VI results. The stereospecificity observed for the reac-



VIII

tion I \rightarrow II also requires that isomer I be stereochemically homogeneous, as implied by its nmr spectrum.¹⁶ (The compound presumably has the *anti* stereochemistry shown in structure VIII, for if it had the *syn* stereochemistry, epimeric at the phosphorus atom, a molecular model allowing an intramolecular rearrangement to II could not be constructed.) The stereochemical homogeneity of I, implied by the simplicity of its nmr spectrum and the stereospecificity of its transformation to II, means that the reaction by which I forms is stereospecific.

It is noteworthy that the compound II produced after normal distillation of the reaction product of dipotas-

(36) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(37) Distances were measured on a Barton³⁸ model constructed from tetrahedral and trigonal carbons and a phosphorus with valencies directed 99° apart.³⁹ The following were the lengths of the bonds: 1,2 and 1,8, 1.54 Å; 2,3 and 7,8, 1.33 Å; 3,4, 1.46 Å; P,1, 1.87 Å; P, phenyl, 1.87 Å; phenyl C-C, 1.40 Å; C-H, 1.07 Å.⁴⁰

(38) D. H. R. Barton, *Chem. Ind. (London)*, 1136 (1956).

(39) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).

(40) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

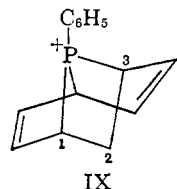
(41) The facility with which allylmethylphenylphosphine racemizes, relative to methylphenyl-*n*-propylphosphine, has been attributed to an allylic rearrangement.^{18a,b,c}

(42) This is thermal suprafacial sigmatropic change of order [1,5]; cf. R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

sium cyclooctatetraenide with dichlorophenylphosphine, which could be the product of a 1,4 addition to the cyclooctatetraene system, is in fact the product of 1,2 addition and subsequent rearrangement. Surprisingly, a nitrogen analog of II is reported to form by direct 1,4 addition of NCN to cyclooctatetraene, and even though the analog of I forms simultaneously, it is claimed not to rearrange to the 1,4 adduct.¹² The analog of I, prepared by addition of carbethoxynitrene to cyclooctatetraene, on the other hand, does undergo thermal rearrangement, but not to the analog of II. IIIa results instead.¹¹

Acid-Catalyzed Inversion of Configuration in the Phosphine II. In view of the configurational stability of trisubstituted phosphines demonstrated by the observation that optically active methyl-*n*-propylphenylphosphine is configurationally stable for long periods of time at room temperature,^{18e} although upon heating to 130° in hydrocarbon solvents it racemizes in hours,⁴³ and that methyl-*n*-butylbenzylphosphine can be resolved into its optical antipodes,^{18a} the stability to epimerization that allows the isolation of the isomers II and II', as well as other geometrically isomeric phosphines recently reported,⁴⁴ is expected, as is the thermal epimerization of II to II'. However, that the inversion of the phosphine II would be catalyzed by acids was not anticipated.

There are a few mechanisms that can account for this catalysis. The reaction might be a skeletal rearrangement initiated by protonation of II at C-2, followed by migration of the bridge from 1 to 3 and deprotonation, but that IX is an intermediate appears specious because if the alkylation¹⁸ (and by microscopic reversibility dealkylation)



of phosphines is stereospecific, then IX can form from only one isomer of II—presumably VII—and can lead to only the same isomer. Alternative mechanisms are (i) protonation on the benzene ring and deprotonation; (ii) protonation on phosphorus and displacement by halide on C-1, followed by rotation about the carbon-phosphorus bond and redisplacement of halide by phosphorus; and (iii) protonation on phosphorus followed by coordination by phosphorus to further ligands that lower the barrier to inversion.

This last possibility is discussed below. It was suggested⁴⁵ recently to account for the acid-catalyzed racemization of an arsine (methyl-*n*-propylphenylarsine).⁴⁵ The following observations—that the rate of racemization of the arsine in methanolic HCl is directly proportional to both the hydrogen ion and chloride ion concentration, and that the rate increases upon changing the anion from F⁻ to Cl⁻ to Br⁻ to I⁻—implied that the halide was present in the transition state for the rate-determining step, and suggested that

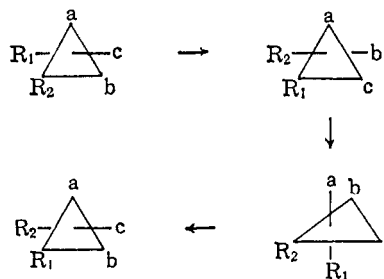
(43) L. Horner and H. Winkler, *Tetrahedron Letters*, 461 (1964).

(44) (a) L. D. Quin, J. P. Gratz, and R. E. Montgomery, *ibid.*, 2187 (1965); (b) L. D. Quin and H. E. Shook, Jr., *ibid.*, 2193 (1965).

(45) L. Horner and W. Hofer, *ibid.*, 4091 (1965).

an octahedral complex AsR₃HCl₂⁻ with *trans* chlorine groups was an intermediate. Formation of such a complex results in the observed configurational inversion, but the first-order dependence of the rate on chloride ion concentration requires that the rate-determining step precede its formation.

A variant on this scheme is one in which the most highly coordinated intermediate formed is the pentavalent R₃ZHX, where Z is phosphorus or arsenic and X⁻ is a halide anion.⁴⁶ Although pentacoordinate derivatives of the group V elements usually assume a trigonal bipyramidal configuration,^{48,49} the ¹⁹F nmr spectra of a number of these compounds^{48,50,51} show that the interchange of apical and equatorial substituents in the trigonal bipyramid can be fast on the nmr time scale⁵² and intramolecular. (For example, PCl₂F₃ inverts intramolecularly about 10³ times per second at -50°;^{51,52} tetramethylenephosphorus trifluoride is similarly rapid.^{50,53}) The low-energy barrier to the interchange is presumably^{48,54} due to the small difference in energy between the trigonal bipyramidal and tetragonal pyramidal configurations.^{49,55} In bicyclic phosphine II, the interchange may occur without both phosphorus-skeletal carbon bonds lying in the equatorial plane, and thus straining the CPC angle. If R₁ and R₂ are ring residues, the sequence below exchanges them without affecting the relative positions of the other groups. If a and b are the phenyl and hydrogen, the inversion presumably occurs^{18a} in the second step of the sequence.



Mechanisms for the acid-catalyzed inversion of phosphines or arsines that proceed through intermediates in which the group V element is bonded to more than four substituents do not account as easily for the slow rate of racemization of quaternary phosphonium or arsonium salts as do the alternative mechanisms that involve protonation on carbon, but the

(46) Silicon is isoelectronic with P⁺, and a pentacoordinated silicon anion has been suggested to intervene in the methanol-catalyzed racemization of α -naphthylphenylmethylfluorosilane.⁴⁷

(47) L. H. Sommer and P. G. Rodewald, *J. Am. Chem. Soc.*, **85**, 3898 (1963).

(48) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964).

(49) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

(50) E. L. Muetterties, W. Mahler, and H. Schmutzler, *ibid.*, **2**, 613 (1963).

(51) W. Mahler and E. L. Muetterties, *ibid.*, **4**, 1520 (1965).

(52) E. L. Muetterties, *ibid.*, **4**, 769 (1965).

(53) Pentamethylenephosphorus trifluoride and dimethylphosphorus trifluoride are slow.⁵⁰

(54) S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(55) Evidence for believing that the tetragonal pyramid is not a prohibitively high-energy configuration for such a molecule is the observation that pentaphenylantimony in the crystalline state assumes nearly this geometry.^{56,57}

(56) P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964).

(57) Pentaphenylphosphorus, however, is found to be in the trigonal bipyramidal configuration in the solid state: P. J. Wheatley, *ibid.*, 2206 (1964).

effect may be steric, nonbonded interactions being severer in more highly coordinated complexes and a proton being smaller than an alkyl group. Ethyl-*n*-butylphenylbenzylarsonium bromide was recently observed to racemize in chloroform at 103°. The methiodides II-M and II'-M, however, do not interconvert under similar conditions.

Intermediates very similar to those that form on addition of the acid HX to tertiary phosphines should also form on LiAlH₄ reduction of tetraalkylphosphonium salts.⁵⁹ The observation that LiAlH₄ reduction of optically active methylethylphenylbenzylphosphonium iodide yields racemic methylethylphenylphosphine^{18d} may, thus, not be unusual.^{18a} The racemization might be a side reaction catalyzed by the acid formed during the reduction.

Ultraviolet Spectra. The electronic spectra of the phosphines should result from absorption by two more-or-less isolated, strongly absorbing chromophores, the diene⁴ and the phenylphosphine.⁶⁰ However, absorption by the latter, like that of phenyldimethylphosphine (Table III), should be greatly diminished in intensity upon formation of the methiodide (Table III) or oxide,⁶¹ and the spectra of II-M, II'-M, II-O, and II'-O should probably all be dominated by the diene chromophore absorption. In agreement with this presumption, the spectra of these compounds are similar (Figure 5 and Table III) and the positions of maximum absorption (about 267 mμ) are not greatly different from those of Xa (256 mμ), Xb (260 mμ), or Xc (255 mμ). But this assignment is not certain because the position of the maxima and their vibrational fine structures are like those of benzenes substituted by only weakly perturbing groups.⁶¹

In contrast to the spectra of the methiodides and oxides, those of the phosphines II and II' differ from each other. A possible reason for these differences is that the unshared pair of electrons on phosphorus occupies an orbital that overlaps appreciably with the π -molecular orbitals of the carbon skeleton. Since the orbital occupied by the unshared pair is symmetrical with respect to reflection in the plane normal to the C-3, C-4 bond axis, while the unfilled molecular orbital of lowest energy in the butadiene system is symmetrical and in the ethylene system antisymmetrical with respect to this reflection, an appreciable charge-transfer⁶² interaction is possible only in the butadiene system, and then, possibly,⁶³ only if the phenyl is on the opposite side, as in VII. The perturbation would raise the energy of the unoccupied orbital (in the butadiene system) and lower that of the filled orbital. The ultraviolet absorption would be shifted to shorter wavelength, which is the way the spectrum of II' (tentatively believed to be VII) differs from its epimer II. Other factors that might cause the ultraviolet spectra of II and II' to differ, but not their methiodides or oxides, are (i) interactions between the benzene ring and the olefin π

electrons resulting from their being closer in the tri-coordinated phosphorus compounds than in the tetra-coordinated ones, and (ii) differences in the phase of rotation about the phenylphosphorus single bond in II and II'. The first hypothesis is not supported by the proton nmr data in Table IV, and there is presently no test of the other.

The spectrum of phosphine I does not closely resemble that of either bicyclo[6.1.0]nonatriene (or cyclooctatetraene oxide) or phenyldimethylphosphine. At-



Xa, X = C(CH₃)OCOCH₃
 b, X = C(CH₃)OH
 c, X = NCN

tempts to prepare either a methiodide or phosphine oxide from I failed, and the spectra of these derivatives are therefore unknown.

Phosphorus Chemical Shifts (Table II). The large difference (65 ppm) in the ³¹P chemical shift of II and II' indicates the difficulty⁶⁴ in assuming that ³¹P chemical shifts of trivalent phosphorus compounds are the sum of group substituent constants,⁶⁵ and in accounting for the wide range of these shifts (−227 ppm for PBr₃ to +240 ppm for PH₃, with triethylphosphine at +20.4 ppm^{64a}) by *a priori* calculation.⁶⁶ This difference might be a consequence of the delocalization of the phosphorus nonbonding electrons proposed above to account for the difference in the ultraviolet spectra of II and II'. The striking phosphorus chemical shift of phosphine I—it is at much higher field than the resonance in any trialkylphosphine known^{64, 65, 67}—is expected from calculations that account for increased shielding in trivalent phosphorus compounds as the phosphorus bonding orbitals increase in p character,^{64b, 66} and from the experimental observations that in PH₃ and P₄, in which the internuclear angle is particularly small,⁶⁸ the ³¹P resonances occur at unusually high field.^{71, 72}

Experimental Section⁷³

Preparation of Dipotassium Cyclooctatetraenide. Dipotassium cyclooctatetraenide was prepared as follows.⁷⁴ Small pieces of

(64) (a) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem. Intern. Ed. Engl.*, **1**, 32 (1962). (b) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3357 (1956).

(65) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956).

(66) H. S. Gutowsky and J. Larmann, *ibid.*, **87**, 3815 (1965).

(67) K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).

(68) The H-P-H angle in phosphine is 93.5°, while the C-P-C angle in trimethylphosphine is 99.1°. ³³ P₄ is tetrahedral.⁷⁰

(69) C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.*, **81**, 798 (1951); D. L. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).

(70) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958.

(71) PH₃ at +241 and P₄ at +488 ppm: H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954); see also ref 64 and 65.

(72) In five- and six-membered cyclic phosphites and phosphates, however, no simple relationship was observed between phosphorus resonance frequency and ring size: R. A. Y. Jones and A. R. Katritzky, *J. Chem. Soc.*, 4376 (1960).

(73) Tetrahydrofuran was dried over potassium hydroxide pellets and distilled from lithium aluminum hydride. Melting points, determined on a Thomas-Hoover melting point apparatus, are uncorrected. Ultraviolet spectra were determined in 95% ethanol with a Cary 14 spectrophotometer. Nmr spectra were determined in CDCl₃ solution using a Varian Associates A-60 spectrometer and tetramethylsilane was the internal standard, unless stated otherwise. However, for the decoupling experiments a 100-Mc/sec instrument described in the text was used.

(58) L. Horner and W. Hoffer, *Tetrahedron Letters*, 3281 (1965).

(59) L. Maier, *Progr. Inorg. Chem.*, **5**, 104 (1963).

(60) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

(61) H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952); H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954).

(62) (a) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); (b) R. C. Cookson and N. Lewin, *Chem. Ind. (London)*, 984 (1956); (c) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); (d) S. Winslein, L. deVries, and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961).

(63) The directionality of the nonbonding phosphorus orbital will increase with its p character.

potassium (24 g, 0.61 g-atom) were added to dry THF (500 ml) under nitrogen. The mixture was cooled to -78° , and cyclooctatetraene (25.0 g, 0.24 mole) was added. The mixture was vigorously stirred for 18 hr at -78° , at 0° for 8 hr, and at room temperature for 14 hr. At the end of this time, a red-brown solution containing excess potassium and pale yellow, crystalline solid was obtained. The mixture was diluted with THF (150 ml) to dissolve the precipitated salt.

9-Phenyl-9-phosphabicyclo[6.1.0]nonatriene (I). Dipotassium cyclooctatetraenide solution (0.24 mole) was added dropwise under nitrogen to 70 ml (93 g, 0.52 mole) of dichlorophenylphosphine at 0° over a 90-min period. The green-black mixture was stirred for 1 hr at room temperature and then carefully quenched by the addition of ice water (150 ml) dropwise. The resulting bright orange mixture was diluted with water (250 ml) and pentane (200 ml) and dried over anhydrous magnesium sulfate. Most of the solvents were removed with a flash evaporator at water-pump pressure at room temperature, leaving an orange, viscous residue, which was further dried by placing it in a slowly rotating flask connected by means of heavy tubing to a high-vacuum manifold. A semicrystalline, dark orange residue was obtained, a portion of which was sublimed at 55° (1×10^{-6} mm) to give 9-phenyl-9-phosphabicyclo[6.1.0]nonatriene (white crystals at -78° but somewhat oily at room temperature). The compound darkens rapidly upon exposure to air.

Anal. Calcd for $C_{14}H_{13}P$: C, 79.23; H, 6.17; P, 14.61. Found: C, 79.19; H, 6.17; P, 14.56.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (II). Dipotassium cyclooctatetraenide solution (0.24 mole) was added dropwise under nitrogen to 70 ml (93 g, 0.52 mole) of dichlorophenylphosphine at 0° over a 60-min period. The green-black mixture was stirred for 2 hr at room temperature. The reaction was quenched with 100 ml of water (dropwise addition), and transferred to a filter flask where more water (250 ml) and pentane (200 ml) were added. Solid sodium carbonate was slowly stirred into the reaction mixture (under N_2) until it was neutralized. The organic material was extracted with pentane (two 100-ml portions) and dried over anhydrous magnesium sulfate, and the solvents were removed. Distillation of the orange, viscous residue (160–170° (0.4 mm)) gave 23.3 g (45.9%) of a pale yellow solid. Recrystallization from acetone and sublimation at 80° (0.1 mm) gave white, needle-like crystals of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (II), mp 85.5 – 86.5° . The crystals darken rapidly upon exposure to air, as do solutions of the compound.

Anal. Calcd for $C_{14}H_{13}P$: C, 79.23; H, 6.17; P, 14.61. Found: C, 79.15; H, 6.29; P, 14.32.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene Methiodide (II-M). 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (3.75 g, 17.7 mmoles) was dissolved in acetone (15 ml) and methyl iodide (3 ml, 6.8 g, 48 mmoles) was added with stirring and cooling. The phosphonium salt precipitated immediately as pale yellow crystals. The first crop consisted of 5.08 g (81.3%). Several recrystallizations from ethanol gave white, rod-like crystals, mp 239 – 240° ; nmr (in deuterium oxide at 100° with sodium 2,2-dimethyl-2-silapentane-5-sulfonate⁷⁵ as internal standard) τ 2.30 (multiplet, 4.86 H), 3.90 (multiplet, 6.11 H), 5.48 (multiplet, 1.99 H), 7.88 (doublet, $J = 14$ cps, 3.03 H).

Anal. Calcd for $C_{15}H_{16}PI$: C, 50.86; H, 4.55; P, 8.75; I, 35.84. Found: C, 50.64; H, 4.83; P, 8.82; I, 35.76.

Hydrogenation of II-M: Preparation of 9-Phenyl-9-phosphabicyclo[4.2.1]nonane Methiodide. 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene methiodide (II-M, 0.230 g, 0.650 mmole) was added to ethanol (20 ml) and 30% palladium over carbon (0.117 g). The mixture was hydrogenated at atmospheric pressure at 70° over a period of 4 days; 60.0 ml of hydrogen was absorbed (125%). The catalyst was removed, the solvent was evaporated, and the residue crystallized spontaneously. Recrystallization from ethanol gave short, white needles of 9-phenyl-9-phosphabicyclo[4.2.1]nonane methiodide, mp 244.5 – 245° ; nmr τ 2.3 (multiplet, 4.91 H), 7.5–9 (multiplet, 17.1 H), no olefinic protons. Analysis of this compound indicated the presence of material other than C, H, P,

and I—presumably Pd. The salt was, therefore, converted to the picrate.

9-Phenyl-9-phosphabicyclo[4.2.1]nonane Methopicate. 9-Phenyl-9-phosphabicyclo[4.2.1]nonane methiodide (II-M, 0.353 g, 1.02 mmoles) dissolved in hot ethanol (10 ml) was mixed with an equivalent amount of a hot sodium picrate solution (10 ml of ethanol containing 0.237 g, 1.03 mmoles, of picric acid and 0.076 g, 1.9 mmoles, of sodium hydroxide). The picrate deposited upon cooling was collected (0.248 g, 54.1%) and recrystallized three times from acetonitrile to give deep yellow crystals, mp 187.1 – 187.6° . A mixture melting point with 9-phenyl-9-phosphabicyclo[4.2.1]cyclooctatriene methopicate (described below) was lower, 182.5 – 184.5° .

Anal. Calcd for $C_{21}H_{24}PN_3O_7$: C, 54.66; H, 5.24; P, 6.71; N, 9.11. Found: C, 54.46; H, 5.16; P, 6.82; N, 9.20.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene Methopicate. 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene methiodide (II-M, 0.443 g, 1.25 mmoles) dissolved in hot ethanol (10 ml) was mixed with an equivalent amount of a hot sodium picrate solution (10 ml of ethanol containing 0.288 g, 1.26 mmoles, of picric acid and 0.051 g, 1.27 mmoles, of sodium hydroxide). The picrate deposited upon cooling was collected (0.365 g, 66.4%) and recrystallized three times from acetonitrile to give deep yellow crystals, mp 186.0 – 186.5° .

Anal. Calcd for $C_{21}H_{24}PN_3O_7$: C, 55.39; H, 3.98; P, 6.80; N, 9.23. Found: C, 55.09; H, 3.98; P, 7.14; N, 9.42.

Conversion of 9-Phenyl-9-phosphabicyclo[6.1.0]nonatriene (I) to 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (II). A. At 70° . 9-Phenyl-9-phosphabicyclo[6.1.0]nonatriene (I, ca. 150 mg) was dissolved in chloroform-*d* (ca. 1.5 ml), sealed into an evacuated (10^{-6} mm) nmr tube, and immersed in a thermostated oil bath and cooled in ice-water at 0.5-hr intervals for the first 2 hr, and at hourly intervals for the next 4 hr. The nmr spectrum was recorded and integrated each time the tube was removed. The relative amounts of phosphines I and II were determined from the peak areas of the cyclopropyl protons of I (at τ 7.4) and the bridgehead protons of II (at τ 6.37). A first-order kinetic plot of the data gives a half-life for I at 70.0° of 1.1×10^2 min.

B. At Room Temperature. 9-Phenyl-9-phosphabicyclo[6.1.0]nonatriene (I) was dissolved in chloroform and kept at room temperature for 2 months. The nmr spectrum of the solution at the end of this time showed that it contained only phosphine II.

Conversion of 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (II) to Its Stereoisomer (II'). A. By Heating in Acidified Chloroform Solution. 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (II) was dissolved in acidified chloroform (normal chloroform which had been acidified with hydrogen chloride gas), and sealed into an evacuated (10^{-6} mm) nmr tube. The tube was immersed in an oil bath and heated at 100° overnight. The nmr spectrum at the end of this time was that of a mixture of phosphines II and II', mainly the latter.

The nmr spectrum of a sample of phosphine II that had been dissolved in normal chloroform, sealed into an evacuated nmr tube, and heated at 100° for 1 month, indicated only the presence of phosphine II. The nmr spectrum of a similarly prepared sample of phosphine II in chloroform-*d* indicated a mixture of II and II' after overnight heating at 100° (chloroform-*d* contains a sufficient amount of acid to catalyze the rearrangement).

Phosphine II rearranges to II' in normal chloroform if heated at 160° for 24 hr. A dark, viscous solution is obtained at this temperature, indicating extensive decomposition.

B. By Pyrolysis. A Vycor pyrolysis column filled with quartz chips was heated to 480° and evacuated to 0.1 mm. Nitrogen was then bled into the column at 10 mm, and 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (II, 10 g, 47.2 mmoles) was sublimed by heating with a small flame from a side arm onto the hot quartz chips. A receiver cooled with liquid nitrogen was used to collect the product. The yellow, semisolid material obtained was sublimed at 100° (0.1 mm) to give 1.1 g (11%) of an oily mixture of phosphines II and II'. Phosphine II' predominated in the mixture. At lower temperatures, little II' was produced and at higher temperatures, much unsublimable material.

Dichlorobis(9-phenyl-9-phosphabicyclo[4.2.1]nonatriene)palladium²⁰ from II. To a solution of dichlorobis(benzonitrile)palladium⁷⁶ (0.475 g, 1.2 mmoles) in chloroform (10 ml) was added a solution of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (II, 0.50

(74) This is a procedure described by P. J. Garratt, Dissertation, Columbia University, 1963. An alternative procedure (E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 1941 (1965)), in which cyclooctatetraene was reacted with potassium near room temperature, was also used.

(75) (a) G. v. D. Tiers and R. I. Coon, *J. Org. Chem.*, **26**, 2097 (1961); (b) G. v. D. Tiers and A. Kowalsky, Abstracts of Papers, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, p 17R.

(76) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

g, 2.4 mmoles) in chloroform (5 ml). The yellow, crystalline precipitate, which formed immediately, was filtered, washed with a little chloroform, and dried. The yield was 0.59 g (82%). An analytical sample was prepared by three recrystallizations from methylene chloride and dried under vacuum (5×10^{-3} mm) at 85° . The analytical sample did not melt, but decomposed over the range $264\text{--}269^\circ$. Treatment of the complex with a basic potassium cyanide solution (see below) regenerated phosphine II. *Anal.* Calcd for $C_{28}H_{26}P_2PdCl_2$: C, 55.85; H, 5.32; Cl, 11.73. Found: C, 55.63; H, 4.18; Cl, 12.07.

Dichlorobis(9-phenyl-9-phosphabicyclo[4.2.1]nonatriene)- μ, μ' -dichlorodipalladium²⁰ from II. To a solution of dichlorobis(benzonitrile)palladium (0.475 g, 1.2 mmoles) in chloroform (10 ml) was added a solution of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (0.25 g, 1.2 mmoles) in chloroform (5 ml). After standing overnight, the reaction consisted of a deep red solution with a trace of precipitate. Filtration, addition of the filtrate to 200 ml of hexane, and filtration again gave 0.39 g of an orange solid. Two recrystallizations from methylene chloride-carbon tetrachloride yielded 0.30 g (42% yield) of the complex as orange crystals ($228\text{--}235^\circ$ dec).

Anal. Calcd for $C_{14}H_{13}PPdCl_2$: C, 43.07; H, 3.33. Found: C, 43.26; H, 3.44. Calcd for $C_{28}H_{26}P_2Pd_2Cl_4$ (osmometry) in CH_2Br_2 : mol wt, 779. Found: mol wt, 743.

Dichlorobis(9-phenyl-9-phosphabicyclo[4.2.1]nonatriene)palladium from II'. The mixture of phosphine II and II' obtained from the pyrolysis of II (1.14 g, 5.36 mmoles) was dissolved in chloroform (5 ml) and treated with a chloroform solution (10 ml) of dichlorobis(benzonitrile)palladium (1.01 g, 2.68 mmoles). Yellow crystals deposited after cooling in a freezer overnight (0.536 g, 33.2%). Three recrystallizations from methylene chloride gave the analytical sample, which did not melt, but decomposed over the range $260\text{--}268^\circ$.

Anal. Calcd for $C_{28}H_{26}P_2PdCl_2$: C, 55.85; H, 4.32. Found: C, 55.60; H, 4.57.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (II'). Dichlorobis(9-phenyl-9-phosphabicyclo[4.2.1]nonatriene)palladium (prepared from II', 0.507 g, 0.844 mmole) was stirred under nitrogen with a basic potassium cyanide solution (1.3 g, 20 mmoles, in 5 ml of 0.1 N sodium hydroxide and 5 ml of chloroform). The complex had completely dissolved after 90 min of stirring. The layers were separated; the chloroform layer was washed with water (two 2-ml portions) and dried over anhydrous magnesium sulfate. Evaporation of the chloroform gave 0.332 g (92.4%) of pure phosphine II'. The nmr spectrum did not show any peaks attributable to phosphine II. Sublimation at 80° (0.1 mm) gave white crystals of II', mp $84.5\text{--}85.5^\circ$.

Anal. Calcd for $C_{14}H_{13}P$: C, 79.23; H, 6.17; P, 14.61. Found: C, 79.42; H, 6.24; P, 14.50.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene Methiodide (II'-M). The mixture of phosphines II and II' obtained from the gas phase pyrolysis of phosphine II at 475° (0.176 g, 0.832 mmole) was dissolved in acetone (1.5 ml) and methyl iodide (0.75 ml, 12 mmoles) was added. A moderately exothermic reaction occurred upon mixing, and a white precipitate deposited (0.180 g, 61.2% based on 100% II'). Recrystallization from ethanol gave glistening white plates, mp $219\text{--}220^\circ$. A mixture melting point with II-M (mp 240°) was $184\text{--}190^\circ$; nmr τ 1.61–2.70 (complex multiplet, 4.7 H), 3.27–4.53 (complex multiplet, 6.23, H), 5.01–5.43 (multiplet, 1.99 H), 7.65 (doublet, $J = 14$ cps, 3.09 H).

Anal. Calcd for $C_{15}H_{16}PI$: C, 50.86; H, 4.55; P, 8.74; I, 35.83. Found: C, 50.81; H, 4.59; P, 8.49; I, 35.86.

Attempted Thermal Rearrangements of Methiodides II-M and II'-M. A sample of methiodide II-M dissolved in chloroform (saturated solution) was sealed in an evacuated (10^{-6} mm) nmr tube. The tube was immersed in an oil bath and heated at 100° for 2 days. Its nmr spectrum at the end of this time did not show any peaks attributable to methiodide II'-M. In a similar experiment, a rearrangement of II'-M to II-M could not be detected.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene Oxide (II'-O). **A. From II and Air.** 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (II, 2.70 g, 12.7 mmoles) was dissolved in chloroform (30 ml), and dry air was bubbled through this solution for 7 hr. Removal of the chloroform and sublimation of the residue at 160° (0.1 mm) gave 1.21 g (41.8%) of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene oxide (II'-O). Recrystallization from acetone gave white needles, mp $197.5\text{--}197.7^\circ$.

Anal. Calcd for $C_{14}H_{13}PO$: C, 73.67; H, 5.74; P, 13.57. Found: C, 73.48; H, 5.90; P, 13.77.

B. From II' and Hydrogen Peroxide. The mixture of phosphines II and II' obtained from the pyrolysis of II at 482° (0.329 g, 1.55 mmoles) was dissolved in chloroform (5 ml) and 30% hydrogen peroxide (1.5 ml, 0.45 mole) was added dropwise. An exothermic reaction occurred. After cooling, water (3 ml) was added, the layers were separated, and the chloroform layer was dried over anhydrous magnesium sulfate. Evaporation left 0.299 g (84.5%) of a crystalline residue. The nmr spectrum was identical with that of phosphine oxide II'-O described in A.

C. From II' and Air. A sample in chloroform of the phosphine mixture II and II' obtained from pyrolysis of II was exposed to air for 4 weeks. The phosphine oxide produced has an nmr spectrum identical with that of II'-O.

9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene Oxide (II-O). 9-Phenyl-9-phosphabicyclo[4.2.1]nonatriene (II, 8.13 g, 38.3 mmoles) was dissolved in chloroform (25 ml) and while the stirred solution was cooled in an ice bath, 30% hydrogen peroxide (10 ml, 4.38 g, 0.129 mole) was added dropwise. The reaction mixture was diluted with water (10 ml) and the organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent and sublimation of the residue at 160° (0.1 mm) gave 6.89 g (78.9%) of white, crystalline material. Recrystallization from benzene gave small, white needles, mp $182.8\text{--}183.4^\circ$, of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene oxide (II-O). A mixture melting point with II'-O was $153\text{--}166^\circ$.

Anal. Calcd for $C_{14}H_{13}PO$: C, 73.67; H, 5.74; P, 13.57. Found: C, 73.68; H, 5.87; P, 13.22.

Attempted Diels-Alder Reactions. **A. Phosphine II and Maleic Anhydride.** Maleic anhydride (0.43 g, 4.39 mmoles) was added to phosphine II (0.93 g, 4.39 mmoles) dissolved in benzene (20 ml). The solution immediately turned deep red, and a dark, viscous material settled to the bottom of the flask. Removal of solvent yielded only tarry material, from which nothing could be sublimed.

B. Phosphine II and Tetracyanoethylene.⁷⁷ Phosphine II (1.05 g, 4.95 mmoles) was added to tetracyanoethylene (0.653 g, 5.09 mmoles) dissolved in THF (15 ml). A red-brown color immediately developed in the solution. Removal of the solvent, and chromatography of the residue on alumina, gave a series of intensely colored products which were not characterized.

C. Methiodide II-M and Maleic Anhydride. Methiodide II-M (0.285 g, 0.805 mmole) and maleic anhydride (0.080 g, 0.816 mmole) were refluxed in xylene (40 ml) overnight. Removal of the solvent gave a crystalline residue whose melting point was similar to that of the starting material.

D. Methiodide II-M and Tetracyanoethylene. Tetracyanoethylene (0.208 g, 1.57 mmoles) was added to 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene methiodide (II-M, 0.557 g, 1.57 mmoles) dissolved in hot methanol (10 ml). A dark red-brown color developed immediately. The methanol was removed, and the dark oily residue gradually crystallized to give the phosphonium salt of methyl dicyanoacetate.²⁶ Recrystallization from acetone gave 0.313 g, 50.9%, of white, needle-like crystals, mp $130.5\text{--}131^\circ$; $\lambda_{\text{max}}^{\text{EtOH}}$ 267 m μ ($\log \epsilon$ 3.63), shoulder at 273 m μ ($\log \epsilon$ 3.57); ν (KBr) 4.54, 4.62 ($C\equiv N$), 6.07 μ ($C-O^-$); nmr τ 2.28 (multiplet, 4.84 H), 3.90 (multiplet, 6.01 H), 5.50 (multiplet, 1.97 H), 6.46 (singlet, 3.04 H), 7.82 (doublet, $J = 14$ cps, 3.14 H).

Anal. Calcd for $C_{20}H_{19}PN_2O_2$: C, 68.56; H, 5.47; P, 8.84; N, 8.00. Found: C, 68.73; H, 5.30; P, 8.93; N, 8.13.

Nmr Spectra and Their Analyses. Nmr spectra were obtained at 100 Mc/sec and at about 31° in a $CDCl_3$ solution containing tetramethylsilane (TMS). The Varian HR-100 spectrometer was equipped with a locally built field-frequency stabilizing system based on the design of Elleman, *et al.*⁷⁸ The field was locked to a side band of TMS at about 2500 cps and all spectra were produced by sweeping the frequency of a second side band provided by a General Radio Model 1107-A interpolation oscillator. Proton decoupling experiments were carried out by irradiating the multiplet of the protons to be decoupled with a third side band of the appropriate frequency and power. Phosphorus decoupling was done with an NMR Specialties Model SD-60 spin decoupler operating at 40.5 Mc/sec. The frequency of the latter was locked to that of an audiooscillator with the Anet stabilization circuit built into the decoupler.

No attempt was made to analyze the nmr spectrum of I in detail because of its broad-band nature. Unsuccessful attempts were

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(78) D. D. Elleman, S. L. Manatt, and C. D. Pearce, *J. Chem. Phys.*, **42**, 650 (1965).

made to sharpen the observed bands by changing the temperature of the sample.

The spectra of the ring protons in II, II', II-O, and II'-O were analyzed in several steps with the aid of the Swalen-Reilly iterative method.¹⁸ The complex spectrum from the nine interacting spins in each of these molecules was first simplified by simultaneously decoupling the nuclear spins of the phosphorus and the protons 1 and 6 (upfield multiplet). Under these conditions protons 7 and 8 gave a single line at their chemical shift and protons 2, 3, 4, and 5 gave an AA'BB' pattern that was readily analyzed¹⁸ to give accurate chemical shifts and interproton spin-spin coupling constants (see Table I). The chemical shift of protons 1 and 6, their spin-spin couplings to protons 2 and 5 and to the phosphorus, were obtained directly from the splittings in the upfield multiplet due to protons 1 and 6. The interproton coupling constants for protons 1, 6, 7, and 8 were obtained from the BB' portion of the AA'BB'CC' pattern from spins 1, 6, 7, 8, 2, and 5 with P decoupled. This procedure is believed to be valid because of the near-zero coupling of protons 7 and 8 (BB') with protons 2 and 5 (CC'). A check on the correctness of the resulting parameters given in Table I was made by comparing the calculated P decoupled spectrum from the eight protons with that observed. Reasonable agreement was obtained as shown for example in Figures 1b and 1c for II. Improved values for some of the parameters quoted in Table I could undoubtedly be made by making an iterative analysis of the P

decoupled spectrum (eight spins interacting). However, the results obtained as outlined above are adequate to establish the structure of II, II', II-O, and II'-O.

For compounds II' and II-O, in addition to the above analysis, the upfield multiplet from protons 1 and 6 was decoupled alone. The resulting AA'BB'CC' portion of the AA'BB'CC'X pattern (X = P) was analyzed by a simple extension⁷⁹ of the Swalen-Reilly iterative method. Where possible to compare them, the results were in satisfactory agreement with the stepwise analysis given above. It was not possible to perform this analysis for II'-O because of incomplete decoupling of protons 1 and 6 from the remaining ones. Also, the sample of II available in solution had deteriorated too much by the time this decoupling could be done to permit meaningful results to be obtained. For this reason only estimated values for $J_{P_2} = J_{P_3}$ and $J_{P_1} = J_{P_4}$ can be given at this time for compounds II and II'-O.

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N-Thionitrosoamines

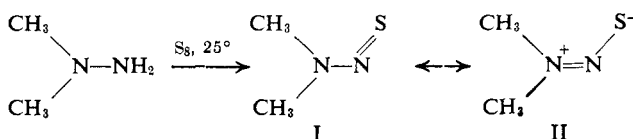
W. J. Middleton

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Abstract: N-Thionitrosodialkylamines, which are organic compounds that contain a new functional group, the thionitroso unit ($-N=S$), have been prepared by reaction of 1,1-dialkylhydrazines with sulfur and by reduction of thionylhydrazines. The thionitrosoamines are highly colored compounds. Spectral evidence suggests that a dipolar resonance structure contributes to their over-all electronic structure.

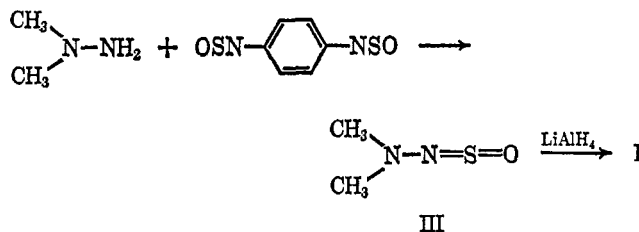
Organic compounds that contain a nitrogen-to-divalent-sulfur double bond appear to be unknown. In particular, the sulfur analogs of common nitrogen-oxygen functional groups, such as nitro and nitroso, have never been reported.¹ Because of the difference in size between the nitrogen atom and the much larger sulfur atom, a π bond connecting these two atoms should be weak due to the restricted overlap of the π orbitals. However, it appeared possible that appropriately substituted thionitro and thionitroso compounds could exist, since thiocarbonyl compounds have a π bond between carbon and sulfur, and carbon is only slightly larger than nitrogen. Of the many classes that can be postulated, N-thionitroso secondary amines should be among the most stable because of the resonance stabilization possible. This paper reports the preparation and properties of amines containing the thionitroso unit ($-N=S$), a new functional group.

Preparation of N-Thionitrosoamines. These compounds have been prepared by two different procedures, one involving a sulfuration (oxidation) and the other a reduction. The most direct process consists in treating a 1,1-dialkylhydrazine with elemental sulfur. For example, N-thionitrosodimethylamine (I) is obtained



from the reaction of 1,1-dimethylhydrazine with a heterogeneous suspension of sulfur in ether at 25°. This reaction is slow and requires 6 days for a 20% conversion of the hydrazine to product. Attempts to speed up the reaction by increasing the temperature or by increasing the concentration of dissolved sulfur by means of better solvents were unsuccessful owing to the instability of the thionitrosoamines under these conditions.

Compound I was also prepared by reduction of thionyl dimethylhydrazine (III) with lithium aluminum hydride in ether. Even under the most favorable



(1) R. J. W. Le Fevré, *J. Chem. Soc.*, 2503 (1932), has reported several unsuccessful attempts to prepare thionitro compounds.