zine hydrate, and 2.0 g of potassium hydroxide and then heated under a water takeoff trap until the temperature of the mixture was 175°. Refluxing was continued for 3 hr. The mixture was cooled and combined with the liquid in the water trap, diluted with water, and extracted with ether. The extract was washed with dilute sulfuric acid and water and dried (sodium sulfate) and the solvent removed to give a yellow oily hydrocarbon mixture which showed no carbonyl absorption in the infrared.

Ozonization.—The hydrocarbon mixture was dissolved in 150 ml of methylene chloride and kept at −5 to −10° while a stream of ozone–oxygen was passed through the solution for 70 min at the rate of about 20 mg of ozone per minute. The solvent was removed under reduced pressure at room temperature. The residue was taken up in 25 ml of acetic acid and mixed with 4.0 g of zinc dust for 5 min. The zinc residue was removed by filtration and washed with ether, and the combined filtrate–wash was made basic with saturated potassium carbonate solution. The ether extract was washed with water and dried and the solvent removed to give a colored oil which appeared to be decomposing and darkening due to ozonide remaining in the mixture; it was again treated with zinc dust and acetic acid for 30 min and worked up as described above. The resulting oil in 25 ml of benzene was chromatographed over Florisil as described earlier[2] to give cyclododecane-1,7-dione, mp 129–133°. The infrared spectrum and paper chromatographic behavior were identical with authentic material.

Paper chromatographic analyses[5] of the appropriate eluate indicated the presence of cyclododecane-1,5-dione.[2]

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[5] We are indebted to Mr. L. M. Reineke for these analyses.

Syntheses of Substituted Phosphetanes and Related Derivatives

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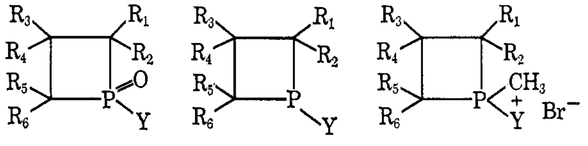
Received April 7, 1967

In the initiation of a general program designed to explore the syntheses, chemical reactions, and physical properties of small-membered ring phosphorus heterocycles, we were prompted to investigate further the previously reported[1] synthesis of 1,1,2,3,3-pentamethyltrimethylenephosphinic acid (Ia) and the acid chloride (Ib). These compounds, which were prepared by treatment of 2,4,4-trimethyl-2-pentene (IV) with phosphorus trichloride in the presence of aluminum chloride, represent one of the few known cases[2] of a four-membered ring containing a single phosphorus heteroatom.

We have now found that treatment of IV with the preformed complex from phenylphosphonous dichloride (V) and aluminum chloride afforded 2,2,3,4,4-pentamethyl-1-phenylphosphetane 1-oxide (Ic) in moderate yield and that similar treatment using methylphosphonous dichloride produced If. Although it was possible to prepare Ic from Ib by treatment with phenyllithium, the yield was low due to the subsequent, rapid reaction of Ic with phenyllithium to give an open-chain compound.[3]



I II III

Ia, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = OH$

Ib, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = Cl$

Ic–IIIc, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = C_6H_5$

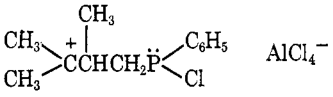
Id–IIId, $R_3 = R_4 = R_5 = R_6 = CH_3$; $R_1 = R_2 = H$; $Y = C_6H_5$

Ie–IIIe, $R_4 = R_5 = R_6 = CH_3$; $R_1 = R_2 = R_3 = H$; $Y = C_6H_5$

If–IIIf, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = CH_3$

IIIg, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = C_6H_5CH_2$

Variation of the olefinic substrate was also investigated. Indeed, reaction of 2,3,3-trimethyl-1-butene (VI) with V and aluminum chloride afforded the crystalline product Id; and both 3,3-dimethyl-1-butene (VII) and 2,3-dimethyl-1-butene (VIII) reacted with V to give the *same* crystalline adduct Ie. The fact that VII and VIII produced the identical substance is consistent with the carbonium ion rearrangement proposed by McBride and co-workers.[1a] The former olefin underwent a methyl migration, whereas the latter olefin proceeded *via* a hydrogen migration to give the same intermediate species IX which can cyclize and subsequently lead to the observed phosphetane 1-oxide after hydrolysis.



$$(CH_3)_2\overset{+}{C}CH(CH_3)CH_2\ddot{P}(C_6H_5)Cl \quad AlCl_4^-$$

IX

Support for the structures Ic–f comes from the corresponding nuclear magnetic resonance (nmr) spectra. Compound Id can be used to illustrate a typical analysis. The nmr ($CDCl_3$) shows each of the unequivalent methyl groups (R_5 and R_6) as a doublet centered at τ 8.62 and 9.07 with ${}^3J_{PCCH} = 17.5$ and 20.0 cps, respectively; each of the unequivalent methyl substituents (R_3 and R_4) occurs as a singlet at τ 8.72 and 9.00. The further assignment of which methyl is *cis* or *trans* relative to the phenyl group cannot be unambiguously made at this time. Finally, the two protons R_1 and R_2 show up as an ABX pattern ($A = R_1$; $B = R_2$; $X = P^{31}$) consisting of eight distinct absorption peaks (τ 6.90–7.92) with ${}^2J_{AB} = 15.0$ cps, ${}^2J_{PCH_A} = 17.0$ cps, and ${}^2J_{PCH_B} = 9.5$ cps; aromatic absorption appears in the region τ 1.97–2.68.

The nmr data were also useful in determining the proportion of geometric isomers which can exist in system Ic. R_3 can be either *cis* or *trans* relative to the phenyl group. For example, a mixture with a melting point range of 104–110° consisted of a 17:3 ratio of isomers (lower melting isomer:higher melting isomer). This ratio was readily obtained from the relative area of the peaks which were unique to each isomer and did not overlap. It was noteworthy that slow addition of water to the reaction mixture (quenching stage) gave a mixture (mp 117–125°) which consisted of

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[1] (a) J. J. McBride, Jr., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962); (b) E. Jungermann, J. J. McBride, Jr., R. Clutter, and A. Mais, *ibid.*, **27**, 606 (1962).

[2] (a) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3739 (1957); (b) M. Green, *ibid.*, 541 (1965); (c) R. I. Wagner, U. S. Patent 3,086,053 (1963); *Chem. Abstr.*, **59**, 10124 (1963); U. S. Patent 3,086,056 (1963); *Chem. Abstr.*, **60**, 559 (1964).

[3] The structure of this compound will be the subject of a future report. There are a number of recorded examples of the reaction of phosphine oxides with organometallic reagents: D. Seyferth, *et al.*, *J. Am. Chem. Soc.*, **86**, 1100 (1964); D. Seyferth and D. E. Welch, *J. Organometal. Chem.* (Amsterdam), **2**, 1 (1964); G. Wittig and R. Rieber, *Ann.*, **562**, 187 (1949).

>90% of the high melting isomer, whereas the reverse addition gave a mixture containing about 82% of the lower melting isomer. The method of quenching also affected the isomer ratio observed for Ie, though not as markedly as in Ic (see Experimental Section). By contrast, the work-up procedure did not change the ratio (approximately 9:1) in the preparation of If.

Conversion of the oxides Ic–f to the corresponding phosphetanes IIc–f was achieved in high yield by treatment with trichlorosilane in the presence of triethylamine (or pyridine) in benzene solution;[4] in turn, the reduction product underwent smooth quaternization with methyl bromide in ether solution to produce the salts IIIc–f. The salt IIIg was prepared from IIf and benzyl bromide. Except for a brief account by Wagner,[2c] the phosphetanes IIc–f constitute the first examples of their kind in the literature; moreover, the quaternary salts represent an unreported class of compounds. That the ring stayed intact during the reduction step was born out by the nmr spectra (Experimental Section) and the fact that oxidation of IIc, e, and f with hydrogen peroxide in acetone gave back the corresponding oxides.

It was also observed that separate reduction [$Cl_3SiH-(C_2H_5)_3N$] of the individual isomers of Ic followed by oxidation gave back the starting isomer in each case; if it is assumed that oxidation occurs with predominant retention of configuration,[5] the reduction step must also proceed with retention. Although Horner and Balzer[6] have found that trichlorosilane–triethylamine reduction gives predominant inversion, their reaction mechanism involves back-side attack with the bulky complex, $(C_2H_5)_3N \rightarrow SiCl_3H$; the large steric requirement of Ic may preclude this type of attack. A mechanism more consistent with our results may involve front-side attack as proposed by Horner for trichlorosilane alone or in the presence of pyridine.

In a similar manner, a 9:1 mixture of isomers of If was reduced [$Cl_3SiH-(C_2H_5)_3N$] and the resultant product oxidized to render the same 9:1 ratio of oxides. However, it was noted that in contrast to Ic and f, the ratio of isomers from the reduction of Ie was markedly dependent on the reaction conditions; the selectivity was sensitive to the nature of the base and the number of equivalents of the reductant used. This variation in selectivity with reaction conditions was also demonstrated by Horner.[6]

The nmr of the individual isomers of IIc revealed interesting differences and features which are worthy of mention. The isomer (neat) from the reduction of higher melting Ic showed the following peaks: τ 7.18 (1 H quartet, $^3J_{\mathrm{HCCH}}$ = 7.0 cps), 8.68 (6 H doublet, $^3J_{\mathrm{PCCH}}$ = 19.5 cps), 8.98 (6 H doublet, $^3J_{\mathrm{PCCH}}$ = 6.5 cps), 9.19 (3 H doublet, $^3J_{\mathrm{HCCH}}$ = 7.0 cps, $^4J_{\mathrm{PCCCH}} \approx 0$), and 2.1–2.9 (5 H multiplet); the phosphetane derived by reduction of the lower melting oxide showed absorption at τ 7.70 (1 H double quartet, $^3J_{\mathrm{HCCH}}$ = 7.2 cps, $^3J_{\mathrm{PCCH}}$ = 3.5 cps), 8.68 (6 H doublet, $^3J_{\mathrm{PCCH}}$ = 19.5 cps), 8.90 (6 H doublet, $^3J_{\mathrm{PCCH}} \approx 6$ cps), 9.22 (3 H double doublet, $^3J_{\mathrm{HCCH}}$ = 7.2 cps, $^4J_{\mathrm{PCCCH}}$ = 1.5 cps), and 2.1–3.0 (5 H multiplet). The four-bond coupling of the phosphorus with the methyl (R_3) protons was also observed in several of the oxides and phosphonium bromides (Experimental Section). In the case of Ic and the quaternary salt IIIc, $P^{31}-H^1$ spin–spin decoupling studies confirmed this long-range coupling in addition to the other assignments. In open-chain, saturated compounds no splitting for protons beyond the β position to the phosphorus has been substantiated.[7] Apparently, there is a geometric dependence for this coupling; such geometrical considerations are well known in rigid systems which show four-bond H^1-H^1 coupling.[8] It was also noted that phosphorus coupling (0–3.5 cps) with the ring proton (R_4) in IIc was smaller than for typical open-chain compounds.[7] By contrast the magnitude of $^3J_{\mathrm{PCCH}_3}$ was 19.5 and 6–6.5 cps; a similar dependence of the size of coupling as a function of geometry has been observed by Quin[9] in the 1,2-dimethyl-3-phospholene system.

Finally, it should be pointed out that although the isomers of IIc are not interconvertible[10] at room temperature or under the reaction conditions of the reduction stage (refluxing benzene), isomerization of the pure liquid (in an evacuated nmr tube) was observed to occur slowly at 110°. For example, a 4:1 mixture goes to a 3:2 mixture (the phosphetane derived from the higher melting Ic predominated in each ratio) in 3 days. Heating the same 4:1 mixture at 165° for 2.5 hr gave a 3:2 ratio (phosphetane derived from the *lower melting* oxide in greater abundance!). Further heating at 165° indicated that this mixture (3:2) was at equilibrium.[11] Although several acyclic phosphines undergo inversion readily (*e.g.*, the half-life of methyl-*n*-propylphenylphosphine in decalin at 130° is about 5.5 hr[6,12]), cyclic systems have exhibited stability toward inversion.[13,14] An exception to this is 9-phenyl-9-phosphabicyclo[4.1.0]nonatriene which undergoes inversion in chloroform with extensive decomposition when heated at 160° for 24 hr; at 100° (for 1 month) no interconversion took place.[15] The facile conversion of isomers in IIc may be due to the high degree of methyl substitution on the ring as well as the phenyl substituent on phosphorus. Such structural features

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[4] H. Fritzsche, U. Hasserodt, and F. Korte, *Ber.*, **98**, 171 (1965); **97**, 1988 (1964).

[5] L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964); L. Horner, *et al.*, *Tetrahedron Letters*, 161 (1961).

[6] L. Horner and W. D. Balzer, *ibid.*, 1557 (1965).

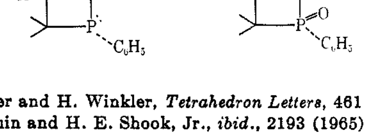
[7] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964); see also, C. E. Griffin, R. B. Davison, and M. Gordon, *ibid.*, **22**, 561 (1966).

[8] A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 233 (1964); K. Takahashi, *Bull. Chem. Soc. Japan*, **39**, 2782 (1966).

[9] L. D. Quin, J. P. Gratz, and R. E. Montgomery, *Tetrahedron Letters*, 2187 (1965).

[10] For a general account of inversion in trivalent phosphorus compounds, see W. E. McEwen in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, pp 17–23; R. F. Hudson and M. Green, *Angew. Chem. Intern. Ed. Engl.*, **2**, 11 (1963); G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967); see ref 20a–f and 21a–b cited therein.

[11] The equilibrium data allow one to assign tentatively the stereochemistry of the predominant isomer (more thermodynamically stable isomer) of IIc and the related oxide Ic (lower melting) as



[12] L. Horner and H. Winkler, *Tetrahedron Letters*, 461 (1964).

[13] L. D. Quin and H. E. Shook, Jr., *ibid.*, 2193 (1965).

[14] B. Fontal and H. Goldwhite, *Tetrahedron*, **22**, 3275 (1966).

[15] T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966).

have been found to lower the energy barrier to inversion in the aziridine system.[16]

Future work will be concerned with equilibrium and rate studies as well as the rearrangement of the oxides and quaternary salts in the presence of aqueous base and organometallic reagents.

Experimental Section

Nmr spectra were recorded on a Varian Associates Model A-60 spectrometer with tetramethylsilane as an internal standard; in those cases in which D_2O was employed as the solvent, Tier's salt [$(CH_3)_3SiCH_2CH_2CH_2SO_3Na \cdot H_2O$] was used as the reference standard. The P^{31}–H^1 decoupling experiments were performed using an NMR Specialties Model HD-60A heteronuclear spin decoupler in conjunction with an HR-60 spectrometer. The infrared spectra were taken on the Perkin-Elmer Model 21 and 237 spectrophotometers. Microanalyses were carried out by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim (Ruhr), West Germany. All boiling and melting points (Thomas-Hoover apparatus) are uncorrected. Solvents were removed during the reaction work-up with a Büchii rotating evaporator. All reactions were conducted under a nitrogen atmosphere.

2,2,3,4,4-Pentamethyl-1-phenylphosphetane 1-Oxide (Ic).—To 133 g (1.0 mole) of aluminum chloride in 700 ml of methylene chloride in a 3-l. flask (equipped with a stirrer, addition funnel, calcium chloride drying tube, and thermometer) was added 179 g (1.0 mole) of phenylphosphonous dichloride in several portions. The homogeneous solution was then cooled with an ice bath as 112 g (1.0 mole) of 2,4,4-trimethyl-2-pentene (Phillips Petroleum Co., 95%) in 300 ml of methylene chloride was added over a 2.5-hr period; the temperature was maintained at 5–10°. The clear solution was stirred for an additional 20 hr at room temperature and then cooled in an ice bath and quenched by slow, dropwise addition of 1.5 l. of water over 2 hr. Additional methylene chloride was added until two distinct layers were formed. The organic layer was separated, washed with dilute sodium bicarbonate and with saturated sodium chloride solution, and finally dried over sodium sulfate. The solvent was evaporated to an oil; an equal volume of cyclohexane was added and subsequently evaporated to give an oil which readily solidified. The solid was recrystallized from cyclohexane to give 114 g (48%) of white solid (mp 115–123°) which consisted of >90% of one isomer. Repeated fractional recrystallization gave long, flat needles, corresponding to the high melting isomer, mp 122–125.3°.

When the reaction mixture was added dropwise to rapidly stirred ice water (temperature maintained at 0°), a 52% yield of crude product (mp 90–99°) was obtained. Recrystallization from cyclohexane raised the melting point to 100–110°; nmr analysis indicated a 4:1 isomer distribution, the lower melting point isomer predominating. Pouring the reaction mixture rapidly over ice gave a 14:11 distribution (lower melting point isomer predominant). Because the 100% pure, lower melting point isomer was never obtained (even by fractional recrystallization) its exact melting point is not known.

The nmr (C_6H_6) of the lower melting point isomer (80%) showed peaks at τ 7.52–8.15 (1 H multiplet), 8.65 (6 H doublet, $^3J_{PCCH} = 16.0$ cps), 9.00 (6 H doublet, $^3J_{PCCH} = 18.0$ cps), and 9.25 (3 H double doublet, $^3J_{HCCH} = 7.0$ cps, $^4J_{PCCCH} = 1.5$ cps). The nmr (C_6H_6) of the higher melting isomer showed peaks at τ 8.01–8.45 (1 H double quartet, $^3J_{HCCH} = 7.0$ cps, $^3J_{PCCH} = 2.0$ cps), 8.66 (6 H doublet, $^3J_{PCCH} = 16.0$ cps), 9.10 (6 H doublet, $^3J_{PCCH} = 18.0$ cps), and 9.23 (3 H double doublet, $^3J_{HCCH} = 7.0$ cps, $^4J_{PCCCH} = 1.5$ cps).

A P^{31}–H^1 double-resonance experiment was performed on the high melting compound in $CDCl_3$; the double quartet gave a quartet, the doublets became singlets, and the double doublet was reduced to a doublet. Substantial chemical shifts were observed on variation of both solvent or concentration for these compounds and others described in this section.[17] The infrared spectra (CCl_4) showed P=O stretching at 1184 and 1191 cm^{-1} for the low and high melting point compounds, respectively.

A sample (containing a mixture of the isomers) was recrystallized from cyclohexane and sublimed (90–100°, 0.05 mm) to give the analytical sample.

Anal. Calcd for $C_{14}H_{21}OP$: C, 71.15; H, 8.96. Found: C, 71.39; H, 8.66.

1,2,2,3,4,4-Hexamethylphosphetane 1-Oxide (If).—The method of preparation was essentially identical with the synthesis of Ic; methylphosphonous dichloride was prepared according to the procedure described by Parshall[18] and treated with IV. The reaction was carried out on a 0.2-mole scale and was quenched by pouring over ice. On work-up a clear, viscous oil was obtained which solidified on standing; the crude solid was recrystallized from cyclohexane to give 22 g of flocculent, white precipitate which was quite hygroscopic. Subsequent recrystallization and sublimation gave 8 g (23%) of purified material, mp 170–171° (sealed, completely immersed, capillary tube).[19] The nmr ($CDCl_3$) due to the major component (>95%) showed peaks at τ 8.44 (3 H doublet, $^2J_{PCH} = 11.5$ cps), 8.73 (6 H doublet, $J = 16.0$ cps), 8.82 (6 H doublet, $J = 18.5$ cps), and 9.08 (3 H double doublet, $^3J_{HCCH} = 7.0$ cps, $^4J_{PCCCH} = 1.0$ cps); the ring proton was hidden under the lower field methyl protons. An infrared spectrum (CCl_4) indicated P=O stretching at 1198 cm^{-1}.

Anal. Calcd for $C_9H_{19}OP$: C, 62.05; H, 11.00; P, 17.79. Found: C, 62.06; H, 10.69; P, 17.89.

Quenching of the reaction was also carried out by slow addition of water to the mixture and the reverse process. The crude product in each case consisted of a 9:1 (qualitative estimate due to close proximity of peaks) mixture of isomers. The nmr ($CDCl_3$) of the minor component had peaks at τ 8.65 (doublet, $^3J_{PCCH} = 16.5$ cps, $PCCH_3$) and 8.84 (doublet, $^3J_{PCCH} = 19.0$ cps, $PCCH_3$); the other peaks were obscured by the major isomer.

2,2,3,3-Tetramethyl-1-phenylphosphetane 1-Oxide (Id).—The general method for the preparation followed that of Ic. The starting olefin, 2,3,3-trimethyl-1-butene (VI), was either prepared from pinacolone and methylenetriphenylphosphorane *via* the Wittig reaction or was obtained commercially (Chemical Samples Co., Columbus, Ohio). The reaction was carried out on a 0.25-mole scale and was quenched by pouring onto ice. A viscous oil was obtained which solidified on cooling and was recrystallized from cyclohexane to give 32 g (58%) of crystalline product, mp 81.5–83.5°.

The nmr ($CDCl_3$) is given in the Discussion section. In *benzene* the following peaks were observed: τ 7.01–8.14 (2 H, ABX pattern, $^2J_{AB} = 15$ cps, $^2J_{PCH_A} = 16.5$ cps, $^2J_{PCH_B} = 9.0$ cps), 8.71 (3 H doublet, $^3J_{PCCH} = 17.0$ cps), 9.22 (3 H doublet, $^3J_{PCCH} = 19.5$ cps), 8.77 (3 H singlet), and 9.16 (3 H singlet). The infrared spectrum (CCl_4) showed P=O stretching at 1205 cm^{-1}.

A sample for analysis was recrystallized from cyclohexane and sublimed (70°, 0.05 mm), mp 82.5–84°.

Anal. Calcd for $C_{13}H_{19}OP$: C, 70.23; H, 8.62; P, 13.93. Found: C, 69.96; H, 8.61; P, 13.91.

2,2,3-Trimethyl-1-phenylphosphetane 1-Oxide (Ie).—The general procedure as described for Ic was followed. Quenching was carried out by pouring the reaction over ice. In the case of the reaction of 3,3-dimethyl-1-butene (VII), a viscous oil was obtained which was distilled [bp 120–121° (0.1 mm)] to give a product (69% yield) which solidified on cooling. Recrystallization of the solid from cyclohexane gave white crystals, mp 81–83° (17:3 mixture of isomers, by nmr). The product derived from 2,3-dimethyl-1-butene (VIII) and V was obtained in 44% yield and was identical (mixture melting point, infrared, and nmr) with the material from the 3,3-dimethyl-1-butene reaction. The nmr (C_6H_6) signals of the major isomer appeared at τ 7.03–8.46 (3 H multiplet), 8.71 (3 H doublet, $^3J_{PCCH} = 17.0$ cps), 9.32 (3 H doublet, $^3J_{PCCH} = 19.5$ cps), and 9.19 (3 H doublet, $^3J_{HCCH} = 6.5$ cps). The nmr (C_6H_6) of the minor component showed separate absorption at τ 8.64 (doublet, $^3J_{PCCH} = 17.0$ cps, $PCCH_3$); the other peaks were hidden by the main component.

Dropwise addition (6 hr) of water to the reaction mixture (from V and VII) gave a 19:1 isomer distribution, mp 84–86°. When the reaction was added slowly (4 hr) to water the ratio

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[16] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

[17] C. E. Griffin and M. Gordon, *J. Organometal. Chem.* (Amsterdam), **3**, 414 (1965).

[18] G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960).

[19] The sharpness of the melting point indicates that some fractional purification probably occurred in the work-up. Samples which had undergone less purification had mp 158–165° and consisted of a 9:1 (approximately) ratio of isomers.

was about 7:3, mp 75–78°. In all cases the major isomer was the same.

Anal. Calcd for $C_{12}H_{17}OP$: C, 69.22; H, 8.23. Found: C, 69.45; H, 8.10.

General Reduction Procedure of Phosphetane 1-Oxides.—To 0.05 mole of the phosphetane 1-oxide in 70 ml of dry benzene, 5.1 g (0.05 mole) of dry triethylamine was added followed by the dropwise addition (20 min) of 6.9 g (0.05 mole) of trichlorosilane in 30 ml of benzene. The solution was allowed to reflux for 3–15 hr under a nitrogen atmosphere. After cooling in an ice bath, the mixture was treated by the dropwise addition of 80 ml of 20% sodium hydroxide solution over 40 min. Additional benzene was added to give two distinct layers; the organic layer was separated, washed four times with saturated sodium chloride solution, and dried over sodium sulfate. The solvent was evaporated and the product was distilled under reduced pressure. The physical properties[20] of the individual phosphetanes follow.

2,2,3,4,4-Pentamethyl-1-phenylphosphetane (IIc) was formed in 82% yield, bp 75–77° (0.05 mm); nmr (Discussion section). The microanalysis was performed on a 1:1 mixture of the isomers.

Anal. Calcd for $C_{14}H_{21}P$: C, 76.32; H, 9.61; P, 14.06. Found: C, 76.27; H, 9.36; P, 14.17.

1,2,2,3,4,4-Hexamethylphosphetane (IIf) was not isolated or purified because of its susceptibility to air oxidation; it was characterized by treatment with methyl bromide in benzene–ether solution to afford the quaternary salt IIIf in 57% over-all yield. The salt was recrystallized from acetonitrile to give white crystals, mp >305° (did not melt up to this temperature). The nmr (D_2O; Tier's salt as the internal reference) showed absorption at τ 7.06–7.50 (1 H double quartet, $^3J_{\mathrm{HCCH}} = 6.5$ cps, $^3J_{\mathrm{PCCH}} = 4.0$ cps), 7.91 (3 H doublet, $^2J_{\mathrm{PCH}} = 14.0$ cps), 8.01 (3 H doublet, $^2J_{\mathrm{PCH}} = 14.0$ cps), 8.52 (6 H doublet, $^3J_{\mathrm{PCCH}} = 20.0$ cps), 8.58 (6 H doublet, $^3J_{\mathrm{PCCH}} = 20.0$ cps), and 9.02 (3 H double doublet, $^3J_{\mathrm{HCCH}} = 6.5$ cps, $^4J_{\mathrm{PCCCH}} \approx 1.0$ cps).

Anal. Calcd for $C_{10}H_{22}BrP$: C, 47.43; H, 8.76; P, 12.24. Found: C, 47.63; H, 8.57; P, 12.41.

The phosphetane was further characterized by treatment with benzyl bromide in benzene solution to give the benzylphosphonium salt (IIIg) (mp 231–232°) in 62% yield. The nmr (D_2O) indicated that this was a 9:1 mixture of isomers. The major component showed absorption at τ 2.37–2.75 (5 H multiplet), 5.97 (2 H doublet, $^2J_{\mathrm{PCH}} = 14.0$ cps), 7.03–7.51 (1 H double quartet, $^3J_{\mathrm{HCCH}} = 7.0$ cps, $^3J_{\mathrm{PCCH}} \approx 2.5$ cps), 8.09 (3 H doublet, $^2J_{\mathrm{PCH}} = 13.0$ cps), 8.40 (6 H doublet, $^3J_{\mathrm{PCCH}} = 19.2$ cps), 8.70 (6 H doublet, $^3J_{\mathrm{PCCH}} = 19.8$ cps), and 8.93 (3 H double doublet, $^3J_{\mathrm{HCCH}} = 7.0$ cps, $^4J_{\mathrm{PCCCH}} \approx 1.0$ cps). The minor isomer exhibited peaks at τ 5.84 (doublet, $^2J_{\mathrm{PCH}} = 14.0$ cps), 8.12 (doublet, $^2J_{\mathrm{PCH}} = 13.5$ cps), 8.42 (doublet, $^3J_{\mathrm{PCCH}} = 19.5$ cps), and 8.61 (doublet, $^3J_{\mathrm{PCCH}} = 19.5$ cps).

Anal. Calcd for $C_{16}H_{26}BrP$: C, 58.38; H, 7.96; Br, 24.27. Found: C, 58.33; H, 7.91; Br, 24.17.

2,2,3,3-Tetramethyl-1-phenylphosphetane (IId) was obtained in 75% yield, bp 74–76° (0.2 mm). The nmr (neat) exhibited peaks at τ 2.6–2.9 (5 H multiplet), 7.75–8.52 (2 H multiplet), 8.83 (3 H doublet, $^3J_{\mathrm{PCCH}} = 18$ cps), 8.72 (3 H singlet), 9.17 (3 H singlet), and 9.23 (3 H doublet, $^3J_{\mathrm{PCCH}} = 5.8$ cps).

Anal. Calcd for $C_{13}H_{19}P$: C, 75.68; H, 9.28; P, 15.02. Found: C, 75.51; H, 9.09; P, 15.23.

2,2,3-Trimethyl-1-phenylphosphetane (IIe) was prepared in 75% yield [bp 71° (0.3 mm)] by reduction (general procedure) of Ie (17:3 mixture of isomers) with 1 equiv of Cl_3SiH–$(C_2H_5)_3N$ (1:1 mole ratio). The nmr of the product indicated a nearly 1:1 mixture of isomers. Adding Ie (19:1) dropwise to 10 equiv of Cl_3SiH–$(C_2H_5)_3N$ (1:1) resulted in a 13:7 distribution of isomers; moreover the dropwise addition of Ie (19:1) to 3 equiv of Cl_3SiH–pyridine (1:1) rendered a 19:1 ratio of isomers. When 2 equiv of the latter reductant was employed a 2:1 ratio resulted. In all of these cases, the major component was the same.

On standing about 1 week in an evacuated tube (at 25°), IIe became very viscous and apparently polymerized or decomposed.

The nmr ($CDCl_3$) of the predominant component showed peaks at τ 1.90–2.60 (5 H multiplet), 6.66–8.63 (3 H multiplet), 8.66 (3 H doublet, $^3J_{\mathrm{PCCH}} = 20.0$ cps), 9.12 (3 H doublet, $^3J_{\mathrm{HCCH}} = 6.5$ cps), and 9.28 (3 H doublet, $^3J_{\mathrm{PCCH}} = 8.2$ cps); the minor isomer showed absorption at τ 8.67 (doublet, $^3J_{\mathrm{PCCH}} \approx 19$ cps), 9.07 (double doublet, $^3J_{\mathrm{HCCH}} = 6.5$ cps, $^4J_{\mathrm{PCCCH}} \approx 1$ cps), and 9.29 (doublet, $^3J_{\mathrm{PCCH}} = 6.0$ cps).

Anal. Calcd for $C_{12}H_{17}P$: C, 74.98; H, 8.92; P, 16.11. Found: C, 74.84; H, 9.03; P, 16.07.

General Method for Quaternization of the Phosphetanes.—A solution of the phosphine in benzene or ether was treated with about 5 equiv of methyl bromide. A suction flask with a sealed side arm and tightly wired stopper served as a reaction vessel. The contents of the flask were allowed to stand for 12–24 hr at room temperature. When carried out on a larger scale, moderate external cooling was required. The solid product was filtered, washed with ether, and recrystallized from acetonitrile–ethyl acetate to give a 90–95% yield of pure salt.

The phosphonium bromide IIIc (derived from Ic, high melting isomer, by reduction and subsequent quaternization) had mp 226–228°; nmr (D_2O; Tier's salt) showed peaks at τ 1.6–2.4 (5 H multiplet), 6.90–7.45 (1 H multiplet), 7.55 (3 H doublet, $^2J_{\mathrm{PCH}} = 14.0$ cps), 8.37 (6 H doublet, $^3J_{\mathrm{PCCH}} = 20.0$ cps), 8.58 (6 H doublet, $^3J_{\mathrm{PCCH}} = 19.5$ cps), and 8.82 (3 H double doublet, $^3J_{\mathrm{HCCH}} = 7.8$ cps, $^4J_{\mathrm{PCCCH}} = 1.2$ cps). A P^{31}–H^1 decoupling experiment was consistent with the above assignment.

From a 4:1 mixture (mp 224–228°) of the salt derived by reduction and subsequent quaternization of Ic (lower melting isomer predominant) the nmr (D_2O; Tier's salt) of the isomeric salt was determined: τ 1.8–2.3 (5 H multiplet), 6.80–7.30 (1 H double quartet, $^3J_{\mathrm{HCCH}} = 7.2$ cps, $^3J_{\mathrm{PCCH}} = 2.8$ cps), 7.57 (3 H doublet, $^2J_{\mathrm{PCH}} = 14.0$ cps), 8.42 (6 H doublet, $^3J_{\mathrm{PCCH}} = 20.2$ cps), 8.47 (6 H doublet, $^3J_{\mathrm{PCCH}} = 19.5$ cps), and 8.89 (3 H double doublet, $^3J_{\mathrm{HCCH}} = 7.2$ cps, $^4J_{\mathrm{PCCCH}} = 1.5$ cps).

Anal. Calcd for $C_{15}H_{24}BrP$: C, 57.15; H, 7.68. Found; C, 57.54; H, 7.50.

The phosphonium bromide IIId had mp 211–212°. The nmr spectrum (D_2O; Tier's salt) exhibited peaks at τ 1.64–2.41 (5 H multiplet), 6.50–6.95 (2 H multiplet), 7.47 (3 H doublet, $^2J_{\mathrm{PCH}} = 15.0$ cps), 8.30 (3 H doublet, $^3J_{\mathrm{PCCH}} = 21.0$ cps), 8.80 (3 H doublet, $^3J_{\mathrm{PCCH}} = 21.0$ cps), 8.59 (3 H singlet), and 8.79 (3 H singlet).

Anal. Calcd for $C_{14}H_{22}BrP$: C, 55.82; H, 7.36; Br, 26.53. Found: C, 55.97; H, 7.28; Br, 26.63.

The phosphonium salt IIIe derived from IIe (9:1 mixture) had mp 184–185° dec; the nmr of the salt indicated a 9:1 ratio of isomers. A 1:1 mixture of IIIe had mp 181–182° dec. Nmr (D_2O) absorption from the major component (in the 9:1 ratio) occurred at τ 1.62–2.42 (5 H multiplet), 6.33–7.22 (3 H multiplet), 7.49 (3 H doublet, $^2J_{\mathrm{PCH}}$ 14.5 cps), 8.37 (3 H doublet, $^3J_{\mathrm{PCCH}} = 21.0$ cps), 8.93 (3 H doublet, $^3J_{\mathrm{PCCH}} \approx 20$ cps), and 8.70 (3 H doublet, $^3J_{\mathrm{HCCH}} \approx 7$ cps). For the minor isomer absorption occurred at τ 7.43 (3 H doublet, $^2J_{\mathrm{PCH}} = 14.5$ cps), 8.45 (3 H doublet, $^3J_{\mathrm{PCCH}} = 21.5$ cps), and 8.83 (3 H doublet, $^3J_{\mathrm{PCCH}} \approx 20$ cps); the remaining peaks overlapped with the other isomer.

Anal. Calcd for $C_{13}H_{20}BrP$: C, 54.36; H, 7.02. Found: C, 54.52; H, 7.00.

Oxidation of IIc, e, and f with Hydrogen Peroxide.—To 2.2 g (0.01 mole) of IIc (from Ic, mp 123–125°; 90–95% one isomer) in 35 ml of acetone, 1.3 g (0.01 mole) of 30% hydrogen peroxide in 5 ml of acetone was added dropwise; the temperature was kept below 20° by ice-bath cooling. The reaction mixture was evaporated to yield an oil which crystallized on standing. The solid was purified by recrystallization from cyclohexane and sublimed to give 1.6 g (68%) of product, mp 117–125°. The nmr was identical with Ic and contained >90% of the high melting isomer; the infrared spectra were also identical.

In a similar manner IIe and f were individually oxidized at 0° to give products which contained an isomer ratio similar to that in the oxides from which they were derived. In the case of IIe some polymer-like product was also formed during the oxidation; the desired product was separated from this material by hot cyclohexane extraction.

Treatment of Ib with Phenyllithium to Yield Ic.—To 10.0 g (0.05 mole) of the acid chloride (Ib)[1a] in 275 ml of dry ether was added 50 ml (1.0 *M*) of phenyllithium in ether solution over 1 hr at 25°. The reaction mixture was quenched with water and the ether layer was separated, washed with saturated sodium chloride solution, and dried. Evaporation of the solvent produced an oil which was dissolved in benzene and

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[20] Several unsuccessful attempts were made to separate the individual isomers of IIc or e by glpc (20 ft × $^3/_8$ in. column packed with 30% SE 30/firebrick) and distillation (24-in. spinning-band column).

chromatographed over 200 g of Woelm (neutral, grade I) aluminum oxide. Elution with ether–ethanol (20:1) gave a crude solid which was purified by recrystallization from cyclohexane to give 2 g (17%) of Ic, mp 120–125°.

Acknowledgment.—The authors are indebted to the National Cancer Institute for U. S. Public Health Service Grant CA-07806, which supported this investigation. We also are grateful to Dr. Bernard Friedman, Sinclair Oil Co., for a generous supply of several olefins and to the Stauffer Chemical Co. for the phenylphosphonous dichloride.

Alumina-Catalyzed Dehydration of 1-Ferrocenylethanol. Formation of 1,3-Diferrocenyl-1-butene

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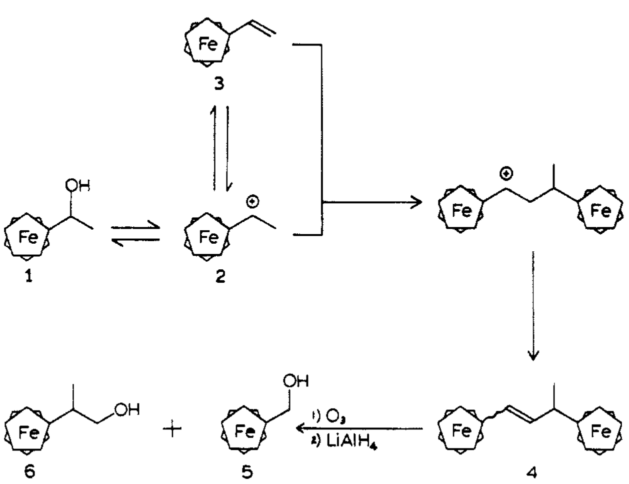
Received June 6, 1967

In 1961, Schlögl and Mohar[1] reported that a brief, room-temperature treatment of 1-ferrocenylethanol (**1**) with acidic Woelm alumina (Brockmann activity I) provided a mild means of effecting dehydration of the carbinol to vinylferrocene (**3**) in about 50% yield. We have found that relatively slight variations in the procedure leads to the formation of 1,3-diferrocenyl-1-butene (**4**).

Thus treatment of 1-ferrocenylethanol with acidic alumina (Merck) in refluxing benzene during 2 hr gave the olefin (**4**) in 77% yield. The structure of the product, possibly a mixture of the *cis* and *trans* forms, was established by the spectrometric data determined from the red, viscous liquid. Its mass spectrum[2] displayed the parent ion peak at 424, and the relative intensities of the $P - 2$, $P + 1$, and $P + 2$ peaks were found to be consistent with the molecular formula, $C_{24}H_{24}Fe_2$. The nmr spectrum showed the presence of the two vinyl protons, the methyl group attached to methine carbon, and the 19 other protons as a broad array of complex signals. The disubstituted, conjugated, olefinic linkage was also clearly indicated in the electronic and infrared spectra obtained from the purified reaction product. The structural assignment was also strengthened by the results obtained from ozonolysis.[3] Lithium aluminum hydride reduction of the ozonide produced from a portion of the purified reaction product gave rise to a two-component mixture; one of which was shown to be hydroxymethylferrocene (**5**), while the other component presumably was the unknown alcohol (**6**).

The formation of 1,3-diferrocenyl-1-butene may be rationalized in terms of the 1-ferrocenylethyl cation (**2**) as illustrated in Scheme I. This rationalization is supported by the fact that both **3** and **4** were obtained when the reaction was carried out for only 30 min at room temperature. A more complete description of the mechanism is not possible, however, principally because of the difficulty in assigning the detailed role which the alumina must play. In this regard it is interesting to note that the use of alkaline alumina, even in refluxing benzene for 2 hr, produces only vinylferrocene and not 1,3-diferrocenyl-1-butene.

Scheme I



An important aspect of this work, in addition to providing a convenient means for the preparation of 1,3-diferrocenyl-1-butene, lies in the fact that all previously reported dimerizations arising from ferrocenylcarbinyl cations are believed to occur *via* radical coupling processes.[4] The present work represents the first-recognized case of a dimerization to which the radical coupling mechanism does not apply, but one which appears to be best-explained in terms of the ionic addition mechanism.

Experimental Section

General.—Temperature measurements were not corrected. Infrared, electronic, and nmr spectra were determined, respectively, on a Perkin-Elmer Model 337 spectrometer, a Perkin-Elmer Model 202 spectrometer, and a Varian A-60 spectrometer. Standard references[5] were used in guiding the interpretation of the spectrometric data.

Treatment of 1-Ferrocenylethanol with Acid-Washed Alumina in Refluxing Benzene.—1-Ferrocenylethanol (0.85 g, 3.7 mmoles), dissolved in 50 ml of benzene, was mixed with 10 g of acid-washed alumina (Merck), which was previously activated (100° for several hours). The mixture was heated under reflux during 2 hr and then allowed to cool to room temperature. After the blue-green alumina was collected in a filter, it was washed with several small portions of benzene. The original benzene filtrate was combined with the washings, and the whole evaporated to **1,3-diferrocenyl-1-butene** (**4**), 0.60 g (77% yield). A portion of the deep red liquid was molecularly distilled [55° (air-bath, 0.25 mm)] to obtain a sample from which the following data were obtained.[6]

The infrared spectrum gave ν^{CCl_4} 3095, 1105, 1000 (ferrocenyl

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[1] K. Schlögl and A. Mohar, *Naturwiss.*, **48**, 376 (1961).

[2] Obtained through the courtesy of Dr. H. M. Fales, National Heart Institute, to whom we acknowledge our sincere thanks.

[3] A general procedure for the ozonolysis of olefinic systems containing a ferrocenyl group, which avoids destruction of the latter, has been recently developed in this laboratory, the details of which will be published elsewhere.

[4] For examples and discussion see, M. Rosenblum, "Chemistry of the Iron Group Metallocenes," John Wiley and Sons, New York, N. Y., 1965, p 121 ff.

[5] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958; K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962; R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966; L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959; J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall Co., Inc., Englewood Cliffs, N. J., 1965; R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967.

[6] The infrared spectrum of the initially obtained reaction product did not differ significantly from that determined with the distilled material, indicating a relatively high purity of the former.