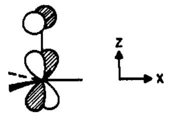
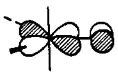
Fund for creating this circumstance. The research of R. H. and J. M. H. was generously supported by the National Science Foundation, the National Institutes of Health (GM 13468), and the Petroleum Research Fund of the American Chemical Society. The initial interest of R. H. in phosphorane chemistry was stimulated by D. A. Usher and F. H. Westheimer. We are grateful to M. Marsh, D. B. Boyd, and A. R. Rossi for discussions of this problem.

Appendix

Equatorial *vs.* Axial d–p π Bonding. The usual argument concerning this point[3,20] goes as follows: Consider a pair of donor orbitals in an axial position, e_x, e_y (**6**), and in an equatorial position, b_1, b_2 (**7**). The P 3d orbitals which can by symmetry interact with these donor orbitals are: $e_x + d_{xz}$, $e_y + d_{yz}$, $b_1 + d_{xz}$, $b_2 + d_{xy}$. The difference between axial and equatorial substitutions comes down to a weighing of the interaction $e_y + d_{yz}$ (axial) *vs.* $b_2 + d_{xy}$ (equatorial). It is assumed that the d_{xy} orbital is partially tied up in improving equatorial σ bonding. Thus the $e_y + d_{yz}$ axial interaction is said to be more stabilizing.

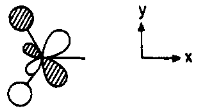


$e_y + d_{yz}$



$b_2 + d_{xy}$

In contrast to this we find that over a wide range of d-orbital positions there is very little interaction with the PH_5 σ orbitals. Instead we see significant mixing with PH_5 σ^* orbitals, depressing the e′ (d_{xy}, $d_{x^2-y^2}$) d orbital combination and making it more available as an acceptor orbital. The combined $d_{xy} + PH_{\sigma^*}$ orbital has the shape shown in **18**. The bonding character in its combination with the donor p orbital is enhanced, **19**.



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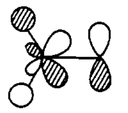


19

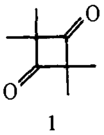
Pentacovalent Phosphorus. IV. Cyclic Pentacovalent Phosphoranes from Reaction of Trivalent Phosphorus Compounds with Dimethylketene

Wesley G. Bentrude,* W. Delmar Johnson,[1] and Wajid A. Khan

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received August 9, 1971*

Abstract: The reaction at −70° of dimethylketene with a wide variety of PXYZ gives a series of new 2:1 adducts containing pentacovalent phosphorus in a five-membered ring (**5**). Spectroscopic and chemical evidences for structure **5** are presented. Their preferred configurations from pmr spectra are discussed on the basis of trigonal-bipyramidal structures. The relative stabilities of the series of adducts (**5**) are shown to be in accord with the expectations based on the strain and polarity rules. They are further shown to undergo clean reaction with water, methanol, CS_2, CO_2, CH_3I, and Br_2 to give structurally novel products often in high yields.

Our interests in the chemistry of pentacovalent phosphorus in general,[2] and especially in the reactions of trivalent phosphorus compounds with the dione and lactone dimers of dimethylketene (**1** and **2**),[3] led us to examine the reaction of dimethylketene itself with trivalent phosphorus nucleophiles. Reactions of **1** and **2** with various PXYZ appear to proceed[3] *via* pentacovalent species of the types **3** and **4**. It seemed quite possible that intermediates of this type might be generated independently by reactions of dimethylketene with PXYZ at low temperatures and stabilized for study under those conditions. Instead we find that near-quantitative amounts of 2:1 adducts of structure **5** are formed in reactions with general applicability to a wide variety of trivalent phosphorus derivatives, PXYZ. The phosphorane ring system containing the functionality



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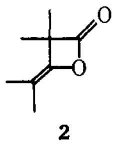

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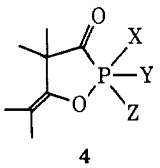

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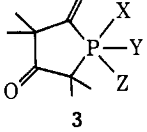

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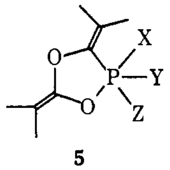

5

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[1] National Institutes of Health Predoctoral Fellow. Taken in part from the Ph.D. Thesis of W. D. Johnson, University of Utah, 1969; published in part in preliminary form: W. G. Bentrude and W. D. Johnson, *J. Amer. Chem. Soc.*, 90, 5924 (1968).

[2] W. G. Bentrude and K. R. Darnall, *Chem. Commun.*, 862 (1969); W. G. Bentrude, *ibid.*, 174 (1967); W. G. Bentrude and K. R. Darnall, *Tetrahedron Lett.*, 2511 (1967); W. G. Bentrude, *J. Amer. Chem. Soc.*, **87**, 4026 (1965).

[3] W. G. Bentrude W. D. Johnson, and W. A. Khan, *ibid.*, **94**, 923 (1972); W. G. Bentrude, W. D. Johnson, W. A. Khan, and E. R. Witt, *J. Org. Chem.*, 37, 631 (1972); W. G. Bentrude, W. D. Johnson, and W. A. Khan, *ibid.*, 37, 642 (1972).

Table I. Phosphoranes from Dimethylketene and PXYZ

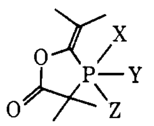
Phosphorane	X	Y	Z	% yield, isolated	Bp, °C[a] (Torr)	Thermal stability[b]
5a	CH_3O	CH_3O	CH_3O	97		2
5b	n-C_3H_7O	n-C_3H_7O	n-C_3H_7O	87		2
5c	CH_3O	$-OCH_2CH_2O-$		85		1
5d	$(CH_3)_2N$	CH_3O	CH_3O	100		3
5e	CH_3O	$-OCH_2CH_2N(CH_3)-$		*c*	75–77 (0.15)	1
5f	CH_3O	$-N(CH_3)CH_2CH_2N(CH_3)-$		*d*		3
5g	$(CH_3)_2N$	$-N(CH_3)CH_2CH_2NCH_3-$		*e*		*e*
5h	$(CH_3)_2N$	$-OCH_2CH_2N(CH_3)-$		96	68–70 (0.1)	1
5i	$(CH_3)_2N$	$-OCH_2CH_2O-$		100	78–80 (0.1)	1
5j	$(CH_3)_2N$	$(CH_3)_2N$	$(CH_3)_2N$	*e*		*e*
5k	C_6H_5	CH_3O	CH_3O	100		
5l	C_6H_5	$-OCH_2CH_2O-$		100		

[a] Obtained for relatively stable adducts only. All are liquids or oils except **5d**, a greasy white solid, and **5l**, a semisolid. [b] Relative thermal stability: 1, little decomposition, in 6 days at 60°; 2, decomposed in 3–5 days at 60°; 3, decomposed almost immediately on warming to 60°. [c] Not precisely determined but at least 80%. [d] Yield undetermined because of product instability. [e] Gave no pentacovalent adduct.

shown in structure **5** is not accessible by the other reasonably general preparative methods available for the synthesis of pentacovalent phosphorus intermediates. These include the peroxide[4a,b] and exchange[4c,d] route, the condensation of α-dicarbonyl compounds with various PXYZ,[5] reactions of 1,2-diols and amino alcohols with trivalent phosphorus,[6] and certain 1,3-dipolar addition reactions of methylene- and aminophosphoranes.[7] In addition, the new adducts (**5**) undergo a series of facile reactions leading to a variety of new products, usually in high yields, which are not easily synthesized by other means.

Results

The adducts **5** (Table I) of dimethylketene and PXYZ are formed in very clean and rapid reactions at Dry Ice temperatures by the addition of dimethylketene in ethyl acetate to solutions of PXYZ in the same solvent. They were characterized structurally by their chemical and spectroscopic properties (Table II). Each showed intense ir absorption in the region 1725–1735 cm^{-1} and a weak peak at 1630–1635 cm^{-1}. We were at first inclined[1] to assign the intense peak to $>C{=}O$ absorption, since olefinic absorption at this frequency is unusual. This would suggest the alternate structure **6** for the adducts. Structure **6** is also consistent with the chemical behavior of the adducts (see below).



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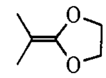

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This structure, however, presents two problems. First, the frequency of the 1725–1735-cm^{-1} band is somewhat low for a carbonyl group in a five-membered ring, although the effect of the phosphorus on such absorption is not known. Second, the structure **6** contains a geminal methyl pair whose pmr resonance should be split into a doublet by the phosphorus.[8] Further, although the pmr spectra of the adducts in $CDCl_3$ or CH_2Cl_2 do show a broad 6-H singlet, which might be assigned to the geminal methyls of structure **6** if some way could be found to explain the lack of spin–spin interaction with the neighboring phosphorus, in C_6H_6 the above hydrogens usually appear as two distinct absorptions (3 H each). That the solvent change affects chemical shifts rather than coupling constants was clearly shown by spectra run at both 60 and 100 MHz. Although the spirophosphoranes are unsymmetrical and may have certain of their pseudorotations which exchange ring substituents inhibited to some degree by the strain rule (see Discussion),[9] the noncyclic adducts should have equivalent geminal methyls if **6** were the correct structure, since the geminal methyls in unsymmetrical forms would be readily interchanged by pseudorotation. Such interconversions would only violate the polarity rule[9] ($\Delta G^{\ddagger}$ = 10–17 kcal/mol)[10] and are normally fast on the nmr time scale near room temperature. In spite of this the methyls in question for adduct **5k** are nonequivalent in $CDCl_3$ as well as in C_6H_6 as is consistent with structure **5**. If the nonequivalency noted for the A methyls of **5k** were the result of nonequivalency in a structure of type **6**, this effect should be accentuated

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(4) (a) D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, **91**, 5821 (1969); (b) D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *ibid.*, **91**, 5243 (1969); (c) B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *ibid.*, **93**, 4004 (1971); (d) F. Ramirez, A. J. Bigler, and C. P. Smith, *Tetrahedron*, **24**, 504, (1968).

(5) The synthetic aspects of these reactions have been thoroughly explored by the Ramirez group. For reviews see (a) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968); (b) F. Ramirez in "Organophosphorus Compounds," International Symposium, Heidelberg, 1964, IUPAC, Butterworths, London, 1964, pp 337–369; (c) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (d) F. Ramirez, *Bull. Soc. Chim. Fr.*, 2443 (1966). For more recent work see (e) F. Ramirez, S. L. Glaser, A. J. Bigler, and J. F. Pilot, *J. Amer. Chem. Soc.*, **91**, 496, 5696 (1969); (f) F. Ramirez and G. V. Loewengart, *ibid.*, **91**, 2293 (1969); (g) F. Ramirez and C. D. Telefus, *J. Org. Chem.*, **34**, 376 (1969).

(6) R. Burgada, D. Houlla, and R. Wolf, *C. R. Acad. Sci., Ser. C*, **264**, 356 (1964); R. Burgada, M. Bon, and F. Mathis, *ibid.*, **265**, 1499 (1967); R. Burgada and H. Germa, *ibid.*, **267**, 270 (1968); M. Sanchez, J. F. Brazier, D. Houlla, and R. Wolf, *Bull. Soc. Chim. Fr.*, 3930 (1967); M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *ibid.*, 773 (1968); M. Sanchez, L. Beslier, and R. Wolf, *ibid.*, 2778 (1969); M. Sanchez, L. Beslier, J. Roussel, and R. Wolf, *ibid.*, 3053 (1969).

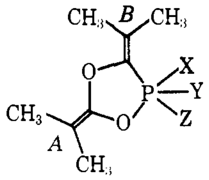
(7) (a) R. Huisgen and J. Wulff, *Chem. Ber.*, **102**, 746, 1833, 1848 (1969); (b) J. Wulff and R. Huisgen, *ibid.*, 102, 1841 (1969); (c) A. Umani-Ronchi, M. Acampora, G. Gaudiano, and A. Selva, *Chim. Ind. (Milan)*, **49**, 388 (1967); (d) H. J. Bestmann and H. Kunstmann, *Angew. Chem., Int. Ed. Engl.*, **5**, 1039 (1966).

(8) Similarly situated geminal methyls have shown 15–21-Hz splittings: ref 7b; D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1970).

(9) These principles are well enunciated in four review articles: K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970); E. L. Muetterties, *ibid.*, 3, 266 (1970); F. H. Westheimer, *ibid.*, **1**, 70 (1968); ref 5a.

(10) (a) D. Gorenstein, *J. Amer. Chem. Soc.*, **92**, 644 (1970); (b) D. Houlla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 443 (1969).

Table II. Spectral Data for Phosphoranes **5**



Phosphorane	δ ^{31}P[a]	Pmr data (δ, J)[b]						Ir ν, cm^{-1};[c] uv λ, nm[e]
		Solvent	Vinyl methyls (A)		Vinyl methyls (B)		X, Y, Z	
5a	53.8 (neat) 53.0 (hexane)	C_6H_6	1.73 (s)	1.77 (s)	1.86 (d, 3.0)	1.92 (d, 2.5)	3.50 (CH_3O) (d, 13.0)	2970, 2930, 2850, 1735, 1630 (w), 1455, 1295, 1215, 1175, 1100, 1080, 1052, 975, 909, 807, 763, 672 (film); λ_{max} 270 (ϵ 2,550),[g] λ_{max} 200 (ϵ 10,700)
	53.6 (CH_2Cl_2)	$CDCl_3$	1.62 (s)		1.91 (d, 3.0)	1.95 (d, 2.0)	3.62 (CH_3O) (d, 13.0)	
5b	53.6 (neat)	C_6H_6	1.77	1.79	1.90 (d, 3.0)	2.04 (d, 3.0)	0.88 (CH_3CH_2O) (t, 6.5) 4.10 (CH_3CH_2O) (m)	2970, 1730, 1630 (w), 1455, 1385, 1295, 1265, 1210, 1168, 1070, 1015, 988, 908, 846, 812, 783, 727, 676 (film)
5c	34.6 (CH_2Cl_2)	CH_2Cl_2	1.58 (s)		1.94 (d, 3.0)	1.99 (d, 3.0)	3.65 (CH_3O) (d, 14.0) 3.90 (OCH_2CH_2O) (m)	2900, 1735, 1630 (w), 1450, 1285, 1265, 1210, 1168, 1058, 970, 945, 908, 829, 756, 738, 687 (CH_2Cl_2)
5d	53.2 (CH_2Cl_2)	CH_2Cl_2	1.59 (s)		1.85 (d, 3.0)	1.90 (d, 3.0)	2.72 [$(CH_3)_2N$] (d, 10.5) 3.49 (CH_3O) (d, 12.5)	1730, 1635 (w), 1280, 1162, 1093, 1057, 993, 785 (Nujol)
5e	50.4 (CH_2Cl_2)	CH_2Cl_2	1.60 (s)		1.87 (d, 3.0)	1.96 (d, 3.0)	3.55 (CH_3O) (d, 14.0) 2.86 (CH_3N) (d, 10.0) 3.10 ($PNCH_2$) (m) 3.80 ($POCH_2$) (m)	2930, 1735, 1635 (w), 1450, 1345, 1290, 1255, 1205, 1180, 1075, 1058, 960, 784, 738, 678 (CH_2Cl_2)
5f	51.8[d] (CH_2Cl_2)							
5h[h]	54.0 (CH_2Cl_2)	CH_2Cl_2	1.61 (s)		1.83 (d, 3.0)	1.90 (d, 3.0)	2.62 [$(CH_3)_2N$] (d, 11.0) 2.78 (CH_3N) (d, 10.5) 2.90 ($PNCH_2$) (m) 3.80 ($POCH_2$) (m)	2930, 2860, 1725, 1630 (w), 1450, 1295, 1275, 1252, 1198, 1176, 1075, 995, 958, 813, 749, 713 (neat film); λ_{max} 255 (ϵ 2035), λ_{max} 200 (ϵ 12,760)[f]
5i	38.5 (CH_2Cl_2)	CH_2Cl_2	1.58 (s)		1.90 (d, 3.0)	1.96 (d, 3.0)	2.75 [$(CH_3)_2N$] (d, 10.5) 3.83 (OCH_2CH_2O) (m)	2920, 1730, 1630 (w), 1450, 1280, 1166, 1075, 1000, 948, 900, 818, 793, 740, 720, 670 (neat film); λ_{max} 265 (ϵ 1970), λ_{max} 200 (ϵ 9000)[g]
5k	43.8 (CH_2Cl_2)	$CDCl_3$	1.55 (s)	1.63 (s)	1.98 (d, 2.5)	2.02 (d, 2.5)	3.52 (CH_3O) (d, 12.5) 7.45 (C_6H_5) (m)	2910, 2840, 1730, 1630 (w), 1440, 1295, 1200, 1150, 1075, 1040, 968, 909, 815, 770, 745, 690, 660 (film)
5l	31.2 (CH_2Cl_2)	$CDCl_3$	1.58 (s)		1.93 (d, 2.5)	2.07 (d, 2.5)	3.95 (OCH_2CH_2O) (m) 7.50 (C_6H_5) (m)	2950, 2900, 2850, 1730, 1630 (w), 1160, 1120, 1070, 965, 945 ($CHCl_3$)
		C_6H_6	1.81 (broad s)		1.93 (d, 2.5)	1.99 (d, 2.5)	3.65 (OCH_2CH_2O) (m)	

[a] In ppm relative to external 85% H_3PO_4. [b] Figures given are chemical shifts (δ) in ppm downfield from internal TMS. In parentheses beneath δ values are indicated peak multiplicity (s, singlet; d, doublet; t, triplet; m, complex multiplet) and J_{PH} or J_{HH} in Hz. [c] Bands are of medium or strong intensity unless otherwise noted. [d] Observed only in reaction mixture. Product not isolated. [e] In hexane. [f] Freshly distilled sample. [g] Freshly prepared sample. [h] On freshly distilled samples. *Anal.* Calcd for $C_{13}H_{25}O_3N_2P$: C, 54.16; H, 8.74; P, 10.74. Found: C, 52.92, 53.15; H, 8.76, 9.12; P, 9.51, 11.36.

in **5l** by the strain rule; however, the A methyls are equivalent coincidentally in both $CDCl_3$ and C_6H_6.

The pairs of pmr doublets at δ 1.85–1.95 and 1.90–2.05 (J_{HP} = 2.5–3.0) (Table II) are assigned to the vinyl methyls (CH_{3B}) closer to the phosphorus atom. As a model compound, the ketene acetal **7** was synthesized.[11] **7** had vinyl methyl pmr absorption at δ 1.55 ($CDCl_3$) and an intense ir band at a surprisingly high frequency, 1740 cm^{-1} (C=C). Thus the intense ir band (1725–1735 cm^{-1}) in the phosphorane adducts is assigned to the ketene acetal double bond in structure **5**.

The pentacovalency of the adducts was also indicated by the ^{31}P shifts[12] (Table II). The shifts for the phosphite adducts occur within the range expected for a species with four oxy and one carbon substituent on phosphorus. A ^{31}P chemical shift of +55 ppm relative to 85% H_3PO_4 was recently reported[13a] for the pentacovalent 2:1 adduct formed from diphenylketene and triethyl phosphite which almost certainly has the structure analogous to **5**. Decreases in chemical shift

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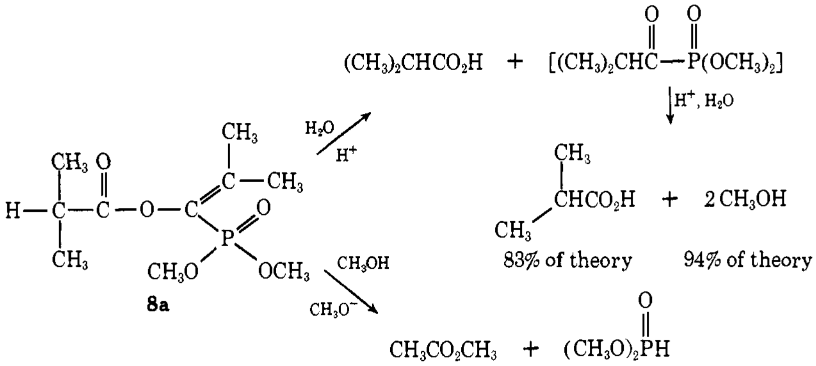
(11) The procedure of S. M. McElvain and C. L. Aldridge, *J. Amer. Chem. Soc.*, **75**, 3993 (1953), was followed.

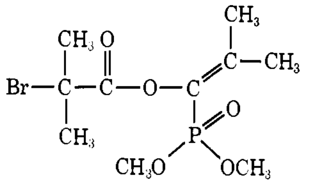
(12) (a) F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *Tetrahedron*, **24**, 2275 (1968); (c) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967); (d) D. B. Denney, D. Z. Denney, and B. C. Chang, *ibid.*, **90**, 6332 (1968). The significance of the ^{31}P shift is discussed quite thoroughly in ref 12a and 5a.

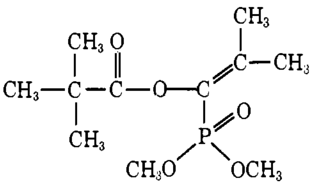
(13) (a) J. E. Baldwin and J. C. Swallow, *J. Org. Chem.*, **35**, 3583 (1970); (b) T. Mukaiyama, H. Nambu, and M. Okamoto, *ibid.*, **27** 3651 (1962).

similar in magnitude to the 19 and 15 ppm changes observed (Table II) in comparing **5a** with **5c**, **5d** with **5i**, and **5k** with **5l** have been noted previously when two exocyclic oxygens become part of a five-membered ring.[14] No effect of that magnitude is seen when an exocyclic nitrogen and oxygen are included in a ring (compare **5d** and **5e**). Also consistent with pentacovalency is the distillable nature of the more stable adducts **5e**, **5h**, and **5i**. That true 2:1 adducts are formed was attested by the experimentally determined molecular weight of **5h**, 288 (289 theory).

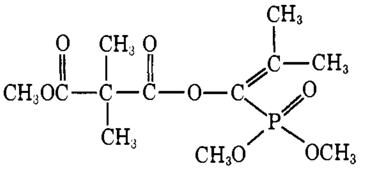
The structures of the adducts **5** were further confirmed by their chemical behavior. This is exemplified by a detailed study of the chemistry of **5a**. At temperatures above 60°, **5a** was converted quantitatively to **2** and trimethyl phosphite. Structures **3**–**6** out of nine isomeric potential 2:1 adducts are the only ones consistent with this result. Spectral data and the chemistry of the adducts exclude structures **3** and **4**. Reaction with water at 25° gave instantaneous near-quantitative conversion to **8a** which had the ir and pmr spectral features expected (Table III). Mass spectral analysis of **8a** gave a parent peak at *m/e* 250 (theory 250) and a fragmentation pattern consistent with **8a**. Base-catalyzed methanolysis and acid-catalyzed hydrolysis[15] of **8a** gave the products shown. Reaction at 0–5° of **5a** with Br_2 led to **9a**. Reaction with methyl iodide yielded **10a** while base-catalyzed methanolysis of **5a** yielded trimethyl phosphite and methyl isobutyrate, in approximate 1:2 ratio, as the only products detectable by vpc. Methanol alone gave largely **8a**.

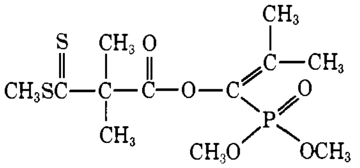



9a


10a

Carbonation of **5a** also proceeded very cleanly at low temperature to give a high yield of product, the ester **11a**. Similarly **12a**, formed on reaction of **5a** with CS_2, appears to result from attack on the carbon atom. The structures of products **8a**–**12a** were determined by quantitative elemental analysis and from their ir and pmr spectra and in some cases also from mass spectral data (see Experimental Section).


11a


12a

The structures of the other pentacovalent analogs were determined from their spectra (Tables I and II) and in most instances by quantitative elemental analysis of their product(s) of reaction, usually with H_2O or CH_3I (Table III and Experimental Section). For **5i** the hydrolysis product was shown to be identical with that from **5c** for which analysis was obtained. Instability of the derivatives formed from **5h** precluded their analysis. In several instances more than one product resulted from a given reaction, as indicated in Table III and the Experimental Section.

The stabilities of the **5** adducts were very structure dependent. As noted in Table I, some of the materials decomposed to **2** and the accompanying trivalent phosphorus compound within hours at 60°. Others required several days, while some could be distilled at reduced pressure and were essentially stable at 60°. In two instances, **5g** and **5j**, no evidence for formation of a stable adduct could be obtained by either ^1H or ^{31}P nmr techniques. From attempts to form **5g**, the lactone **2** and the phosphorus nucleophile were detected. These are the same products formed on thermal decomposition of the pentacovalent species (**5**).

Discussion

Synthesis and Structures. The formation of the phosphoranes **5** probably occurs in several steps. Apparently the relatively hard phosphonium electrophilic center combines preferentially with the hard oxygen nucleophile rather than with the soft carbon center which would have given structure **6**. The above reaction sequence also involves preferential O- rather than C-acylation of the initial 1:1 adduct. The structure **5** must also be the thermodynamically more stable

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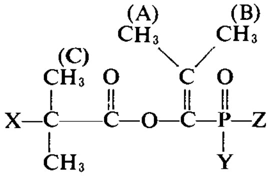
(14) F. Ramirez, M. Nagabhushanam, and C. P. Smith, *Tetrahedron*, **24**, 1785 (1968).

(15) Hydrolysis of **8a** should give initially 1 mol of isobutyric acid and 1 mol of the ketophosphonate which would not survive the reaction conditions but be rapidly converted to the products shown.[16]

(16) A. J. Kirby and S. G. Warren, "The Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, p 153; K. D. Berlin and H. A Taylor, *J. Amer. Chem. Soc.*, **86**, 3862 (1964).

Table III. Spectral and Analytical Data for Derivatives of **5**



Product	Solvent	Pmr chemical shifts[a]					Ir, ν, cm^{-1}	Formula	Elemental analyses[h]			
		ν_A	ν_B	ν_C	ν_X	ν_Y or ν_Z			% C	% H	% P	% N
8b, X = H; Y = Z = $OCH_2CH_2CH_3$	C_6H_6	1.58 (d, 2.5)[b]	2.12 (d, 3.0)	1.20 (d, 7.0)	2.60 (m, ~7)	0.83 ($OCH_2CH_2\mathit{CH}_3$) (t, 7.0) 1.6 ($OCH_2\mathit{CH}_2CH_3$) (m) 4.0 ($O\mathit{CH}_2CH_2CH_3$) (m)	2970, 1745, 1635 (w), 1460, 1385, 1270, 1135, 1063, 995, (neat film)	$C_{14}H_{27}O_5P$	54.89 (54.94)	8.88 (9.13)		
9b, X = Br; X = Y = $OCH_2CH_2CH_3$	$CDCl_3$	1.82 (d, 2.5)	2.14 (d, 3.0)	2.00 (s)		0.96 ($OCH_2CH_2\mathit{CH}_3$) (t, 7.0) 1.7 ($OCH_2\mathit{CH}_2CH_3$) (m) 4.0 ($O\mathit{CH}_2CH_2CH_3$) (m)	2970, 1750, 1640 (w), 1460, 1395, 1370, 1270, 1150, 1110, 995 (neat film)					
8c, X = H; Y, Z = OCH_2CH_2O	C_6H_6	1.47 (d, 2.5)	2.03 (d, 3.0)	1.12 (d, 7.0)	2.50 (m, ~7)	3.9 (OCH_2CH_2O) (m)	3000, 1750, 1645 (w), 1473, 1383, 1370, 1285, 1240, 1225, 1120, 1100, 1035, 921, 815, 809, (neat film)	$C_{10}H_{17}O_5P$	48.39 (48.23)	6.90 (7.15)	12.48 (12.18)	
10c,[c] X = CH_3; Y = OCH_2CH_2I; Z = OCH_3	C_6H_6	1.5 (d, 2.5)	2.05 (d, 3.0)	1.28 (*tert*-C_4H_9) (s)		3.09 ($OCH_2\mathit{CH}_2I$) (t, 7.0) 4.1 ($O\mathit{CH}_2CH_2I$) (m) 3.56 (OCH_3) (d, 11.5)	2970, 1748, 1640 (w), 1482, 1460, 1370, 1266, 1235, 1125, 1034, 1000, 803, 760, 743, 686, (neat film)	$C_{12}H_{22}O_5PI$	35.66 (36.16)	5.49 (5.59)		
10c′, X = CH_3; Y, Z = OCH_2CH_2O	C_6H_6	1.43 (d, 2.5)	2.08 (d, 3.0)	1.22 (*tert*-C_4H_9) (s)		3.8 (OCH_2CH_2O) (m)	2960, 1745, 1635 (w), 1482, 1370, 1280, 1235, 1110, 1080, 1030, 930, 828, 808, 758, 684					
8d,[d] X = H; Y = $(CH_3)_2N$; Z = CH_3O	C_6H_6	1.49 (d, 2.5)	2.05 (d, 3.0)	1.12 (d, 7.0)	2.51 (m, ~7)	2.53 [$(CH_3)_2N$] (d, 10.5) 3.42 (CH_3O) (d, 11.0)	2950, 1750, 1645 (w), 1470, 1310, 1258, 1225, 1128, 1033, 996, 804, 716, (neat film)	$C_{11}H_{22}NO_4P$	50.18 (50.85)	8.42 (8.51)		5.32 (5.12)
10d, X = CH_3; X = $(CH_3)_2N$; Z = CH_3O	C_6H_6	1.50 (d, 2.5)	2.04 (d, 3.0)	1.23 (*tert*-C_4H_9) (s)		2.57 [$(CH_3)_2N$] (d, 10.0) 3.45 (CH_3O) (d, 11.0)	2970, 1745, 1635 (w), 1480, 1460, 1305, 1280, 1255, 1230, 1130, 1035, 993, 803, 760, 713, (neat film)	$C_{12}H_{24}NO_4P$	51.98 (51.86)	8.72 (8.90)	5.05 (5.05)	11.17 (11.32)

10e,[e] X = CH_3; Y = Z = $N(CH_3)CH_2CH_2O$	C_6H_6	1.46 (d, 2.5)	2.20 (d, 3.0)	1.15 (*tert*-C_4H_9) (s)		2.48 (CH_3N) (d, 9.5) 2.8 ($PN\mathit{CH_2}CH_2O$) (m) | CH_3 3.7 ($PNCH_2\mathit{CH_2}O$) (m) | CH_3	2930, 1745, 1635 (w), 1463, 1372, 1270, 1230, 1122, 1068, 1030, 940, 827, 807, 759, 716, (Nujol)	$C_{12}H_{22}NO_4P$	52.36 (52.20)	8.06 (8.25)	11.25 (11.29)	
10e′,[g] X = CH_3; Y = CH_3O; Z = $N(CH_3)CH_2CH_2I$	C_6H_5	1.50 (d, 2.5)	2.00 (d, 3.0)	1.20 (*tert*-C_4H_9) (s)		2.50 (CH_3N) (d, 9.5) 3.43 (CH_3OP) (d, 11.5)						
10f, X = CH_3; Y = Z = $-N(CH_3)CH_2CH_2N(CH_3)-$	$CDCl_3$	1.69 (d, 2.5)[b]	2.25 (d, 3.0)	1.28 (*tert*-C_4H_9) (s)		2.60 (CH_3N) (d, 10.0) 3.15 (NCH_2CH_2N) (m)	1740, 1630 (w), 1265, 1250, 1223, 1168, 1115, 1063, 1038, 945, 758, 726, 705 (Nujol)	$C_{13}H_{25}N_2O_3P$	54.16 (54.65)	8.74 (8.53)	9.72 (9.65)	10.74 (10.48)
10h, X = CH_3; Y = $(CH_3)_2N$; Z = $N(CH_3)CH_2CH_2I$	C_6H_6	1.52 (d, 2.0)	2.11 (d, 3.0)	1.20 (*tert*-C_4H_9) (s)		2.50 [$(CH_3)_2N$] (d, 10.0) 3.17 (CH_2I) (t, 7.0)						
8h, **8h′**,[f] X = H; Y, Z = $N(CH_3)CH_2CH_2O$ (**8h′**); Y = $HN(CH_3)CH_2CH_2O$; Z = $(CH_3)_2N$ (**8h′**)	C_6H_6	1.53 (d, 2.5)	2.10 or 2.15 (d, 3.0)	1.17 (d, 7.0)	2.53 (m, 7.0)	2.59 or 2.62 [$(CH_3)NP$] or [$(CH_3)_2NP$] (d, 9.5) 2.31 [$C\mathit{H_3}NHCH_2$] (s)						
10i, X = CH_3; Y = $(CH_3)_2N$; Z = OCH_2CH_2I	C_6H_6	1.48 (d, 2.5)	2.02 (d, 3.0)	1.22 (*tert*-C_4H_9) (s)		2.53 [$(CH_3)_2NP$] (d, 10.0) 3.04 (CH_2I) (t, 7.0) 4.0 (OCH_2) (m)	2960, 1740, 1645 (w), 1485, 1465, 1370, 1282, 1255, 1227, 1128, 1074, 993, 948, 762, 720, 680 (neat film)					
8k, X = H; Y = C_6H_5; Z = OCH_3	$CDCl_3$	1.67 (d, 2.0)	2.06 (d, 2.5)	1.14 (d, 7.0), 1.16 (d, 7.0)	2.53 (septet 7.0)	3.70 (CH_3OP) (d, 11.0) 7.57 (C_6H_5) (m)	2960, 2920, 1750, 1640 (w), 1485, 1440, 1385, 1365, 1342, 1250, 1225, 1180, 1125, 1030, 1000, 910, 794, 752, 720, 695 (film)	$C_{15}H_{29}O_4P$	60.81 (61.27)	7.09 (7.07)	10.48 (10.42)	
8l, X = H; Y = C_6H_5; Z = OCH_2CH_2OH	$CDCl_3$	1.65 (d, 2.0)	2.02 (d, 2.5)	1.14 (d, 7.0), 1.16 (d, 7.0)	2.54 (septet, 7.0)	3.54 (OH) (s) 7.68 (C_6H_5) (m) 4.08 (OCH_2CH_2O) (m)	3350, 2900, 1745, 1640 (w), 1473, 1440, 1390, 1365, 1250, 1220, 1125, 1100, 1030, 955, 750, 722, 695 (film)	$C_{16}H_{23}O_4P$	58.89 (58.89)	7.10 (7.22)	9.49 (9.12)	
10l, X = CH_3; Y = C_6H_5; Z = OCH_2CH_2I	$CDCl_3$	1.65 (d, 2.0)	2.06 (d, ~3)	1.17 (*tert*-C_4H_9) (s)		3.29 (CH_2I) (t, 7.0) 4.17 ($POCH_2$) (m) 7.5 (C_6H_5) (m)						

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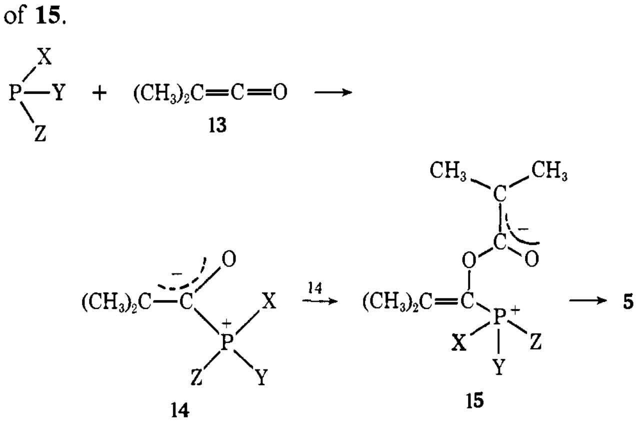
[a] In ppm downfield from internal TMS. [b] Coupling constant J_{HH} or J_{HP}. [c] Ratio **10c**/**10c′**, 80/20. [d] Ratio **8d**/**8a**, 67/33. [e] Ratio **10e**/**10e′**, 50/50. [f] Ratio **8h**/**8h′**, ~50/50. Pmr analysis on mixture of **8h** and **8h′**. [g] Pmr absorptions in a mixture with **10e**. [h] Found values are given in parentheses.

form if **5** is in rapid equilibrium with a small amount of **15**.



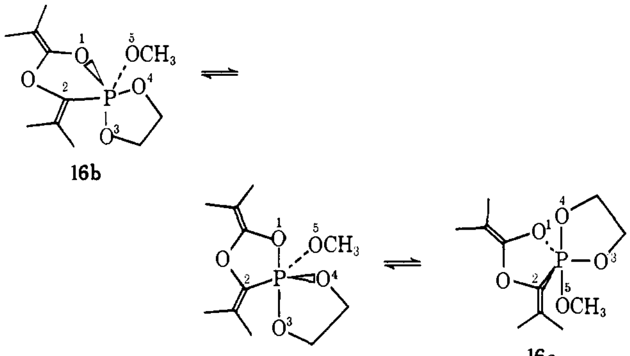
13

14

15

Any zwitterionic species (**15**) must be present in small concentrations as its contribution to the ^{31}P shifts is not great enough to shift them appreciably downfield from that expected for a purely pentacovalent species. It should also be noted that the ^{31}P shift for **5a** (Table II) is the same in CH_2Cl_2 as in hexane. This is in contrast to the sizable variation in the ^{31}P shift found on change from hexane or benzene to CH_2Cl_2 with certain other cyclic phosphoranes for which a dipolar–pentacovalent equilibrium has been proposed.[4b,12]

Careful examination of the J_{HP} values for the methoxyl hydrogens for the phosphoranes **5** shows that in the spiro compounds (**5c**, **5e**) J_{HP} is larger than in the monocyclic cases **5a** and **5d**. This effect is noted[5a,17] in other systems in which the methoxy is constrained to be primarily in the equatorial position. Shown below for **5c** are the two types of pseudorotation processes available to a spirophosphorane of configurations **16**. In **16a** ⇄ **16b**, the methoxyl group remains equatorial. Processes like the above, which violate the polarity rule[9] by placing a less polar substituent in the axial position, have $\Delta G^{\ddagger}$ of only 10–17 kcal/mol.[1c] On the other hand, violation of the strain rule[9] by placing the ring atoms diequatorial as in **16c** was shown to be associated with a $\Delta G^{\ddagger}$ of 18–22 kcal/mol.[10a] Even if the barrier to **16a** ⇄ **16c** is readily crossed with **5c** and **5e**, forms **16a** and **16b** with the methoxy equatorial should be most greatly populated as suggested by the coupling constants observed. Interchange of equatorial and axial methoxys in **5a** occurs readily (one peak) as expected, as this can be done without violation of the strain rule.

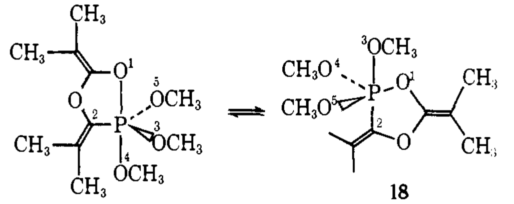


16b

16a

16c

It may be significant that the pmr spectrum of **5a** is unchanged at −90°. Although it is realized that coalescence temperatures for pmr exchange processes depend on peak separations as well as $\Delta G^{\ddagger}$, the lack of resolution of the methoxy doublet into a pair of doublets in 2:1 area ratio may mean that an abnormally low $\Delta G^{\ddagger}$ obtains. Inspection of molecular models shows that for the configuration of **5a**, which the strain and polarity rules predict should be most stable (structure **17**), a vinyl methyl will be forced into close proximity to the axial methoxy, thus raising the energy of that form. This could lower the energy difference between **17** and **18** through which the methoxys are interchanged.

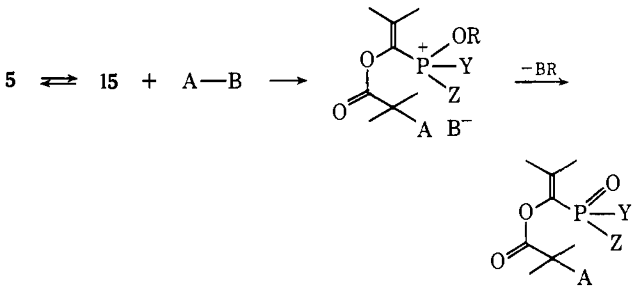


17

18

Reactions of 5. The reactions of **5a** observed with Br_2, CH_3I, CO_2, and CS_2 are completely consistent with the presence of either a polar species (**15**) or a completely covalent compound with an easily polarized P–O bond. This is represented in general terms by Scheme I in which a quasi-phosphonium salt intermediate gives product in an Arbuzov-like reaction. However, no experimental evidence concerning the actual mechanism operative is available. The synthetic potential of these reactions is suggested by the high yields and structural novelty of the products formed. Particular features of certain of these reactions and those with the H_2O and CH_3OH will be discussed individually.

Scheme I



A	B
Br	Br
CH_3	I
O=C	O
S=C	S
H	OCH_3

The hydrolyses of **5a** and its analogs probably initially involve replacement of a noncarbon substituent on phosphorus as has been suggested before in analogous systems.[18] With methanol, the reaction route depends on whether sodium is added. Sodium methoxide

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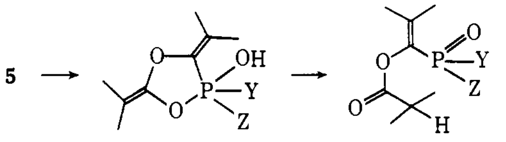
(17) (a) F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, **90**, 1275 (1968); (b) D. G. Gorenstein and F. H. Westheimer, *ibid.*, **89**, 2762 (1967); (c) *ibid.*, **92**, 634 (1970); (d) *Proc. Nat. Acad. Sci. U. S.*, **58**, 1747 (1967); (e) F. Ramirez, *Trans. N. Y. Acad. Sci.*, 30, 410 (1968).

(18) D. Swank, C. N. Caughlan, F. Ramirez, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6503 (1967); F. Ramirez, N. B. Desai, and N. Ramanathan, *ibid.*, **85**, 1874 (1963); F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson, and E. M. Banos, *ibid.*, **85**, 2681 (1963); F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *ibid.*, **87**, 549 (1965); F. Ramirez, S. B. Bhatia, and C. P. Smith, *ibid*, **89**, 3026 (1967).

apparently attacks the ring carbon between the acetal oxygens. This is likely followed by fragmentation to methyl isobutyrate, trimethyl phosphite, and dimethylketene. The latter should be rapidly converted to

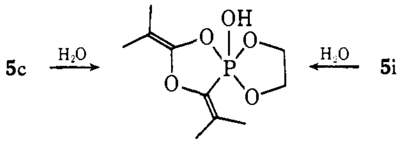


19

methyl isobutyrate which accounts for the approximate 2:1 methyl isobutyrate:trimethyl phosphite ratio observed. However, neutral absolute methanol apparently reacts according to Scheme I to yield the same product (**8a**) as does H_2O.

In no instance in hydrolyses of adducts **5** was any product noted in which the ring containing the P–C bond was preserved. Exclusive P–C cleavage from intermediate **19** probably reflects the relatively great stability of the enolate ion formed. As with other cyclic phosphoranes,[18] hydrolyses of **5c**, **5h**, and **5i** all give at least some product in which the other ring is retained.

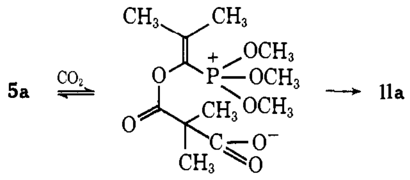
It is likely that hydrolyses of **5c** and **5i** proceed *via* the same intermediate (**21**) since the same product results from both reactants. This result is also support for the mechanism as depicted. Reaction *via* protonation of the ring double bond or of **15** should have given ring-opened product from the amino compound **5i**. The same may be said for the hydrolysis of **5h** which involves both P–N$(CH_3)_2$ (50%) and P–N$(CH_3)CH_2$ (50%) cleavages. It is interesting to note that in contrast to **5i**, **5d** hydrolysis features both P–O (67%) and P–N (33%) scissions. Interpretation of the effects of the second five-membered ring on hydrolysis reaction patterns awaits a better understanding of the mechanism of the first step. It seems likely that with neutral methanol and **5a** a step analogous to **5** → **19** may occur rapidly. But since this merely regenerates **5a**, a slower attack *via* Scheme I is product controlling. With H_2O **5** → **19** gives a very reactive intermediate which collapses quickly to product so that reaction *via* Scheme I cannot compete.



21

The methylation reactions of adducts **5** with CH_3I appear to be straightforward C-alkylation processes, perhaps *via* **15**, followed by iodide displacement on an alkoxy group. The exclusive C-alkylation is consistent with the generally observed mode of alkylation of α carbanions of carboxylic esters.[19] In reaction with **5c** and **5e** displacement both on methoxy and on ring alkoxyl occurs in the postulated phosphonium iodide intermediate. The Arbuzov reaction of 2-methoxy-1,3,2-dioxaphospholane with methyl iodide is reported to occur with exclusive ring opening.[20] However, we have rechecked this report using vpc analysis and find that two products result in about 2:1 ratio on reaction at 25°. The major product is the ring-retained methyl phosphonate, and the other is ring-opened ester $CH_3P(O)(OCH_3)OCH_2CH_2I$. This may be compared with the reaction pattern noted for **5c** in which the ratio of methyl to methylene attack is 1:4. Hydrolysis of **10a** from **5a** alkylation should proceed smoothly to pivalic acid. Use of other alkyl iodides with **5a** should lead to a general synthesis of alkyldimethylacetic acids.

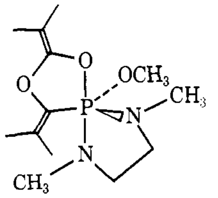
The reactions with CO_2 and CS_2 are the reverse of the ready decarboxylation of 1,1-dicarboxylic compounds. The ease of these reactions, which might otherwise not proceed with favorable equilibrium constants, is probably the result of the initial adduct such as **22** being trapped by a rapid subsequent Arbuzov-like reaction. This suggests that other condensations typical of active methylene compound such as aldol and Claisen condensations, which are sometimes difficult to carry out efficiently because of equilibrium problems, may proceed readily.



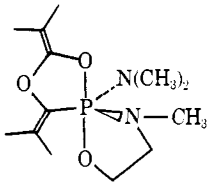
22

Stability of Phosphoranes (5). Other workers have noted that the stability of pentacovalent phosphorus compounds is enhanced by strongly electronegative substituents.[4b,12] Thus, replacement of alkoxy groups in a phosphorane by amino substituents, which can also better stabilize a positive charge on phosphorus (structure **15**), decreases the stability of the phosphorane. In addition steric interactions[21] seem to be reduced by placing any two phosphorus substituents in a five-membered ring, thus increasing phosphorane stability.[12,22] The effect of the second ring is readily seen in the stability data recorded in Table I and is clearly demonstrated by comparing **5a** to **5c** and likewise **5d** to **5e** and **5i**. Further, compounds **5e**, **5h**, and **5i** were distillable even though they all contain at least one amino substituent. The destabilizing effect of increasing the number of aminos is also illustrated. Three amino substituents, even if two are part of a ring, render the potential phosphorane too unstable for detection (**5g** and **5j**).

Phosphoranes **5f** and **5h** make for an interesting comparison as they both have two nitrogen substituents



5f



5h

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[19] A. C. Cope, H. L. Holmes, and H. O. House, *Org. React.*, **9**, 107 (1957).

[20] A. E. Arbuzov and V. M. Zoroastrova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 770 (1952).

[21] R. D. Spratley, W. C. Hamilton, and J. Ladell, *J. Amer. Chem. Soc.*, **89**, 2272 (1967); W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967).

[22] (a) F. Ramirez, A. S. Gulati, and C. P. Smith, *ibid.*, **89**, 6283 (1967); F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Org. Chem.*, **33**, 13 (1968).

but widely different stabilities. While **5h** was distillable, any **5f** formed decomposed to dimer **2** and the 2-methoxy-1,3-dimethyl-1,3,2-diazaphospholane immediately on warming to room temperature. In fact, dimerization of dimethylketene to **2** is catalyzed at −70° by 2-methoxy-1,3-dimethyl-1,3,2-diazaphospholane when excess dimethylketene is used. The greater stability of **5h** is explained if one makes the following assumptions: (1) that oxygen, being more electronegative than nitrogen, has the greater preference[9] for the axial position in the trigonal-bipyramidal structure assumed for **5h**; (2) that the five-membered rings preferably will span equatorial–axial positions.[9] Then **5h** would have the structure shown in which the ring oxygen is able to occupy the axial position. In **5f** the methoxy would be forced into the equatorial position, and one ring nitrogen is axial, both unfavorable constraints. **5e** and **5i** are of comparable stability because each has only one atom in an unfavorable position, an oxygen equatorial.

The dissociation of all **5** to **2** and PXYZ will occur at sufficiently high temperatures. We believe that this explains the ready catalysis of dimethylketene dimerization by trivalent phosphorus noted previously.[23] The less stable the potential phosphorane is, the lower the temperature at which catalysis should occur.

Experimental Section

Pmr spectra at 60 MHz were taken on either a Varian A-60 or A-56-60 spectrometer. Pmr spectra at 100 MHz were measured on a Varian XL-100 spectrometer. Proton chemical shifts are reported in δ (ppm downfield from TMS as internal standard). Mass spectra were taken on a Perkin-Elmer 270 instrument operated at 70 eV. Ir spectra were recorded on a Perkin-Elmer 5A infrared spectrophotometer. Bands recorded are ones of medium to strong intensity unless otherwise noted. Ultraviolet spectra were run on a Cary 14 spectrophotometer. Preparative vpc work was carried out on a Varian Aerograph A-90-P3 gas chromatograph while analytical data were obtained on an F and M Model 810 thermal conductivity instrument. Columns and flow rates were: column A, 6 ft × 0.25 in. 20% SE-30 on 60–80 mesh Chromosorb W, 120 ml/min; column B, 10 ft × $^3/_8$ in. 20% SE-30 on Chromosorb W, 200 ml/min; column C, 6 ft × 0.25 in. 30% Celanese Ester No. 9 on 60–80 Chromosorb W, 120 ml/min; column D, 15% Carbowax 20M on Chromosorb W. The chemiionization mass spectrum was obtained on a modified[24] CED 21-110B instrument.

Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. Molecular weights were determined osmometrically at the Laboratories of the Phillips Petroleum Co., Bartlesville, Okla.

The trivalent phosphorus nucleophiles were prepared as described elsewhere.[3]

Syntheses of Phosphoranes 5. General Procedure. The preparation of **5a** is typical. Trimethyl phosphite (0.53 g, 0.0043 mol) in 3 ml of ethyl acetate was stirred and cooled in a Dry Ice–acetone bath and to it was slowly added, under a nitrogen atmosphere, a 5% solution of dimethylketene (**13**) in ethyl acetate. The dark yellow color of the dimethylketene solution at first faded immediately on contacting the phosphite solution and then more slowly until 2 mol had been added per mole of phosphite. The consumption of **13** then ceased, and the yellow color persisted. An additional 1 ml of the **13** solution was added, and stirring at Dry Ice temperatures was continued for 1 hr followed by removal of volatile materials under vacuum at 5°. The yield of product was determined from the weight of nearly pure (nmr) adduct. **5a** and the other phosphoranes gave only decomposition products on attempted vpc analysis. All the other phosphoranes were prepared by essentially the same procedure. Phosphoranes **5e**, **5h**, and **5i** were distillable. For distilled **5h**, a molecular weight (osmometric, benzene) of 288 (theory 289) was obtained. Uv spectra were obtained in 0.1-cm cells using nitrogen-flushed solvent and cell compartment.

On attempted preparation of **5f**, addition of an excess of **13** failed to give the usual yellow solution. Consumption of **13** continued even after twice the calculated amount was added. Vpc and ir analysis showed production of **2** which increased as more **13** was added. Evaporation of volatiles left a dark yellow viscous liquid impure by ir and pmr analysis but which showed a strong ^{31}P nmr peak (CH_2Cl_2) at 51.8 upfield from external 85% H_3PO_4. Reaction with methyl iodide gave the product expected of **5f** (Table III), isolated by preparative vpc. The impure **5f** slowly decomposed at room temperature to **2** and 2-methoxy-1,3-dimethyl-1,3,2-diazaphospholane. Similar attempts to synthesize **5g** and **5j** gave only **2** and impure mixtures which showed no ^{31}P absorbances above 85% H_3PO_4.

Derivatives of 5a. **5a** decomposed completely to **2** and trimethyl phosphite in 2 weeks at room temperature, in about 65 hr at 60°, or in 17 hr at 80° as shown by pmr analysis. A slightly exothermic reaction of neat **5a** with 1 equiv of water at room temperature was complete in about 10 min to give **8a** as the only high-boiling product (vpc column A), a colorless viscous liquid. Purification was effected by preparative vpc (column B): pmr δ 1.19 (6 H, d, $J_{HH} = 7$ Hz, $(CH_3)_2CH$), 1.67 (3 H, d, $J_{HP} = 2.5$ Hz, vinyl CH_3), 2.07 (3 H, d, $J_{HP} = 3.0$ Hz, vinyl CH_3), 2.66 (1 H, septet, $J_{HH} = 7$ Hz, methine H), 3.62 (6 H, d, $J_{HP} = 11.5$ Hz, $POCH_3$); ir (neat film) 2970, 1750, 1645 (w), 1470, 1270, 1240, 1188, 1130, 1028, 828, 794, 770; mass spectrum *m/e* (relative intensity, ion) 250 (5, M^{+}), 180 (100, M − $(CH_3)_2CHCO$ + H), 110 (M − $(CH_3)_2CHCO_2C{=}C(CH_3)_2$ + H).

Anal. Calcd for $C_{10}H_{19}O_5P$: C, 48.00; H, 7.65; P, 12.38. Found: C, 48.03; H, 7.76; P, 12.22.

A mixture of **8a** (0.084 g, 0.34 mmol) and 0.75 ml of 0.1 *M* aqueous trifluoroacetic acid in a sealed tube was heated for 48 hr at 110°. Quantitative vpc (column D)[25] showed only 5% of **8a** remaining and formation of 0.60 mmol of methanol (94%) and 0.53 mmol of isobutyric acid (83%). With methanol containing a trace of sodium methoxide, **8a** reacted in 9 days at 100° to give methyl isobutyrate and dimethyl phosphite (approximate 2:1 ratio) as the only products observable by vpc (columns A and D).

5a in benzene was treated at 0–5° with Br_2 in CCl_4 with vigorous shaking after each addition until the Br_2 color persisted. A single high-boiling product (**9a**) was obtained (vpc column A) accounting for >95% of total peak area and was purified by collection on column B at 240°: pmr ($CDCl_3$) δ 2.00 (6 H, s, geminal CH_3's), 1.82 (3 H, d, $J_{HP} = 2.5$ Hz, vinyl CH_3), 2.12 (3 H, d, $J_{HP} = 3.0$ Hz, vinyl CH_3), 3.83 (6 H, d, $J_{HP} = 11.5$ Hz, CH_3OP); ir (neat film) nearly identical with that of **8a** except for intense peaks at 1110 and 1150 cm^{-1} rather than at 1130 cm^{-1} as in **8a**.

Anal. Calcd for $C_{10}H_{18}O_5PBr$: C, 36.49; H, 5.51; Br, 24.28. Found: C, 36.83; H, 5.38; Br, 24.28.

5a underwent base-catalyzed, room-temperature methanolysis rapidly and exothermically to yield trimethyl phosphite and methyl isobutyrate in approximate 1:2 ratio as the only products observable by vpc (column C). They were also identified by comparison of an nmr spectrum of the above mixture with that of an authentic mixture.

With excess absolute methanol (no Na added) at room temperature **5a** reacted completely overnight to give methyl isobutyrate (14%), **8a** (62%), and a long-retention-time material (24%) which was not identified. Methyl iodide in excess reacted at room temperature in 2 days to give a single high-boiling product (vpc), **10a**, which was purified by preparative vpc on column B: pmr (C_6H_6) δ 1.28 (9 H, s, *tert*-butyl), 1.51 (3 H, d, $J_{HP} = 2.5$ Hz, vinyl CH_3), 2.07 (3 H, d, $J_{HP} = 3.0$ Hz, vinyl CH_3), 3.54 (6 H, d, $J_{HP} = 11.5$ Hz, $POCH_3$); ir (neat film), 2940, 1745, 1640 (w), 1475, 1455, 1395, 1370, 1265, 1235, 1183, 1125, 1085, 828, 790, 773, 685 cm^{-1}.

Anal. Calcd for $C_{11}H_{21}O_5P$: C, 50.00; H, 8.01; P, 11.72. Found: C, 49.96; H, 8.01; P, 11.66.

Neat **5a** underwent a clean, exothermic reaction with excess CS_2 to give a single intense peak in the vpc corresponding to **12a**. Nmr of the reaction mixture showed no peaks not assignable to **12a**. The analytical sample, a yellow viscous liquid, was prepared by collection on vpc column B: nmr (C_6H_6) δ 1.82 (6 H, s, geminal CH_3's), 1.62 (3 H, d, $J_{HP} = 2.5$ Hz, vinyl CH_3), 2.00 (3 H, d, J_{HP} = 3.0 Hz, vinyl CH_3), 2.35 (3 H, s, $CH_3SC{=}S$), 3.53 (6 H, d, J_{HP} =

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(24) J. H. Futrell and L. H. Wojcik, *Rev. Sci. Instrum.*, **42**, 244 (1971).

(25) In this instance peak areas were sensitivity corrected using authentic samples.

11.5 Hz, CH_3OP); ir (neat film), 2950, 1750, 1645 (w), 1455, 1265, 1235, 1125, 1025, 830, 790; chemiionization spectrum *m/e* (ion, relative intensity) 341 ($M^+ + 1$, 30), 309 ($M^+ - OCH_3$, 4), 293 ($M^+ - CH_3S$, 4), 163 ($M^+ - OC{=}C(CH_3)_2P(O)(OCH_3)_2 + 2$, 12), 162 ($M^+ - OC{=}C(CH_3)_2P(O)(OCH_3)_2 + 1$, 10), 161 ($M^+ - OC{=}C(CH_3)_2P(O)(OCH_3)_2$, 100), 133 ($(CH_3)_2CC(S)SCH_3$, 18), 91 ($S{=}CSCH_3$, 4).

Anal. Calcd for $C_{12}H_{21}O_5PS_2$: C, 42.34; H, 6.22; P, 9.10. Found: C, 42.00; H, 6.33; P, 8.94.

Carbon dioxide (from Dry Ice) was bubbled through neat **5a** at room temperature for 1 hr at which time all **5a** had been consumed (as observed by vpc analysis). **8a** was obtained in 20% yield (because of the difficulty encountered in obtaining moisture-free Dry Ice), and **11a** was obtained in 80% yield (based on percentage of total peak area). **11a**, isolated by collection at 218° on vpc column B, solidified into white crystals, mp 35–36°, on standing at room temperature: pmr ($CDCl_3$) δ 1.50 (6 H, s, geminal CH_3's), 1.73 and 2.12 (3 H each, d, $J_{HP} = 2.5$ and 3.0 Hz, vinyl CH_3's), 3.71 (3 H, s, CO_2CH_3), 3.75 ppm (6 H, d, $J_{HP} = 11.5$ Hz, $POCH_3$); ir (neat film) 2950, 1750, 1740, 1640 (w), 1390, 1370, 1265, 1235, 1162, 1122, 1025, 878, 829, 790 cm^{-1}; mass spectrum *m/e* (relative intensity, ion) 308 (5, M^+), 280 (27, $M^+ - CH_3O$), 150 (25, unknown), 140 (12, unknown), 129 (6, $M^+ - OC{=}C(CH_3)_2P(O)(OCH_3)_2$), 128 (65, $M^+ - HOC{=}C(CH_3)_2P(O)(OCH_3)_2$), 100 (100, $M^+ - CO_2C{=}C(CH_3)_2P(O)(OCH_3)_2$).

Anal. Calcd for $C_{12}H_{21}O_7P$: C, 46.75; H, 6.86; P, 10.25. Found: C, 46.16; H, 6.70; P, 10.22.

Reactions of Other Phosphoranes (5). The above procedures were used to make derivatives of other phosphoranes (**5**) for elemental analysis using either the hydrolysis or methyl iodide reaction. With **5b**, a bromo derivative was also made but could not be purified by vpc. All products were oils except **10c**′, **10e**, and **8l**, which were white solids with mp 92–94, 69.5–70.5, and 69–70°, respectively, and **10h**, which proved to be unstable in isolation and purification attempts. Analytical samples generally were prepared by vpc (column B). As noted in Table III analytically pure derivatives were obtained from **5b**, **5c**, **5d**, **5e**, **5f**, **5k**, and **5l**. Hydrolysis of **5i** gave as the sole product material identical with **8c** as shown by ir, nmr, and vpc. Products from reactions of **5h** were all too unstable for purification, as were some of the other products in Table III for which elemental analyses are not given. Their structures were clear from nmr spectra of the unpurified reaction product mixtures. In most cases all nmr peaks could be assigned even if purification was not possible. However (Table III), broad multiplets could not always be assigned with certainty. For this reason nmr data for some products in Table III are incomplete. **5l** reacted with methyl iodide but the product **10l** was not detectable by vpc and decomposed on standing at room temperature. Product **8l** was purified by column chromatography on Florisil.

The reactions were generally very clean as shown by vpc (column A). In some instances, however, more than one major product resulted. The relative product proportions were determined either from vpc peak areas, where possible, or estimated from nmr spectra of the mixtures. Hydrolysis of **5f** yielded 66 and 34% (based on total vpc peak area) of products **8d** and **8a**. From hydrolysis of **5h** approximately equal amounts of **8h** and **8h**′ resulted (by pmr analysis). The nmr spectrum of the mixture (Table III) showed clearly two low-field vinyl methyl absorptions and a single vinyl methyl at higher field (δ 1.53) equal to the area sum for the other two. A single doublet with approximately correct area was readily assigned to overlapping isopropyl groups for the two products. Methyl and dimethylamino groups coupled to phosphorus were clearly present as was a methylamino not split by phosphorus coupling.

Methyl iodide and **5c** gave 80% **10c** and 20% **10c**′, based on total vpc peak areas, as the only products detectable by vpc. The same reaction with **5e** led to about equal amounts of **10e** and **10e**′ (by pmr). Only **10e** could be purified. Ir data are reported for all compounds which were isolated in reasonably pure form even if an analytically pure sample was not obtained. Unless otherwise indicated a given reaction gave no more than 5% of a single second product. Analyses were obtained for all products purifiable by vpc.

Reaction of Methyl Ethylene Phosphite with Methyl Iodide. Methyl ethylene phosphite (0.5 g, 4 mmol) and methyl iodide (0.6 g, 4 mmol) were mixed under nitrogen and left at room temperature. Vpc monitoring showed starting phosphite to be almost completely reacted after 70 hr giving ethylene methylphosphonate and methyl 2-iodoethyl methylphosphonate. The area ratio of the phosphonates was ~2:1.

Preparation of Dimethylketene Ethylene Acetal. Preparation was effected according to the procedure of McElvain and Aldridge[11] and isolated by preparative vpc. It had ir absorptions in agreement with those reported in the literature:[26] ir, 2900, 1740, 1140, 960, 810 (neat); nmr ($CDCl_3$) δ 1.55 (6 H, s, vinyl CH_3's), 4.07 (4 H, s, OCH_2CH_2O); uv (hexane) ϵ_{190} 4020.

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