$COCH_3$), 2.87 (s, 3 H, 7-CH_3), 3.17 (s, 3 H, 12-CH_3)), and 6-acetoxy-7,12-dimethylbenz[a]anthracene (9), mp 138–139° (nmr 2.30 (s, 3 H, $COCH_3$), 3.02 (s, 3 H, 7-CH_3), 3.18 (s, 3 H, 12-CH_3), 7.12 (s, 1 H, 5-H)), respectively. We had hoped to prepare the pure hydroxy compounds corresponding to 8 and 9 by acid-catalyzed methanolysis of 8 and 9. However, on standing with methanol containing hydrogen chloride at room temperature, *the methoxy compounds,* 6 *and* 7, *were obtained in almost quantitative yields!* As far as we know this represents unparalleled behavior for phenolic acetates.

Since methanolysis surely produces methyl acetate and the phenolic tautomer first, we have two cases in which a phenol is converted into its methyl ether by mild treatment with methanolic HCl. Neither 1- or 2-naphthol exhibits this behavior. Our interpretation of these unexpected results is that the benzanthracene phenols rapidly tautomerize to the ketonic tautomers which add methanol to form hemiketals. The latter lose water to yield the methyl ethers, 6 and 7,[9] as shown (only for the 5-substituted case) in Scheme I. Similarly, both the material obtained on sublima-

Scheme I
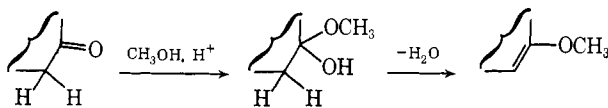
tion of 5 over acid alumina and the dihydrodiol, 4, were converted into 6 in high yield by methanolic HCl.

The tendency for 2 and the 6-hydroxy isomer to exist in the keto form may be explained by the steric strain due mainly to the 12-methyl group.[10] This strain is relieved more in the keto form than in the phenol form. The question as to whether similar equilibria exist in other derivatives of benz[a]anthracene is under investigation.

The fact that the keto form, 4, is so reactive may be of significance in the metabolic processes by which 7,12-dimethylbenz[a]anthracene, DMBA, induces cancer. From evidence we have adduced, it seems probable that carcinogenic metabolism involves the 5-position in 7-methylbenz[a]anthracene and DMBA.[11] Current hypotheses suggest that 3 has a role in carcinogenesis.[12] *We suggest that the reactive intermediate in the case of DMBA may be the ketonic substance* 4 *which in principle could readily be formed from an epoxide precursor or some alternate intermediate.* The reason why DMBA is more active as a carcinogen than 7-methylbenz[a]anthracene may be related to the increased steric strain in DMBA which causes 2 to have a much larger ketonic component than 5-hydroxy-7-methylbenz[a]anthracene. Further studies to test the above hypothesis are under way. The carcinogenic activity of hydroxy (part keto?) derivatives of 7-methyl-

benz[a]anthracene and of 12-methylbenz[a]anthracene are to be assayed.[13]

(13) We hope to be able to supply samples of these materials and of 2 and 4 to interested investigators in the near future.
(14) Postdoctoral Research Associate.
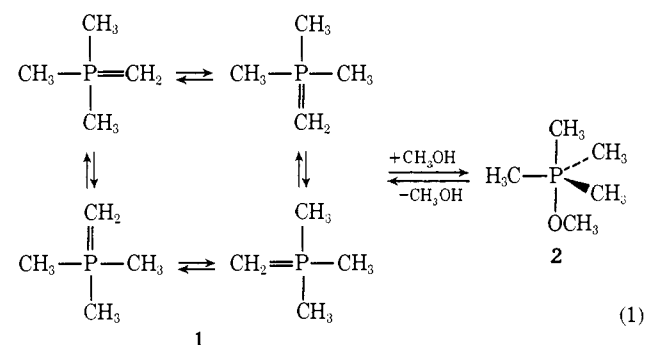
Melvin S. Newman,* Daniel R. Olson[14]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

A Carbon-13 and Phosphorus-31 Study of Tetramethylmethoxyphosphorane

Sir:

The title compound (2) has recently been prepared[1] from salt-free trimethylmethylenephosphorane (1)[2] and methanol (eq 1). It was assigned a trigonal bipyra-

$$\text{(1)}$$

midal molecular structure on the basis of analytical and spectral data.[3] One of the most interesting implications of this geometry is the appearance of one of the methyl groups in an *axial* position. This proposal rested primarily on the strong shielding of the phosphorus nucleus, which is characteristic of pentacoordinate phosphorus (δ_p −88 ppm, *i.e.*, upfield of the H_3PO_4 standard), and on the low temperature proton nmr spectrum.[3] However, the overall pmr behavior of compound 2 is extremely complex due to facile exchange of protons between the methoxyphosphorane and the various ylidic species,[3,4] as well as the methanol, and the corresponding scrambling of the methoxy groups (eq 1). Ambiguities arising from these dynamic phenomena[5] should be greatly reduced in the ^{13}C nmr spectra, and it was therefore felt desirable to support the proposed structure by additional, more detailed nmr studies and to further characterize the state of

(9) A somewhat related example of the formation of an aryl ether from a ketone is supplied by the conversion of 1,2-dihydrobenz[de]-anthracen-3-one to 3-ethoxy-7H-benz[de]anthracene, on heating in ethanol. See D. W. Cameron, D. G. I. Kingston, and P. E. Schutz, *J. Chem. Soc. C*, 2113 (1967).
(10) A discussion of the steric effect of the 12-methyl group on carcinogenic activity has been presented by M. S. Newman and R. F. Cunico, *J. Med. Chem.*, 15, 323 (1972).
(11) M. S. Newman and R. F. Cunico, *J. Med. Chem.*, 15, 323 (1972), and references therein.
(12) E. Boyland, *Biochem. Soc. Symp.*, 5, 40 (1950); D. M. Jerina, J. W. Daly, B. Witkop, P. Zaltzman-Nirenberg, and S. Udenfriend, *J. Amer. Chem. Soc.*, 90, 6525 (1968).

(1) H. Schmidbaur and H. Stühler, *Angew. Chem.*, 84, 166 (1972); *Angew. Chem., Int. Ed. Engl.*, 11, 145 (1972).
(2) H. Schmidbaur and W. Tronich, *Chem. Ber.*, 101, 595 (1968).
(3) H. Schmidbaur, H. Stühler, and W. Buchner, *Chem. Ber.*, 106, 1238 (1973).
(4) H. Schmidbaur and W. Tronich, *Chem. Ber.*, 101, 604 (1968).
(5) The mechanism of the proton exchange of ylids has been under continuing experimental[4,6,7] and theoretical study,[8] but no final conclusion has been reached as yet.
(6) K. Hildenbrand and H. Dreeskamp, *Z. Naturforsch. B*, 28, 226 (1973).
(7) H. Schmidbaur, W. Buchner, and D. Scheutzow, *Chem. Ber.*, 106, 1251 (1973).
(8) R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, 92, 3929 (1970); D. B. Boyd and R. Hoffmann *ibid.*, 93, 1064 (1971).

Table I. Nmr Parameters of Tetramethylmethoxyphosphorane, $(CH_3)_4POCH_3$, 2, in Toluene-d_8

Nucleus	Temp, °C	¹H decoupling	Position	Chem. shift, δ^a	Multiplicity	Coupling constant (Hz)
¹H	−80	No	H_{eq}	1.17	d	$^2J(PH) = 14.0$
		No	H_{ax}	−0.04	s(broad)	$^2J(PH) = {}^d$
		No	H_{OMe}	2.80	d	$^3J(PH) = 8.5$
	+30	No	$H_{eq/ax}$	1.04	s	
		No	H_{OMe}	2.79	s	
¹³C	−90	Yes	C_{eq}	19.4	d	$^1J(PC) = 116.0$
		No	C_{eq}	19.4	dq	$^1J(HC) = 127.7$
		Yes	C_{ax}	34.3	d	$^1J(PC) = 7.3^b$
		No	C_{ax}	34.3	dq	$^1J(HC) = 120.1$
		Yes	C_{OMe}	49.5	d	$^2J(CP) = 6.8$
		No	C_{OMe}	49.5	dq	$^1J(HC) = 135.7$
	+27	Yes	$C_{eq/ax}$	23.1	d	$^1J(PC) = 87.9$
		No	$C_{eq/ax}$	23.1	Broad	
		Yes	C_{OMe}	49.7	s	
		No	C_{OMe}	49.7	q	$^1J(HC) = 135.7$
³¹P	−90	Yes		−88	s	$^1J(PC_{eq}) = 113^c$ $^1J(PC_{ax})^d$
	+80	Yes		−89	s	$^1J(PC_{eq/ax}) = 88^c$

^{a} ¹H relative to external TMS, ±0.05 ppm; ¹³C relative to TMS after conversion of shifts measured relative to $C_6D_5CD_3$ (δ 20.5), ±0.1 ppm; ³¹P relative to external H_3PO_4, ±0.5 ppm. ^{b} ±2.4 Hz, other values ±1.0 Hz. ^{c} From satellites. ^{d} Signals are broadened, but no coupling is resolved.

bonding between phosphorus and the axial and equatorial methyl groups.

The *low temperature, proton-decoupled* ¹³C *nmr spectra*, in both the continuous wave and pulse Fourier transform mode,[9] fully confirmed the earlier suggestions (Figure 1a). The high intensity doublet of the three equatorial methyl carbons and the doublet of the methoxy carbon are clearly distinguished from the signal of the axial methyl carbon, which shows only a very small ^1J (PC_{ax}) coupling, whereas ^1J (PC_{eq}) is much larger than in related tetracoordinate methyl phosphorus(V) compounds (Table I).[10]

The *non-¹H-decoupled* ¹³C *spectra* finally showed the expected quartet structure of all the lines and yielded the data for the ¹H–¹³C couplings in the three different types of methyl groups at the low temperature limit. Interestingly ^1J (HC) is also significantly different in the equatorial and axial methyl groups at phosphorus. ^1J(HC) for the methoxy group is normal.[11]

The spectra of samples *at or above ambient temperature* are also as expected. The couplings ¹H₃CO³¹P and ¹³CO³¹P as well as ¹H₃C³¹P are absent, and there is only one singlet signal for all PCH₃ hydrogens and *only one doublet signal for the* PC_4 *carbon atoms* (Figure 1b). The ^1J (PC) value of 88 Hz of the latter is exactly the weighted average (3:1) of ^1J (PC_{eq}) and ^1J (PC_{ax}), as measured at −90° (calcd 88.9 Hz). Likewise, the ³¹P resonance signal carries only one ¹³C satellite doublet of 88 Hz spacing at 30°.

The room temperature, non-hydrogen-decoupled ¹³C spectra show the expected quartet structure for the methoxy carbon but still no hydrogen coupling for the methyl groups attached to phosphorus. These results can again be interpreted in terms of the exchange processes depicted in eq 1, which indicate intermolecular scrambling of the methoxy groups as well as of all methyl hydrogens at phosphorus. All four carbon

(9) Varian XL 100-15, −90°, Bruker HX 90, −80°.

(10) $^1J(PC_{eq})$ now also was observed in the *low temperature*, ¹H decoupled CW ³¹P nmr spectra (−96°), through location of the corresponding satellite lines to the phosphorus signal. (Detection of ^1J (PC_{ax}) was less reliable because of the minute intensity of these lines and their poor spacing from the main signal.)

(11) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972, p 337.
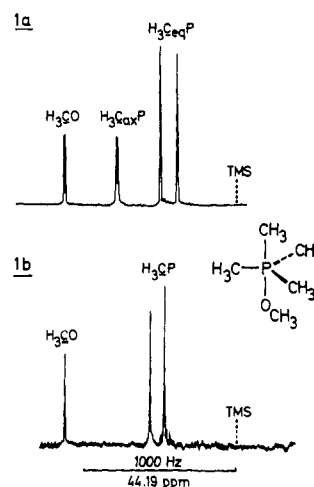
Figure 1. PFT-¹³C-nmr-spectrum of $(CH_3)_4POCH_3$, 2, in toluene at −90° and (b) at +35°, both hydrogen decoupled.

atoms remain attached to phosphorus at any time and are only subject to a positional exchange, thereby retaining an *averaged* ¹³C–³¹P coupling. In addition, the agreement of observed and calculated ^1J (PC) values is proof for identical signs for ^1J (PC_{eq}) and ^1J (PC_{ax}).

Current theories of bonding in a trigonal bipyramidal polyhedron[12] call for little or no phosphorus s character in the axial bonds and roughly an sp^2 hybrid configuration in the equatorial orbitals. Together with the earlier results on the $(CH_3)_4P^+$ cation,[5,6] and other tetracoordinate onium species, the ^1J (PC) values of 2 show a remarkably good correlation with this picture: sp^2 (eq) 114 Hz, sp^3 (tetrahedral) 56, p_z (or p_zd_z) (axial) 7.8. The last figure should be close to zero in the ideal case, but obviously the presence of a methoxy group in the second axial position is not without consequences.

The high ionic character of the P–O bond is likely to

(12) (a) R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 112 (1963); *Surv. Progr. Chem.*, **1**, 81 (1963); (b) J. I. Musher, *Angew. Chem.*, **81**, 68 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); (c) F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963, p 114.

induce some deviations from the TBP geometry in the sense that there will be a bending of the equatorial bonds toward the oxygen atom.[13,14] This, however, is equivalent to appearance of more s character in the axial and an s decrease in the equatorial orbitals. Interestingly, a ^1J (PC_{eq}) of as much as 128 Hz has been found[15] for $(CH_3)_3PF_2$, where such a distortion is ruled out by symmetry. In this case, however, a special inductive effect of the fluorine atoms on ^1J (PC_{eq}) is also to be considered. Thus only the investigation of the hitherto unreported $(CH_3)_5P$ is likely to provide pertinent unequivocal evidence. Pentamethylantimony[16] and the recently reported pentamethylarsenic[17] are unfortunately undergoing too rapid reorganization processes even at very low temperatures to yield straight-forward information.

(13) A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, **91**, 297 (1969). In the crystal structure of $(C_6H_5)_4SbOH$ an average bond angle of 86.7° was found for $C_{eq}-Sb-O!$

(14) K. Shen, W. E. McEven, S. I. La Plata, W. C. Hamilton, and A. P. Wolf, *J. Amer. Chem. Soc.*, **90**, 1718 (1968). In the crystal structure of $(C_6H_5)_4SbOCH_3$ an average bond angle of 87.3° was found for $C_{eq}-Sb-O$.

(15) H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Commun.*, 671 (1970). ^1J (HC) is 129.3 Hz for $(CH_3)_3PF_2$, ^2J ($PC_{eq}H$) is 17.5 Hz.

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

(17) K.-H. Mitschke and H. Schmidbaur, *Chem. Ber.* **106**, 3645 (1973).

(18) Address correspondence to this author at Anorganisch-Chemisches Laboratorium, Technische Universität München.

H. Schmidbaur,*[18] W. Buchner, F. H. Köhler

Anorganisch-chemisches Laboratorium Technische Universität München, 8000 Munich, Germany and Institut für Anorganische Chemie, Universität Würzburg 8700 Würzburg, Germany

The Second Triplet State of Naphthalene in a Sensitized Reaction in Solution[1]

Sir:

In a series of papers we reported examples of triplet–triplet energy transfer from the second triplet states of anthracene[2] and substituted anthracenes.[3-5] It was shown that the average lifetime of 9,10-dibromoanthracene T_2 is $(2.2 \pm 0.5) \times 10^{-10}$ sec,[3] much longer than that commonly assumed for a higher excited state in condensed media.[6] We now wish to report a case of energy transfer from naphthalene T_2 and the determination of its lifetime.[7]

One of the common and successful approaches to study the second triplet states of anthracenes is chemical sensitization where the excited state properties can be derived from examination of yields of products of acceptors.[3-5] However, direct application of this method to naphthalene T_2 as donor may present diffi-

(1) The Role of Second Triplet States in Solution Photochemistry. VIII. For No. VII, see ref 5.

(2) R. S. H. Liu and R. E. Kellogg, *J. Amer. Chem. Soc.*, **91**, 250 (1969).

(3) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 213 (1969).

(4) K. S. Y. Lau, R. O. Campbell, and R. S. H. Liu, *Mol. Photochem.*, **4**, 315 (1972).

(5) R. O. Campbell and R. S. H. Liu, *J. Amer. Chem. Soc.*, **95**, 6560 (1973).

(6) See, *e.g.*, F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

(7) A possible case of reaction from the T_2 of a substituted naphthalene is in the literature, see p 4371 in H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **92**, 4366 (1970).

culties at least in two ways. One is that many of the olefin acceptors when used at high concentrations are known to quench the S_1 state of naphthalene.[8] Secondly, because of closer spacing between the T_1 and T_2 states (see Chart I),[9] its lifetime may become too short for the bimolecular energy transfer process to be competitive with its unimolecular decay, particularly at acceptor concentrations where singlet quenching is negligible. Some modifications will have to be introduced.

The procedure we used with some success is one parallel to that used in studies of energy transfer in solid[2]; *i.e.*, a host compound (solvent) with appropriate triplet energy is introduced which serves both as a T_2 trapping agent and a carrier of excitation energy to the eventual acceptor *via* excitation-hopping among like molecules. This approach has been successfully tested in the anthracenes.[4] The system described below involves the following compounds: donor, naphthalene (N); T_2 trap and energy carrier, benzene (B); inert cosolvent, hexane; acceptor, *endo*-dicyclopentadiene (E) which is known to undergo internal cycloaddition in the triplet state.[10] The key energy levels of the compounds involved are shown in Chart I. Clearly, the
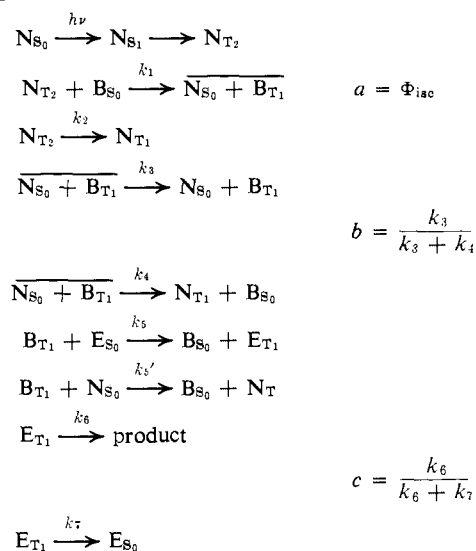
Chart I
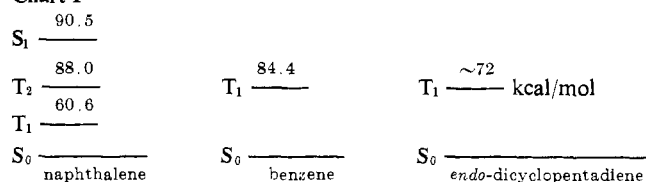
level of benzene T_1 makes it ideal both to trap N_{T_2} and to excite E.[11]

With this four component mixture, the scheme of naphthalene sensitized reaction of *endo*-dicyclopentadiene becomes that shown in Scheme I.

Scheme I

(8) (a) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); (b) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972).

(9) The energy of N_{T_2} was based on absorption study on a single crystal of naphthalene: D. M. Hanson and G. W. Robinson, *J. Chem. Phys.*, **43**, 4175 (1965).

(10) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

(11) We assumed the E_{T_1} energy is close to that of norbornene which is estimated to be close to 72 kcal/mol: D. R. Arnold, *Advan. Photochem.*, **6**, 330 (1968).