benzene (536 mg, 5.0 mmol), and *n*-tridecane (460.9 mg, 2.5 mmol, internal standard) in 5.5 ml of dry benzene was stirred under nitrogen at 70°. At appropriate intervals (Table I and Figure 1), the reaction solution was analyzed by glpc (column B) using predetermined detector response factors for the products which were identified by glpc retention times and, in the case of **8**, by preparative glpc and comparison with an authentic sample (see below).

Preparation of Imine 8.—The procedure described by Pickard and Tolbert[15] afforded **8** (66%), bp 127–129° (1.75 mm) [lit.[15] bp 127° (3.5 mm)].

Reaction of 8 with Diphenylmethylamine. Preparation of Imine 9.—A solution of **8** (1.83 g, 0.01 mol) and diphenylmethylamine (1.81 g, 0.01 mol) in 20 ml of dry benzene was refluxed for 30 hr. Removal of solvent on a rotary evaporator and recrystallization of the resulting white solid from ethanol gave 2.8 g (81%) of **9** as white flakes, mp 149–150° (lit.[6b] mp 153). An attempted preparation of **9** by refluxing benzophenone and diphenylmethylamine in benzene for 48 hr with azeotropic distillation of any water formed resulted in recovery of starting materials with no evidence of **9** detected by glpc.

Registry No.—**8** (Ar = Ph), 1013-88-3; **9** (Ar = Ph), 5350-59-4; nitrosobenzene, 586-96-9; benzylamine, 100-46-9; *p*-methoxybenzylamine, 2393-23-9; diphenylmethylamine, 91-00-9.

Dimerization of Phospholium Ions[1]

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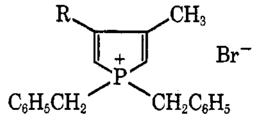
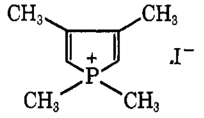
Quaternary salts have been prepared for many of the phospholes synthesized since the recognition of the existence of this ring system in 1959. In every case,[2] the salts have been assigned monocyclic structures with alkylation at phosphorus, although spectral changes in solutions of the benzyl bromide salt of 1-methylphosphole were suggestive of dimerization.[3] On the other hand, dimerization of phosphole 1-oxides can be quite rapid, and in some instances only the dimer can be isolated.[2] This behavior is consistent with the 4-π-electron system of the phosphole oxides and indeed might be expected for the phospholium salts as well. In characterizing some phospholes prepared in a recent study,[4] salts have been isolated which do indeed exhibit dimeric structure. They are described in this paper.

When monomeric structure is present in a salt, it is easily recognized from the simplicity of the proton nmr spectrum. Some examples are given in Table I. Furthermore, monomer character is also revealed by the presence of only one ^{31}P nmr signal; for a D_2O solution of **3**, for example, the signal appeared at −34.4 ppm.[5]

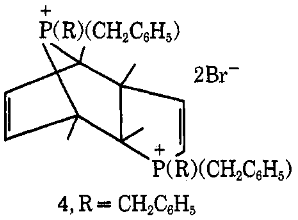


1, R = CH_3
2, R = H



3

The benzyl bromide salt (**4**) of 1-benzylphosphole, as well as the benzyl bromide salt (**5**) of 1-(2-phenylethyl)phosphole, had much more complex nmr spectra. They were incompatible with monomeric structure, but were suggestive of the molecular framework demonstrated[6] for phosphole oxide dimers. In particular, the presence of signals attributable to protons on saturated ring carbons (3.2–4.1 ppm) and the complexity of the *P*-benzyl signal point in this direction. Dimer structure imposes different character on the benzyl groups of each phosphorus atom; in **4**, all four benzyls are in structurally different environments, and in **5** stereoisomeric forms may be present. The *P*-benzyl absorption in both structures would then be a complex composite, rather than a doublet as observed in the monomer. The ^{31}P nmr spectrum for one salt (**4**) provided confirmation of the dimeric structure; two signals were observed (−51.6 and −53.1 ppm in $CDCl_3$), indicating that two structurally different phosphorus atoms were present. Furthermore, the signals were present in equal intensity.



4, R = $CH_2C_6H_5$
5, R = $CH_2CH_2C_6H_5$

It is of significance that we have encountered dimeric salts only for phospholes without a C substituent;[7] 3,4-dimethylphospholium ions (**1** and **3**) remain monomeric, probably through steric crowding encountered in the construction of the bicyclic structure. 3,4-Dimethyl substitution in phosphole oxides has been noted to reduce the east of dimerization in this family

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[1] Taken in part from the Ph.D. Dissertations of S. G. B. (1972) and J. F. E. (1971). Supported by Public Health Service Research Grant CA-05507 from The National Cancer Institute. The Bruker nmr system was purchased in part with funds from the National Science Foundation (Grant No. 10301).

[2] The earlier work has been reviewed: A. N. Hughes and C. Srivanavit, *J. Heterocycl. Chem.*, **7**, 1 (1970). See also ref 7, and F. Mathey and R. Mankowski-Favelier, *Org. Magn. Resonance*, **4**, 171 (1972).

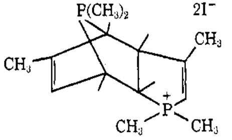
[3] L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, **91**, 3308 (1969).

[4] L. D. Quin, S. G. Borleske, and J. F. Engel, *J. Org. Chem.*, **38**, 1858 (1973).

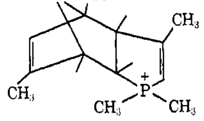
(5) All ^{31}P measurements in this study were performed under conditions of proton decoupling; this gives a sharp singlet and eliminates overlapping of two ^{31}P signals of similar chemical shift, as seen in the phosphole dimers. Spectra were determined at 36.4 MHz on a Bruker HFX-10 spectrometer.

(6) Y. H. Chiu and W. Lipscomb, *J. Amer. Chem. Soc.*, **91**, 4150 (1969).

(7) Two phosphole salts with one C substituent have been prepared that also appear to be dimeric from their ^{31}P nmr spectra. The methiodide (**6**) of 1,3-dimethylphosphole had 1:1 signals at −55.3 and −56.4 ppm (D_2O solution), and the methiodide of 1,2-dimethylphosphole had signals at −58.4 and −59.4 ppm (CF_3COOH solution), also 1:1 in intensity. The C substituent introduces the possibility of positional isomerism in the dimers (*e.g.*, **6a** and **6b** for **6**) and the exact structures of these salts remains unknown at this time.



6a



6b

TABLE I

PROTON NMR SPECTRA[a] OF SALTS OF PHOSPHOLES

		PCH_3		$PCH_2C_6H_5$		C=CH			
Salt	Solvent	δ	$^2J_{PH}$, Hz	δ	$^2J_{PH}$, Hz	δ	$^2J_{PH}$, Hz	C_3CH, δ	CCH_3, δ
				A. Monomers					
1	CF_3COOH[b]			3.99	15.4	6.43	32.4		2.00
2	$CDCl_3$[c]			4.94	16.8	6.2–7.84[d]			1.85
3	$CDCl_3$[b]	3.05	15			7.53	33		2.81[e]
				B. Dimers					
4	$CDCl_3$[b]			5.3–5.7		5.9–6.3, 7.1–7.2[f]		3.8–4.1	
5	$CDCl_3$[c]			4.5–4.8		5.72–7.60[d]		3.2–3.4[g]	

[a] Taken with a Varian A-60 spectrometer. [b] External TMS as standard. [c] Internal TMS as standard. [d] Overlapped by C_6H_5 signals. [e] J_{PH} = 3 Hz. [f] Complex multiplet. [g] Overlapped by phenethyl CH_2 signals.

as well.[8] The nature of the P substituents may also play a role in preventing dimerization of phospholium ions; thus, the *P,P*-dimethyl derivative of the 3-methylphospholium ion appears to be dimeric[7] while the *P,P*-dibenzyl derivative (2) remains monomeric. It would seem to be necessary to consider carefully the structure assigned to a new phosphole salt in view of these results.

The two ^{31}P signals of the dimers are due to the presence of 3-phospholenium and 2-phospholenium moieties. In the dimers examined, the signals are separated by only 1–1.5 ppm. Normally, isomeric 3-phospholenium and 2-phospholenium ions have a greater spread in their ^{31}P shifts (*e.g.*, for the 1,1,3-trimethyl ions, −47.1 and −54.5 ppm, respectively). However, in the dimeric salts, the 3-phospholenium and 2-phospholenium moieties have differences in the substitution at saturated carbons. Thus, as seen in structures **4** and **5**, the 3-phospholenium moiety has carbon substituents at the two α positions, whereas the 2-phospholeniun moiety is substituted at one α and one β position. An analysis of substitution effects on ^{31}P shifts in several families of acyclic phosphorus compounds has shown the shifts to be dependent on the number of carbons in positions β and γ to the phosphorus atom.[9] As in ^{13}C nmr spectra, deshielding is associated with β carbons and shielding (a relatively weaker effect) with γ carbons. The leveling of the ^{31}P shifts for the two components of the phospholium ion dimers is a result of the different substitution patterns in the components. In particular, phosphorus in the 2-phospholenium moiety is deshielded by only one β carbon, and in the 3-phospholenium by two.

Experimental Section[10]

1,1,3-Trimethyl-2-phospholenium Iodide.—To 0.4 g of 1,3-dimethyl-2-phospholene[11] in pentane was added 1 g of methyl iodide. The salt that had precipitated after 1 day at room temperature was recrystallized from a mixture of 2-propanol and ether, mp 135–137°, $\delta_{^{31}P}$ ($CDCl_3$) −54.5 ppm.

Anal. Calcd for $C_7H_{14}IP$: C, 32.83; H, 5.51; P, 12.09. Found: C, 32.70; H, 5.52; P, 12.23.

1,1,3-Trimethyl-3-phospholenium Iodide.—This salt was prepared similarly from 1,3-dimethyl-3-phospholene;[12] it had mp 133–135° and $\delta_{^{31}P}$ ($CDCl_3$) −47.1 ppm.

Anal. Calcd for $C_7H_{14}IP$: C, 32.83; H, 5.51; P, 12.09. Found: C, 32.73; H, 5.45; P, 12.08.

Registry No.—**1**, 38864-31-2; **2**, 38857-58-8; **3**, 37737-13-6; **4**, 38863-80-8; **5**, 38863-82-0; 1,1,3-trimethyl-2-phospholenium iodide, 38857-60-2; 1,1,3-trimethyl-3-phospholenium iodide, 38857-61-3.

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[8] F. B. Clarke, III, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **93**, 4541 (1971).

[9] L. D. Quin and J. J. Breen, *Org. Magn. Resonance*, in press.

[10] All phosphole salts were available from another study.[4] Proton nmr spectra are recorded in Table I, and phosphorus spectra for **3** and **4** are in the text.

[11] D. K. Myers and L. D. Quin, *J. Org. Chem.*, **36**, 1285 (1971).

[12] L. D. Quin and D. A. Mathewes, *ibid.*, **29**, 836 (1964).

1*H*-Imidazo[1,2-*a*]imidazoles.
II. The Chemistry of 1,6-Dimethyl-1*H*-imidazo[1,2-*a*]imidazole

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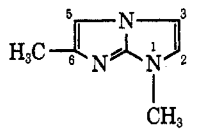
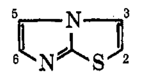
In a previous paper[2] we described the preparation of a series of 1*H*-imidazo[1,2-*a*]imidazoles which were intended as anthelmintic agents. As part of this project, the chemistry of one member of the series, 1,6-dimethyl-1*H*-imidazo[1,2-*a*]imidazole (1), was investigated. At the time the synthetic work was carried out no unsaturated imidazo[1,2-*a*]imidazoles were reported in the literature; however, the reactions of the closely related imidazo[2,1-*b*]thiazole ring system had been studied. The investigations of Paolini[3] and Pyl[4] had revealed that in this ring system the 5 position was the most susceptible to electrophilic attack. It was, therefore, not unexpected to find similar results for the reactions of **1**.



1



imidazo[2,1-*b*]thiazole

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[1] The chemical portion of this work was carried out at the Hess and Clark Division of Richardson-Merrell Inc., Ashland, Ohio, now a division of Rhodia, Inc.

[2] L. F. Miller and R. E. Bambury, *J. Med. Chem.*, **15**, 415 (1972).

[3] J. P. Paolini and L. J. Lendvay, *J. Med. Chem.*, **12**, 1031 (1969).

[4] T. Pyl, R. Giebelmann, and H. Beyer, *Justus Liebigs Ann. Chem.*, **643**, 145 (1961).