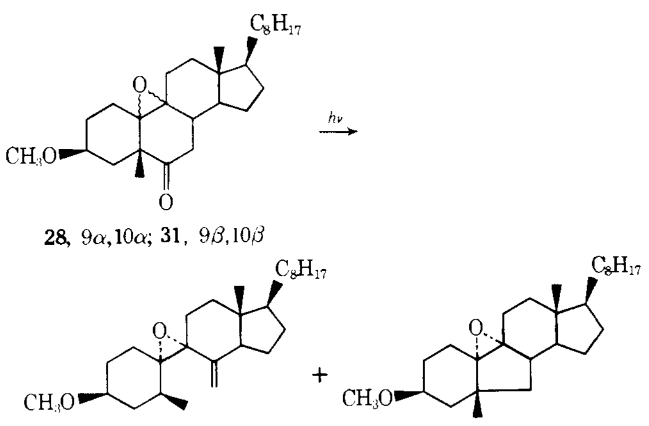

28, 9α,10α; 31, 9β,10β

29

30

ucts.[4] By contrast, the 9β,10β-epoxy ketone **31** remains unchanged when irradiated under comparable conditions.[4] In view of Scheme I, an examination of molecular models suggests that it would appear to be more likely that epoxy ketone **31** rather than **28** would undergo photodecarbonylation. This point is currently under active investigation.

Acknowledgment. This work was supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University of Delaware Research Foundation, and the Delaware Institute of Medical Education and Research.

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(1) For reviews see A. Padwa, *Org. Photochem.*, **1**, 91 (1967); R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N.Y., 1966, pp 129–140; J. A. Waters, Y. Kondo, and B. Witkop, *J. Pharm. Sci.*, **61**, 321 (1972). Also see H. J. Wuthrich, A. Siewinski, H. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **56**, 239 (1973).

(2) A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Am. Chem. Soc.*, **89**, 4435 (1967).

(3) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

(4) R. J. Chambers and B. A. Marples, *J. Chem. Soc., Chem. Commun.*, 1122 (1972).

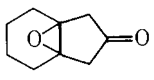
(5) R. G. Carlson, J. H.-A. Huber, and D. E. Henton, *J. Chem. Soc., Chem. Commun.*, 223 (1973).

(6) R. K. Murray, Jr., T. K. Morgan, Jr., H. Hart, and V. J. Hull, *J. Org. Chem.*, **38**, 3805 (1973).

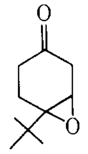
(7) R. K. Murray, Jr., and D. L. Goff, *J. Chem. Soc., Chem. Commun.*, 881 (1973).

(8) For a detailed investigation of the photochemistry of an *acyclic* β,γ-epoxy ketone see ref 2.

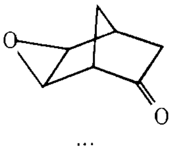
(9) The dearth of information concerning the photochemistry of β,γ-epoxy cyclic ketones may follow from the observation of Starr and Eastman[3] that irradiation of cyclohexane or methanol solutions of i "gave small amounts (less than 0.2 mol/mol of ketone) of a mixture of carbon monoxide and carbon dioxide. The product consisted of a tarry fraction (ca. 50%) and a volatile fraction containing mainly unreacted ketone along with small amounts of a number of products which were not identified." We have found irradiation of ii and iii in a variety of solvents to be similarly unrewarding. It appears that in order for product formation to become significant in the photochemistry of most β,γ-epoxy cyclic ketones that the α-carbon of the β,γ-epoxy ketone moiety must be substituted with either two alkyl groups or one exceptionally good radical stabilizing group (e.g., phenyl or cyclopropyl).



i



ii



iii

(10) Epoxy ketone **12** was prepared by treatment of 2,2-dimethylcyclohept-3-enone[11] with *m*-chloroperbenzoic acid.

(11) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Am. Chem. Soc.*, **90**, 5153 (1968).

(12) All new compounds reported gave analytical data and had spectroscopic properties consistent with the proposed structures.

(13) Carlson et al. have suggested that lactone **18** may arise by initial formation of the thermally unstable *E* isomer of **16** which undergoes an oxy-Cope rearrangement.[5]

(14) Epoxy ketone **19** was prepared by *m*-chloroperbenzoic acid epoxidation of 2,2,4,6,6-pentamethylcyclohex-3-enone which was obtained by exhaustive methylation of 2,4-dimethylcyclohex-2-enone with excess methyl iodide and sodium *tert*-pentoxide in refluxing anhydrous ether.

(15) The disappointing low yield of **20** appears to be a consequence of the extensive competitive photodecomposition of **20** which occurs under the photolysis conditions employed.

(16) Epoxy ketone **21** was prepared by treatment of the corresponding β,γ-unsaturated ketone[17] with *m*-chloroperbenzoic acid.

(17) J. Ipaktschi, *Chem. Ber.*, **105**, 1840 (1972); K. Alder, H.-J. Ache, and F. H. Flock, *ibid.*, **93**, 1888 (1960).

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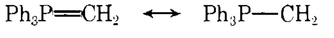
Nuclear Magnetic Resonance Studies. III. Carbon Nuclear Magnetic Resonance of Triphenylphosphonium Ylides

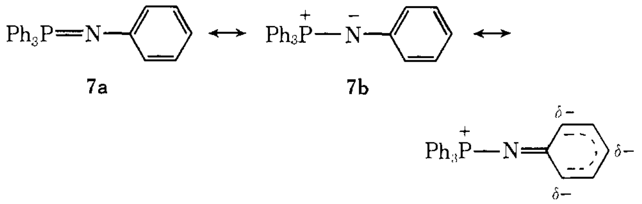
Sir:

We wish to report the preliminary results of a ^{13}C NMR study of several alkylidene triphenylphosphoranes, triphenylphosphinimines, triphenylphosphazenes, and their corresponding phosphonium salts. Stabilized ylides contain a strong electron withdrawing group adjacent to the carbon bearing the formal negative charge. The ^{13}C NMR of several stabilized ylides[1] and only one nonstabilized ylide, methylenetrimethylphosphorane,[2] have been reported previously. There has been no carbon NMR study of phosphinimines or phosphazenes, which contain formal P═N bonds. Utilization of the ^{13}C chemical shift and P-^{13}C coupling data can provide sensitive tests for models which propose[3] d orbital participation in these compounds. Contribution from the following resonance structures are considered in this study.



$$\mathrm{Ph_3P{=}CH_2} \longleftrightarrow \mathrm{Ph_3\overset{+}{P}{-}\overset{-}{C}H_2}$$

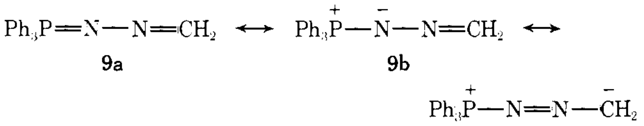
3a 3b



7a

7b

7c



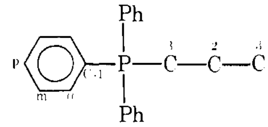
$$\mathrm{Ph_3P{=}N{-}N{=}CH_2} \longleftrightarrow \mathrm{Ph_3\overset{+}{P}{-}\overset{-}{N}{-}N{=}CH_2} \longleftrightarrow \mathrm{Ph_3\overset{+}{P}{-}N{=}N{-}\overset{-}{C}H_2}$$

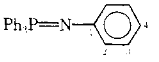
9a 9b 9c

Bart[4] has determined by means of the X-ray structure of methylenetriphenylphosphorane, that the methylene carbon is trigonally hybridized. In addition, other X-ray studies[4-6] indicate a shortened ylide bond in nonstabilized ylides. These studies have suggested a bonding picture in which there is some transfer of electronic charge from carbon to phosphorus presumably via d orbitals.[7] We recognize that the amount of dπ–pπ overlap may be relatively small between phosphorus and carbon.

Due to the rather limited NMR studies dealing with carbon involved in dπ–pπ bonding with second-row elements, we wish to examine the above effects of such interactions on

Table I. ^{13}C Chemical Shifts in Some Phosphorus Ylides



Compound	No.	Carbon chemical shift, ppm[c] 1	2	3	4	C-1	o	m	p	Solvent
$\overset{2}{\mathrm{Me}}_3\mathrm{P{=}}\overset{1}{\mathrm{C}}\mathrm{H_2}$[a]	1	-1.5	19.7							C_6D_6
$Me_3P^+{-}Me\ I^-$[b]	2	11.3								$CDCl_3$
$Ph_3P{=}CH_2$	3	-4.1				132.3	133.1	128.6	131.3	6:1 $C_6D_6-Et_2O$
$Ph_3P^+{-}Me\ I^-$	4	11.4				118.8	133.7	130.5	135.2	$CDCl_3$
$Ph_3P{=}CMe_2$	5	9.0	20.8			133.6	133.8	128.3	130.6	6:1 $C_6D_6-Et_2O$
$Ph_3P^+{-}CHMe_2\ Br^-$	6	21.5	16.4			117.5	133.8	130.6	134.9	$CDCl_3$
	7	151.0	123.4	128.5	117.3	131.2	132.4	128.4	131.5	$CDCl_3$
$Ph_3P^+{-}NHPh\ Br^-$	8	137.8	123.5	129.2	121.8	119.8	133.5	130.0	135.2	DMSO-d_6
$Ph_3P{=}N{-}N{=}CH_2$	9	137.7				129.4	133.2	128.6	132.0	$CDCl_3$
$\mathrm{Ph_3P^+{-}\underset{\underset{Me_1}{\vert}}{N}{-}N{=}\underset{2}{C}H_2\ I^-}$	10	34.1	136.6			118.6	134.1	130.4	135.7	$CDCl_3$

[a] Values taken from H. Schmidbauer, W. Buchner, and D. Scheutzow, *Chem. Ber.*, 106, 1251 (1973). [b] Value taken from W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968). [c] The solutions were examined with a Bruker HFX-90 spectrometer at an operating frequency of 22.63 MHz. The carbon chemical shifts are relative to internal TMS. All phosphorus compounds were prepared by standard procedures.

Table II. $^{31}P-^{13}C$ Coupling for Some Phosphorus Ylides

Compound	No.	$^{31}P-^{13}C$ coupling, Hz[d] 1	2	3	4	C-1	o	m	p
$Me_3P{=}CH_2$[a]	1	90.5 (J_{CH} = 149)	56 (J_{CH} = 127)						
$Me_3P^+{-}Me\ I^-$	2	56[b] (J_{CH} = 134)[c]							
$Ph_3P{=}CH_2$	3	51.9 (J_{CH} = 133)				83.6	9.8	11.6	2.4
$Ph_3P^+{-}Me\ I^-$	4	57.1				88.6	10.7	12.9	3,0
$Ph_3P{=}CMe_2$	5	121.5	13.4			81.2	8.5	11.6	2.4
$Ph_3P^+CHMe_2\ Br^-$	6	47.0	2.0			83.1	9.2	12.1	3.0
$Ph_3P{=}N{-}Ph$	7	2.4	17.5	*	*	98.7	9.6	11.9	2.8
$Ph_3P^+{-}NHPh\ Br^-$	8	2.4	18.3	*	6.7	102.5	11.6	13.4	*
$Ph_3P{=}N{-}N{=}CH_2$	9	45.9				93.6	8.3	11.4	2.7
$\mathrm{Ph_3P^+{-}\underset{\underset{Me}{\vert}}{N}{-}N{=}CH_2\ I^-}$	10	6.7	12.2			103.3	11.0	13.4	2.7

[a] Values taken from H. Schmidbauer, W. Buchner, and D. Scheutzow, *Chem. Ber.*, 106, 1251 (1973). [b] Value taken from W. McFarlane, *Proc. Roy. Soc., Ser. A*, **306**, 185 (1968). [c] Value taken from F. J. Petracek, et al., *Tetrahedron Lett.*, 707 (1970). [d] The numbering system is as in Table I. An asterisk indicates unresolved coupling.

the ^{13}C spectra in these compounds, We do this with the assumption that differences in the amount of dπ-pπ bonding are important for the title compounds and that the effects observed in the $^{13}C-^{31}P$ and $^{13}C-^{1}H$ coupling constants are due largely to changes in effective nuclear charge as the amount of dπ-pπ overlap varies. Also we feel that the observed changes in the ^{13}C chemical shifts are largely due to changes in the charge density of the ylide carbon. The above assumptions regarding the effects in the ^{13}C spectra are only tentative and are subject to revision as more theoretical studies of dπ-pπ bonding with second and lower row elements come to light.

The values of the ^{13}C chemical shifts and $^{31}P-^{13}C$ couplings for the phosphonium ylides and their salts are given in Tables I and II, respectively. The carbons bearing the formal negative charge in methylenetriphenylphosphorane (**3**), methylenetrimethylphosphorane (**1**), and isopropylidenetriphenylphosphorane (**5**), are shielded by 15.5, 12.8, and 12.5 ppm, respectively, from carbon-1 in their corresponding phosphonium salts. Furthermore, $^1J_{^{31}P-^{13}C}$ for this carbon increases dramatically in the order: **3** < **1** < **5** while $^1J_{^{31}P-^{13}C}$ remains relatively constant for the phosphonium salts. A model which is consistent with these results is as follows; in going from an sp^3 hybridized carbon in the phosphonium salts **2**, **4**, and **6** to an sp^2 hybridized carbon in the ylides **1**, **3**, and **5** the amount of s character in the hybrid orbital of carbon making up the P-C bond increases; thus one would expect a larger $^1J_{^{31}P-^{13}C}$ coupling for carbon-1. However, if the effective nuclear charge on carbon is considered to be an important factor in determining the magnitude of $^1J_{^{31}P-^{13}C}$,[8] then the magnitude of the coupling must correspondingly decrease in going from a phosphonium salt to an ylide since carbon-1 assumes a formal negative charge. The contribution of resonance structures analogous to that of **3a** for these ylides will shorten the P-C bond thereby increasing the amount of s character in the carbon hybrid of the P-C bond and increase the effective nuclear charge on carbon. Thus the data in Table II are consistent with the notion that transfer of electron density from carbon to phosphorus in **5** is greater than in **1** or **3**.[9] This is also borne out by molecular orbital calculations.[10] The high field chemical shifts for carbon-1 in ylides **1**, **3**, and **5** compared to that found for typical carbon-heteroatom double bonds (i.e., carbon-2 in **10**) is considered to be a natural consequence of overlap utilizing the diffuse d orbitals since a portion of the negative charge will still be concentrated near carbon (a discussion of this phenomena is given in the references of footnote 7).

The ^{13}C chemical shifts for *N*-phenyltriphenylphosphinimine (7) indicate that there may be some contribution of **7c** to the total electron distribution in this compound. Thus the para carbon of the phenyl group adjacent to nitrogen (carbon-4) is shielded by 4.5 ppm in **7** compared to *N*-anilinotriphenylphosphonium bromide (**8**). The similarity of the chemical shifts for the methylene carbons in formyltriphenylphosphazene (**9**) and its phosphonium salt, **10**, suggests that **9c** does not contribute appreciably toward the electronic structure of **9**. It is also interesting that there is a large difference in $^3J_{^{31}P-^{13}C}$ for the methylene carbon in **9** compared to $^3J_{^{31}P-^{13}C}$ for carbon-2 in **7**. Part of this difference is assuredly due to the substitution of an additional nitrogen atom in **9**. This is analogous to the large values of $^3J_{C-C}$ and $^3J_{C-H}$ when one of the coupled carbons is adjacent to a nitrogen, in pyridine for example.[11] It is also found that the methylene protons are nonequivalent in **9** which implies that the P=N and N=CH$_2$ groups lie solely in a cisoid or transoid configuration. Framework molecular models clearly show the transoid geometry to be less sterically hindered. Thus part of the difference in $^3J_{^{31}P-^{13}C}$ in **7** and **9** results from the fact that the coupling in **9** is transoid, while that in **7** is an average of cis and transoid.

Acknowledgment. We wish to thank the National Institutes of Health for partial financial support of this project.

References and Notes

(1) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).
(2) H. Schmidbauer, W. Buchner, and D. Scheutzow, *Chem. Ber.*, **106**, 1251 (1973).
(3) (a) A. W. Johnson, "Ylide Chemistry," Academic Press, New York, N.Y., 1966; (b) H. J. Bestmann and R. Zimmermann in, "Organic Phosphorus Compounds," Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, p 1.
(4) J. C. J. Bart, *J. Chem. Soc. B*, 350 (1969).
(5) M. J. E. Newlins, *ibid.*, 942 (1971).
(6) R. M. Wing, *J. Am. Chem. Soc.*, **90**, 4828 (1968).
(7) There also exists the possibility of a hybrid combination of empty 3d and 4p orbitals which could provide energetically more favorable overlap. This remains a matter for theoretical chemists to sort out. For recent reviews of this subject see C. A. Coulson, *Nature (London)*, **221**, 1106 (1969); K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969); M. E. Dyatkina and N. M. Klimenko, *Zh. Strukt. Khim.*, **14**, 173 (1973).
(8) See, for example, J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N.Y., 1972, pp 324-325, 377-378, and references therein.
(9) A referee has suggested that estimations of the percent s character in the C-H bond by J_{C-H} using the Muller-Pritchard relationship for **2** and **3** indicate that the hybridization of carbon-1 in **2** and **3** is not substantially changing. This is contrary, however, to the X-ray data for **3**. This relationship, also, is of dubious merit for compounds other than hydrocarbons; see, for example, ref 8 for a full discussion.
(10) R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **92**, 3929 (1970); D. B. Boyd and R. Hoffmann, *ibid.*, **93**, 1064 (1971).
(11) Reference 8, p 378; Y. Takeuchi and N. Dennis, *J. Am. Chem. Soc.*, **96**, 3657 (1974).

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Crystal and Molecular Structure of $(NbCl_5)_2(C_{10}H_{20}S_4)$. An Adduct of $NbCl_5$ with an "Inside Out" Bridging Macrocyclic Ligand

Sir:

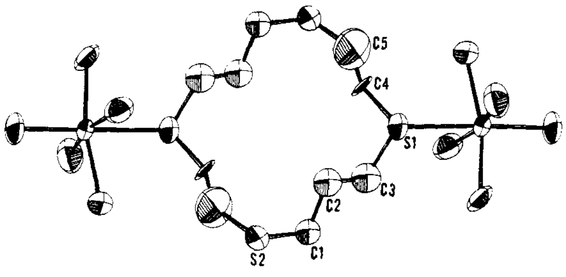
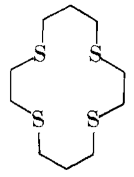
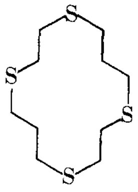


Figure 1.

Numerous structural studies of macrocyclic amine complexes[1-3] have appeared in recent years. We now wish to report the first structure of a transition metal complex containing a four-sulfur macrocyclic ligand (I). Following Ochrymowycz,[4] we shorten the full name 1,4,8,11-tetrathiacyclotetradecane to S$_4$-ethano-propano[14], or S$_4$-e-pr-[14], thus denoting a 14-membered ring containing four sulfur atoms separated by alternating ethano and propano fragments.[5] Reaction of NbCl$_5$ with (I) in benzene yields dark, wine-red crystals of (NbCl$_5$)$_2$(S$_4$-e-pr[14]) which slowly deposit over a period of hours.[6] Unlike any other macrocycle for which structural data are available, the ligand exists in the complex as II, an "inside out" conformation.



I



II

Since structure I is found in the complex Cu(S$_4$-e-pr[14])(ClO$_4$)$_2$,[7] it is likely that interaction with the metal ion aids in an interconversion to II. The entire process requires considerable conformational reorganization as can be seen from examination of a molecular model, and likely proceeds in a stepwise fashion through several energetic barriers. The structure of S$_4$-e-pr[14] in solution is uncertain, and the interconversion may be substantially aided by a pseudo-rotation process,[8] In the complex, the ring is not completely inside-out, presumably due to repulsions among the eight hydrogen atoms directed toward the center of the ring. This can be seen in the disordered structure looking down the *a* axis of the crystal (Figure 1) where the carbon atoms in the ethano bridges are twisted out of the "plane" of the ring.

The complex, (NbCl$_5$)$_2$(S$_4$-e-pr[14]), crystallizes in the space group $P2_1/n$ with unit cell contents of two complex molecules and two molecules of solvent benzene. The cell constants are $a = 7.925 \pm 0.006$ Å, $b = 19.516 \pm 0.012$ Å, $c = 10.212 \pm 0.005$ Å, and $\beta = 88.62 \pm 0.05°$. Intensity data were collected on a Syntex P2$_1$ diffractometer using graphite-monochomatized Mo Kα radiation to a 2θ of 50°. Due to the disorder, revealed clearly in rotation photographs of over 12 crystals, the scan range was set to ±1.2°, slightly wider than normal, to ensure that the entire broadened peak was scanned. Since the crystals are nearly opaque, the disorder at this point could not be distinguished from twinning. Of the 3071 reflections, the intensities of 1062 were $>3\sigma(I)$ above background and were used in the