Reaction of Tertiary Phosphines with Hexafluoroacetone and with *o*-Quinones. Attack by Phosphorus on Carbonyl Oxygen and Isolation of 2,2,2-Trialkyl-2,2-dihydro-1,3,2-dioxaphospholanes

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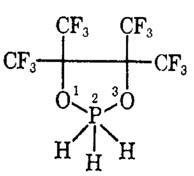
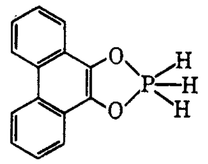
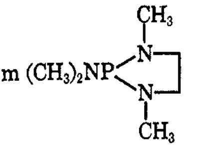
The phosphorus of trialkyl-, alkylaryl-, and triarylphosphines attacked the carbonyl oxygen of hexafluoroacetone at low temperatures (*ca.* −70°). The 1:1 adducts with P–O–C bonds added to more ketone and gave 2:1 adducts with pentavalent phosphorus, which were derivatives of the 1,3,2-dioxaphospholane ring system. The dioxaphospholanes made from the **trialkyl-** and **alkylarylphosphines** underwent relatively slow decompositions at 20°, but were rapidly destroyed at *ca.* 80°. The dioxaphospholane made from **triphenylphosphine** behaved differently. At 120°, this adduct gave hexafluoroacetone, triphenylphosphine, triphenylphosphine oxide, difluorotriphenylphosphorane, and other products. Stable 1,3,2-dioxaphospholenes were obtained from all the tertiary phosphines and phenanthrenequinone, in the range 20–120°. The ^{31}P, ^{19}F, and variable-temperature ^{1}H nmr spectra were recorded. The groups on the pentavalent phosphorus of all the 2,2,2-trialkyl-2,2-dihydro-1,3,2-dioxaphospholanes and phospholenes underwent rapid positional exchange in the time scale of the nmr phenomenon, even at −70°. The tertiary phosphines, the triaminophosphines, and the trialkyl phosphites tend to attack the oxygen of carbonyl functions which are activated by electron-withdrawing groups.

The purpose of this investigation was to compare the behavior of tertiary phosphines, R_3P, triaminophosphines, $(R_2N)_3P$, and trialkyl phosphites, $(RO)_3P$, toward carbonyl compounds. We were concerned with three problems: (1) the mode of attack of the phosphine on the carbonyl function, (2) the relationship between the ^{31}P nmr shift and the nature of the atoms attached to pentavalent phosphorus, and (3) the stereochemistry of the oxyphosphoranes and the ease with which different groups on trigonal-bipyramidal phosphorus undergo positional exchange.

Hexafluoroacetone and phenanthrenequinone were selected for this study because their behavior toward triaminophosphines[2] and trialkyl phosphites[3,4] was known. The phosphorus of these compounds added to the carbonyl oxygen and became part of the 2,2-dihydro-1,3,2-dioxaphospholane ring system (**1–3**) and of the 2,2-dihydro-1,3,2-dioxaphospholene ring system (**4–6**).





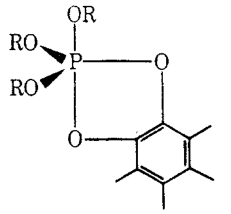


1 derived from $(CH_3)_2NP$ 4

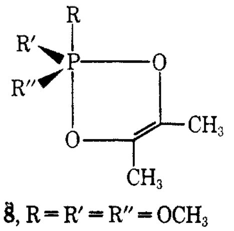
2 derived from $(C_2H_5O)_3P$ 5

3 derived from $(CH_3O)_3P$ 6

The stereochemistry of one of these systems (**7**) was elucidated by X-ray crystallography,[5] and it was found that the phospholene ring occupied an apical-equatorial plane of a trigonal bipyramid. Variable-temperature ^{1}H nmr spectrometry has shown[6] that the groups attached to pentavalent phosphorus in derivatives of the 1,3,2-dioxaphospholene ring, such as **7** and **8–10**, underwent rapid positional exchange[7,8] in the temperature range −60 to +120°.



7, R = i-C_3H_7
$\delta^{31}P = +49.8$ ppm *vs.* H_3PO_4



8, R = R′ = R″ = OCH_3
9, R = R′ = OCH_3; R″ = C_6H_5
10, R = OCH_3; R′ = R″ = C_6H_5

Stereoisomerism at phosphorus has been observed, in solution at 20°, among derivatives of the 2,2-dihydro-1,2-oxaphospholene-4 ring system,[9,10] for example **11a** and **11b**. These isomers were essentially "frozen" in the range −60 to −10°. There was positional exchange among the methoxy groups of each isomer (without their interconversion) in the range 0–40°. Stereomutation **11a** ⇄ **11b** occurred in the range 50–70°, and above this temperature rupture of the ring P–O bond took place. The relative rates at

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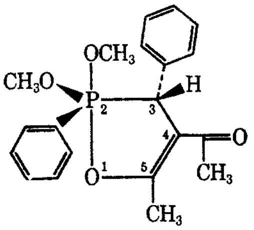
TABLE I

ELEMENTAL ANALYSES AND MAIN INFRARED BANDS OF ADDUCTS[a] DERIVED FROM THE REACTIONS OF TERTIARY PHOSPHINES, $(X_2Y)P$, WITH HEXAFLUOROACETONE AND WITH PHENANTHRENEQUINONE

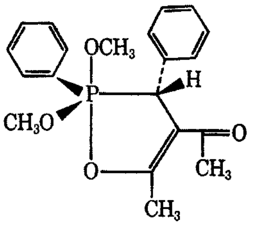
	$(X_2Y)P$		Registry		Molecular	Calcd, %			Found, %			
No.	X	Y	no.	Mp, °C	formula	C	H	P	C	H	P	Ir bands,[b] μ
					Hexafluoroacetone adducts							
16	CH_3	CH_3	17244-54-1	15[c]	$C_9H_9O_2PF_{12}$[d]	26.5	2.2	7.6	26.6	2.3	7.3	7.80, 8.2, 8.50, 8.62, 8.98, 10.00, 10.30, 10.60, 11.3
20	CH_3	C_6H_5	17244-57-4	51–54[e]	$C_{14}H_{11}O_2PF_{12}$	35.7	2.3	...	36.3	2.6	...	7.80, 8.10, 8.30, 8.65, 8.97, 10.05, 10.32, 10.80, 11.30
21	C_2H_5	C_6H_5	17244-58-5	44–47[e]	$C_{16}H_{15}O_2PF_{12}$	38.6	3.0	6.2	39.1	3.1	5.6	7.80, 8.12–8.30, 8.65, 8.97, 9.58, 9.70, 10.05, 10.45, 11.35
22	C_6H_5	C_2H_5	17244-59-6	69–73[e]	$C_{20}H_{15}O_2PF_{12}$[f]	43.9	2.7	5.7	43.5	2.8	5.8	7.80, 8.20, 8.30, 8.70, 9.05, 9.20, 10.05, 10.40, 11.38
24	C_6H_5	C_6H_5	6509-85-9	105–106[e]	$C_{24}H_{15}O_2PF_{12}$	48.5	2.5	5.2	49.3	2.7	5.0	8.92, 10.1, 10.5, 11.4
					Phenanthrenequinone adducts							
29	CH_3	CH_3	17244-66-5	*g*	$C_{17}H_{17}O_2P$	71.8	6.0	...	70.7[g]	6.3	...	6.10, 6.25, 6.65, 6.90, 7.24, 7.50, 7.75, 8.50, 9.40, 9.71, 10.25
30	CH_3	C_6H_5	17244-67-6	95–96[h]	$C_{22}H_{19}O_2P$	76.7	5.5	8.9	76.2	5.7	8.8	6.15, 6.23, 6.70, 6.92, 7.30, 7.58, 8.70, 9.00, 9.82
31	C_2H_5	C_6H_5	17244-61-0	150–151[i]	$C_{24}H_{23}O_2P$	77.0	6.2	8.3	77.0	6.2	8.0	6.10, 6.25, 6.68, 6.90, 7.30, 7.50, 8.50, 8.95, 9.45, 9.72, 10.50
32	C_6H_5	C_2H_5	17244-62-1	125–126[h]	$C_{28}H_{23}O_2P$	79.6	5.4	7.3	79.7	5.5	7.2	6.10, 6.25, 6.68, 6.90, 7.00, 7.28, 7.50, 8.10, 8.50, 8.90, 9.46, 9.70, 10.50
33	C_6H_5	C_6H_5	6546-78-7	165–166[j]	$C_{32}H_{23}O_2P$	81.7	4.9	6.6	82.0	5.1	5.8	6.10, 6.25, 6.70, 6.80, 6.92, 7.32, 8.20, 8.96, 9.50, 9.72, 10.52

[a] 2,2,2-Trisubstituted 1,3,2-dioxaphospholanes (from hexafluoroacetone) and 1,3,2-dioxaphospholenes (from phenanthrenequinone). [b] In CH_2Cl_2 solution. [c] Analysis on adduct as obtained from the reaction; can be recrystallized from hexane at −20°. [d] F, 55.6 (calcd 55.9). [e] From pentane. [f] Mol wt, calcd 546; found 559 (thermoelectric method in benzene). [g] No satisfactory melting point and elemental analysis could be obtained for this relatively unstable adduct. [h] From benzene–hexane. [i] From CH_2Cl_2. The melting point varied with the rate of heating. [j] From benzene. Mol wt, calcd 470; found 466 (cryoscopic in benzene).

which these positional exchanges occurred in the oxyphosphoranes were rationalized[6,9,10] in terms of the steric[5] and electronic[8,11] factors associated with pentavalent phosphorus.



11a, $\delta^{31}P = +16.7$ ppm



11b, $\delta^{31}P = +13.3$ ppm

The reactions of α,β-unsaturated ketones with trialkyl phosphines, triaminophosphines, and trialkyl phosphites have been the subject of a systematic study.[12] The literature is very rich with examples of the behavior of α-halo ketones toward assorted members of these three families of phosphorus compounds.[13]

A recent study[14] concluded that the phosphorus of tributylphosphine attacked the carbonyl carbon of trifluoroacetophenone. This would be in direct contradiction to our findings in the case of triaminophosphines and the same ketone.[2]

The reaction of o-chloranil with triphenylphosphine[15] was reported to yield a 1:1 dipolar adduct with a P–O–C bond.[16] As far as we know, no cyclic oxyphosphorane derived from the reaction of a tertiary phosphine with an o-quinone has been isolated and fully characterized.[17]

Results

Reactions of Tertiary Phosphines with Hexafluoroacetone.—Trimethylphosphine reacted with hexafluoroacetone at −70° in hexane solution. The product was 2,2,2-trimethyl-4,4,5,5-tetrakistrifluoromethyl-2,2-dihydro-1,3,2-dioxaphospholane (**16**).

Structure **16** was based, in part, on the data given in Tables I and II. The elemental analysis disclosed that

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(11) For recent discussions and previous references see (a) P. C. Van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966); (b) L. S. Bartell, *Inorg. Chem.*, **5**, 1635 (1966); (c) R. F. Hudson, "Structure and Mechanisms in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965; (d) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

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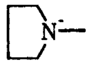
(15) For the reaction of p-quinones with tertiary phosphines see (a) F. Ramirez, D. Rhum, and C. P. Smith, *Tetrahedron*, **21**, 1941 (1965); (b) E. A. C. Lucken, F. Ramirez, V. P. Catto, D. Rhum, and S. Dershowitz, *ibid.*, **22**, 637 (1966); and references therein.

(16) L. Horner and K. Klupfel, *Ann.*, **591**, 69 (1955); see pp 76, 93.

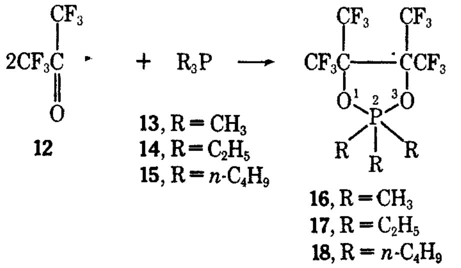
(17) A. N. Hughes and S. Vaboonkul [*Chem. Ind.* (London), 1253 (1967)] investigated the reaction of phenanthrenequinone with triphenylphosphine and water under photochemical activation. See also F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **24**, 1704 (1959).

TABLE II

^{31}P AND ^{19}F SIGNALS[a] OF TERTIARY PHOSPHINES, TRISDIALKYLAMINOPHOSPHINES, AND TRIALKYL PHOSPHITES AND OF THEIR ADDUCTS WITH HEXAFLUOROACETONE AND WITH PHENANTHRENEQUINONE

	$(X_2Y)P$				Adducts with hexafluoroacetone			Adducts with phenanthrenequinone	
No.	X	Y	Registry no.	$\delta^{31}P$ of $(X_2Y)P$	$\delta^{31}P$ of adduct	Δ $P^{III} \rightarrow P^V$	$\delta^{19}F$	$\delta^{31}P$ of adduct	Δ $P^{III} \rightarrow P^V$
16, 29	CH_3	CH_3		62.0	3.2[b]	−59	−9.3	3.0[c]	−59
18, . . .	n-C_4H_9	n-C_4H_9		32.6	−7.3	−40	−9.8	. . .	. . .
17, . . .	C_2H_5	C_2H_5		19.1	−11.7	−32	. . .	. . .	. . .
20, 30	CH_3	C_6H_5		46.0	10.9	−35	−9.7	9.6[d]	−36
21, 31	C_2H_5	C_6H_5		17.0	1.1[e]	−16	−9.8	−0.9[f]	−18
22, 32	C_6H_5	C_2H_5		12.1	6.1[g]	−6	−10.4	9.3[h]	−3
24, 33	C_6H_5	C_6H_5		5.7	22.2[i]	15	−10.6	15.6[j]	10
. . .	$CH_2—CH_2$ $CH_3·N\quad N·CH_3$		17244-65-4	−104.8	30.9	136	. . .	35.1	140
1, 4	$CH_2—CH_2$ $CH_3·N\quad N·CH_3$	$(CH_3)_2N$−	15607-03-1	−114.2	28.3	142	. . .	29.8	144
2, 5	C_2H_5O	C_2H_5O		−138.5	53.2	191	−9.1	47.1	186
3, 6	CH_3O	CH_3O		−140.0	50.1	190	−8.9	44.7	185

[a] $\delta^{31}P$ in parts per million *vs.* H_3PO_4 as 0; measured at 40.5 Mc/sec, at 25°, in CH_2Cl_2 unless otherwise specified. $\delta^{19}F$ in parts per million *vs.* CF_3COOH as 0; measured at 94.1 Mc/sec, at 25°, in $CDCl_3$. [b] In benzene; $\delta^{31}P = 3.2$ ppm in CH_2Cl_2. [c] In benzene; $\delta^{31}P = -1.3$ ppm in CH_2Cl_2. Rapid equilibration of major phosphorane and minor open dipolar ion suspected. [d] In benzene; $\delta^{31}P = 2.4$ ppm in CH_2Cl_2; equilibration of major-P^V and minor-P^{IV} suspected. [e] In benzene; $\delta^{31}P = -1.1$ ppm in CH_2Cl_2. [f] In benzene; $\delta^{31}P = -10.8$ ppm in CH_2Cl_2; equilibration of major-P^V and minor-P^{IV} suspected. [g] In benzene; $\delta^{31}P = 4.1$ ppm in CH_2Cl_2. [h] In benzene; $\delta^{31}P = 7.3$ ppm in CH_2Cl_2. [i] In benzene; $\delta^{31}P = 21.6$ ppm in CH_2Cl_2; 21.0 ppm in nitrobenzene. [j] In benzene; $\delta^{31}P = 15.5$ ppm in CH_2Cl_2.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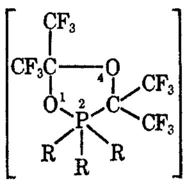
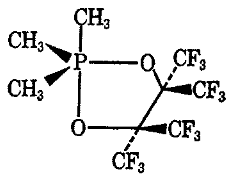
13, R = CH_3
14, R = C_2H_5
15, R = n-C_4H_9

16, R = CH_3
17, R = C_2H_5
18, R = n-C_4H_9

the compound was a simple adduct of 2 mol of the ketone and 1 mol of the phosphine. The ^{19}F spectrum had one sharp singlet, which showed that all the fluorines were magnetically equivalent and thus excluded the 1,4,2-dioxaphospholane structure (**19**). The ^{1}H spectrum in $CDCl_3$ solution had *one doublet*, τ 8.32 (J_{HP} = 9.4 cps), in the temperature range −62 to 30°. The spectrum in *o*-dichlorobenzene had the doublet at τ 8.48 (J_{HP} = 9.4 cps) in the range 30–79°. This behavior was consistent with the trigonal-bipyramidal configuration (**16a**) in which the groups attached to phosphorus were undergoing rapid positional exchange in the time scale of the nmr phenomenon even at the lowest temperature examined.


19, not formed

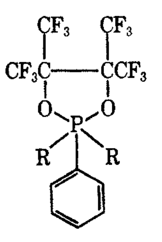

16a

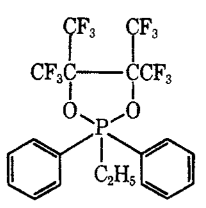
The ^{1}H nmr spectrum of **16** underwent rapid and irreversible changes above 79°, when the original doublet gradually disappeared and was replaced by new doublets at τ 8.14 (J = 15 cps) and 6.0 (J = 20 cps). This behavior proved to be quite general among 1,3,2-dioxaphospholanes of type **16**, in which at least one of the three remaining ligands attached to the phosphorus was an alkyl group carrying an α hydrogen. The nature of these changes will be discussed elsewhere.[17a]

The ^{31}P nmr signal of **16** was weakly positive in relation to the signals of other oxyphosphoranes,[2-4] as can be seen in Table II. This should be emphasized to avoid the growing impression that *all* pentacovalent phosphorus compounds have highly positive chemical shifts *vs.* the usual standard H_3PO_4.

Analogous 1,3,2-dioxaphospholanes **17** and **18** were made from the reaction of hexafluoroacetone with triethyl- and tri-n-butylphosphine (*cf.* Tables I and II). The arylalkylphosphines yielded similar types of compounds, **20–22**. The ^{1}H spectrum of **20** in $CDCl_3$ had one doublet, τ 8.20 (J_{HP} = 9.4 cps), in the range −69 to 30°. In *o*-dichlorobenzene, in the range 30–94°, the doublet was at τ 8.24 (J_{HP} = 9.4 cps). Above this temperature new doublets appeared at τ 7.90 (J = 15 cps) and at 5.80 (J = 20 cps). Likewise, the spectrum of **21** was not significantly different at various temperatures between −69 and 74°; *i.e.*, τ 7.78 (J = *ca.* 8 cps) and 8.89 (J_{HP} = 19.0 cps, J_{HH} = 7.5 cps). The corresponding signals of **22** were τ 7.35 (J = *ca.* 9 cps) and 9.03 (J_{HP} = 22.8 cps, J_{HH} = 7.5 cps) (in $CDCl_3$ at 30°).

The following order of increasing stability was noted in the series of tertiary phosphine–hexafluoroacetone

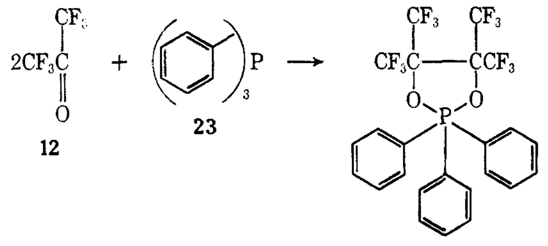

20, R = CH_3
21, R = C_2H_5


22

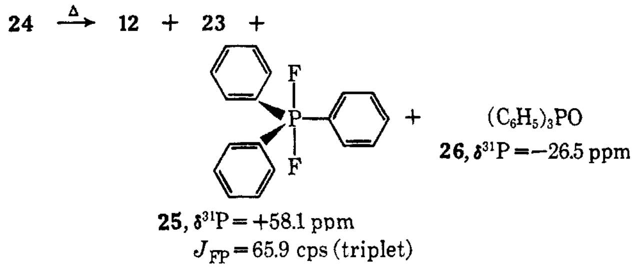
[17a] NOTE ADDED IN PROOF.—The change involves the conversion of the 1,3,2-dioxaphosphopane ring into the 1,2-oxaphosphetane ring, both rings having pentacoordinated phosphorus. See F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, in press.

adducts: $(n\text{-}C_4H_9)_3P \lesssim (C_2H_5)_3P \lesssim (C_2H_5)_2PC_6H_5 < C_2H_5P(C_6H_5)_2 < (CH_3)_2PC_6H_5 < (CH_3)_3P$.

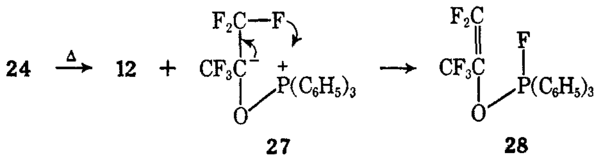
Reaction of Triphenylphosphine with Hexafluoroacetone.—These reagents formed the 1,3,2-dioxaphospholane 24 at −70°, as shown by the data of Tables I and II. Structure 24 was first proposed in two simultaneous preliminary communications.[4a,18]



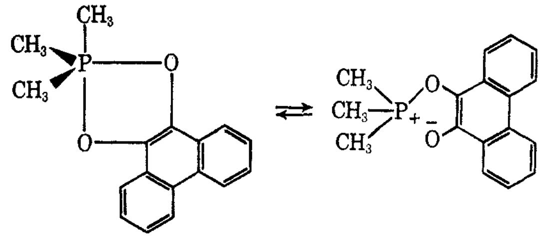
The triarylphosphine adduct 24 and the alkylarylphosphine adducts 20–22 behaved quite differently. Compound 24 was indefinitely stable below 120°, but above that temperature it dissociated into several products: hexafluoroacetone (12), triphenylphosphine (23), difluorotriphenylphosphorane[19] (25), and triphenylphosphine oxide (26), all of which were isolated.



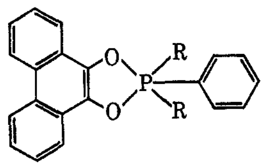
The detailed mechanisms for the formation of these products are not known, but they may involve the intermediates 1:1 adduct 27 and fluorophosphorane 28.



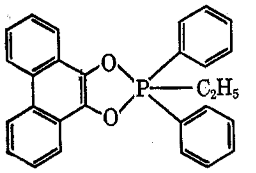
Reaction of Tertiary Phosphines with Phenanthrenequinone.—The reaction of trimethylphosphine with the o-quinone gave a rather unstable pale yellow adduct which was formulated as the 1,3,2-dioxaphospholane 29 from the data of Tables I and II. The configuration 29a was based on previous data,[5] but the groups attached to the phosphorus must be undergoing rapid positional exchange in solution in the temperature range −64 to 30°, since the ^{1}H nmr spectrum in $CDCl_3$ had one doublet, τ 8.31 ($J_{HP} = 9.7$ cps), at those temperatures. The value of the ^{31}P nmr shift of 29 was solvent dependent suggesting that the oxyphosphorane 29a and the open dipolar ion 29b had comparable energies.[2] In solution, both forms probably existed in rapid equilibrium, with the oxyphosphorane form greatly predominating. When phenanthrenequinone was added to a benzene solution of the yellow adduct 29, a deep red-brown color was generated. This may be due to the formation of a charge-transfer complex related[15] to the quinhydrones.



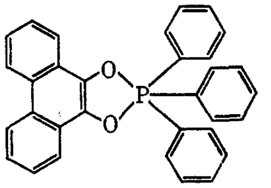
The alkylphenylphosphines gave analogous 1:1 adducts 30, 31, and 32, with the o-quinone. Triphenylphosphine was rather unreactive, but it gave the adduct 33 when the reagents were heated to 120°. Adduct 33 had the same ^{31}P nmr shift in benzene and in methylene chloride solutions. These oxyarylphosphoranes should be compared with the related pentaarylphosphoranes.[20]



30, R = CH$_3$
31, R = C$_2$H$_5$



32



33

Discussion

^{31}P Nmr Shifts of Oxyphosphoranes.—Several conclusions can be drawn from the data of Table II.

(1) The shifts of all the oxyphosphoranes derived from hexafluoroacetone were similar in benzene and in methylene chloride solutions, but the shifts of some of the adducts made from phenanthrenequinone were at higher magnetic field in benzene than in methylene chloride. This is probably related to the relative stabilities of the oxyphosphorane form and the dipolar ion form of a given adduct. If the two forms have comparable stability, and if the establishment of an equilibrium between the two is rapid in solution in the time scale of the nmr, the value of the ^{31}P nmr shift will simple reflect the position of that equilibrium. In the adducts under discussion, the shift of the phosphorane is at a higher magnetic field[21] than that of the dipolar ion; therefore, the greater the proportion of phosphorane at equilibrium, the more positive (or less negative) the shift. In this interpretation, the oxyphosphorane is favored over the dipolar ion to a greater extent if the solvent is benzene than if it is methylene

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(18) R. F. Stockel, *Tetrahedron Lett.*, 2833 (1966).

(19) (a) W. C. Firth, S. Frank, M. Garber, and V. P. Wystrach, *Inorg. Chem.*, **4**, 765 (1965); (b) R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964).

(20) (a) G. Wittig, *Bull. Soc. Chim. Fr.*, 1162 (1966); (b) D. Hellwinkel, *Ber.*, **99**, 3628, 3642, 3660, 3668 (1966).

(21) The larger the positive value, or the smaller the negative value, of the ^{31}P nmr shift (*i.e.*, the higher the magnetic field at which the signal appears), the more effective is the shielding of the ^{31}P nucleus by electrons.

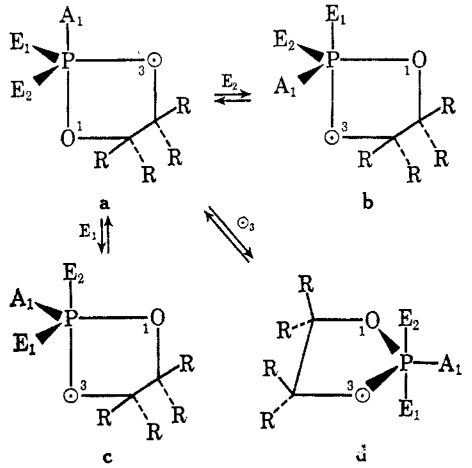
chloride. This is in agreement with our previous findings[2] in the case of the adduct made from benzil and trisdimethylaminophosphine.[22]

All the data now available concerning the tendency of these adducts to exist in the oxyphosphorane or in the dipolar ion forms can be summarized as follows. (a) *For a given tertiary phosphine* there is a greater tendency toward oxyphosphorane when the carbonyl compound is hexafluoroacetone than when it is phenanthrenequinone. (b) *For a given o-quinone* the presence of phenyl rings instead of alkyl groups on the phosphorus favors the oxyphosphorane structure. Note the sequence in the adducts from triphenylphosphine > ethyldiphenylphosphine > diethylphenylphosphine ~ dimethylphenylphosphine > trimethylphosphine. (c) *For all types of carbonyl compounds*, the tendency toward the formation of an oxyphosphorane decreased in the order trialkyl phosphites > trisdialkylaminophosphines > tertiary phosphines.[2-4,6] This reflects the different effects of stereoelectronic factors on the stability of pentavalent and tetravalent phosphorus.

(2) The values of the ^{31}P nmr shifts of 2,2,2-trialkyl-1,3,2-dioxaphospholanes depend in a regular manner on the values of the shifts of the corresponding trivalent phosphorus compound. The shift of pentavalent phosphorus was always at a much lower magnetic field than that of the trivalent phosphorus precursor. The less positive the shift of the phosphine, the smaller the displacement of the oxyphosphorane shift toward lower magnetic field. The same relationship operated among the alkylaryl-1,3,2-dioxaphospholanes. The presence of phenyl rings on pentavalent phosphorus led to a displacement of the shift toward higher magnetic field relative to the corresponding compound lacking the phenyl. These effects resulted in an "inversion" of the displacement of the ^{31}P shift in going from trivalent phosphorus to pentavalent phosphorus. Now, the phosphorane shift was at a higher magnetic field than that of the phosphine. Note how strongly positive are the shifts of the pentaoxyphosphoranes made from trialkyl phosphites, whose shifts are strongly negative. The trisdialkylaminophosphines represent a case which is intermediate between the phosphines and the phosphites, in this respect. These observations could be of value in theoretical interpretations of ^{31}P nmr spectra[23] and are helpful in the diagnosis of the valence state of the phosphorus in related compounds. Certainly, not all compounds with pentavalent phosphorus have strongly positive chemical shifts relative to the usual standard H_3PO_4.

Stereochemistry of the Oxyphosphoranes.—Variable temperature ^1H nmr spectrometry showed that the three methyl groups attached to the phosphorus in the hexafluoroacetone–phosphine adduct (**34**) undergo rapid positional exchange in solution in the temperature range −62 to 79°. The shift and the coupling constant of the doublet observed represent an average of the corresponding values of apical and equatorial methyl groups on the trigonal bipyramid. Note also that the four CF_3 groups gave only one ^{19}F signal, a sharp singlet at 30°.

Previous studies[6,9,10] have shown that the positional exchange of groups on the phosphorus of certain derivatives of the 2,2-dihydro-1,2-oxaphospholene-4 ring system (**11**) can be inhibited at certain temperatures. It was suggested that, at least at low temperatures, the positional exchange occurred by the "pseudorotation" mechanism.[7,8] An application of this mechanism to the ketone–phosphine adducts is shown in formulas **34**–**37**. To convert bipyramid *a* into *b* by pseudorotation, group E_2 (the pivot) was fixed, while groups A_1 and O_1 were pushed back (closing the A_1PO_1 angle from 180 to 120°), and groups E_1 and O_3 were pulled forward (opening the E_1PO_3 angle from 120 to 180°). This gave the new bipyramid b lying on its side; this was rotated 90° counterclockwise about the pivot axis, E_2–P, and then turned upside down by a 180° rotation about the P–O_1 axis. In this way, it is immediately apparent that the pivot group, E_2, remained equatorial, but the other four groups exchanged positions. The ring remained in an apical–equatorial plane with a 90° O_1PO_3 angle.



34, $A_1 = E_1 = E_2 = CH_3$; $R = CF_3$
35, $A_1 = E_1 = CH_3$; $E_2 = C_6H_5$; $R = CF_3$
36, $A_1 = E_1 = C_2H_5$; $E_2 = C_6H_5$; $R = CF_3$
37, $A_1 = C_2H_5$; $E_1 = E_2 = C_6H_5$; $R = CF_3$

The pseudorotation of a using group E_1 as pivot can be carried out as indicated, after the proper reorientation of the bipyramid a; when this is done, the result is bipyramid c. Likewise, it can be shown that pseudorotation of a using O_3 as pivot gives bipyramid d, where the ring is in a diequatorial plane.[24,24a]

In the **trimethylphosphine adduct** (**34**), bipyramids a, b, and c, are identical, but d is different. In the **dimethylphenylphosphine adduct** (**35**), b is an enantiomer of a, but c and d are diastereomers of a, and are both *meso* forms; another *meso* form similar to d,

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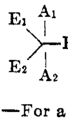
[22] For other work on the reaction of benzil with trisdimethylaminophosphine see R. Burgada, *C. R. Acad. Sci., Paris*, **258**, 4789 (1964); *Bull. Soc. Chim. Fr.*, 347 (1967).

[23] (a) J. H. Lechter and J. R. VanWazer, *J. Chem. Phys.*, **44**, 815 (1966); (b) *ibid.*, **45**, 2916, 2926 (1966).

[24] In the general case, $P(A_1A_2E_1E_2E_3)$, where the five groups on phosphorus are different but symmetric, there are ten pairs of enantiomers: a–a′, b–b′, . . ., j–j′. The pseudorotation of a to b using E_2 as pivot can be denoted by a(E_2)b. The other diastereomers can be derived as follows: a(E_1)c; a(E_3)d; b(A_1)e; b(A_2)f; c(A_1)g; c(A_2)h; d(A_1)i; d(A_2)j. Five *consecutive* pseudorotations using *different* groups as pivots convert a bipyramid into its enantiomer, for example, a(E_2)b(A_1)e(E_1)j′(A_2)d′(E_3)a′ (see ref 8).



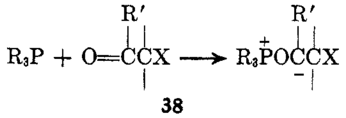
[24a] NOTE ADDED IN PROOF.—For a systematic geometrical analysis of isomerizations of trigonal bipyramidal molecules by pseudorotation, see P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, in press.

but with the phenyl ring in an equatorial position, is possible. The stereochemical analysis of the other adducts, **36** and **37**, can be made by proper substitution of the groups A_1, E_1, and E_2 in the various bipyramids. The experimental results show that the energy barriers for the pseudorotations which cause the positional exchanges are too low to permit inhibition at −62°. The energetic consequences of the conversion of a into d are not entirely clear at this time, but it may be that the expansion of the OPO angle in a *saturated*, and in an *unsaturated*, five-membered ring[6,7,10] represents an unfavorable process relative to other possible isomerizations. As the temperature is increased above 30°, the rupture of a ring P–O bond becomes a distinct possibility. In fact, irreversible decompositions occurred slowly at 30° and rapidly at 80°.

Mechanism of the Reactions of Trivalent Phosphorus Compounds with Carbonyl Functions.—This investigation showed that tertiary phosphines behaved like triaminophosphines and trialkyl phosphites toward mono- and polycarbonyl compounds.[2,3] In these reactions, the trivalent phosphorus became attached to the carbonyl oxygen, provided that the carbonyl function was under some activation by electron-withdrawing substituents. Any feature in the molecule which was capable of providing some degree of delocalization of negative charge on carbonyl carbon enabled the phosphorus to exercise its tendency to become bonded to oxygen. In this manner, a 1:1 adduct with $\geqslant P^{+}\text{–O–}C^{-}$ structure was formed. The 1:1 adduct cyclized to an oxyphosphorane in the case of an *o*-quinone or reacted with a second molecule of the carbonyl compound in the case of hexafluoroacetone. The 2:1 adduct also was stabilized by formation of an oxyphosphorane. In fact, *the tendency to form a 1,3,2-dioxaphospholene or a 1,3,2-dioxaphospholane ring with pentavalent phosphorus seems to be the driving force for all of these reactions.*

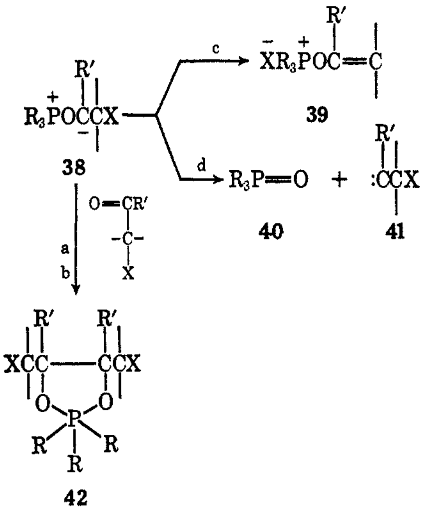
The quantitative differences in the degree of stability of pentacovalent phosphorus are due to two factors: (1) the electronegativity of the element directly attached to the phosphorus, and (2) the steric requirements of the groups once removed from the phosphorus. The operation of these factors has been discussed in detail in previous papers from this laboratory.[2-5,25] In summary we find (1) the lower the electronegativity of the element attached to the phosphorus (O > N > C), the lower the stability of the oxyphosphorane, and (2) the larger the steric requirements of the group attached to the phosphorus ($OR < NR_2 < CR_3$), and the larger the steric requirements of the alkyl groups themselves (R), the lower the stability of the oxyphosphoranes (this steric effect is related to the significant intramolecular overcrowding[5] associated with the trigonal-bipyramidal configuration of pentacoordinated phosphorus).

A great deal has been written on the mechanism of the reactions of tertiary phosphines and of trialkyl phosphites with α-halo ketones.[11c,13] There is no doubt that some of the halogens, in the order I > Br > Cl, can be attacked directly by the phosphorus of certain trivalent phosphorus compounds. Likewise, direct nucleophilic displacements at the α carbon can occur in certain cases. However, the evidence is rather compelling for the *addition of the phosphorus of triaminophosphines, tertiary phosphines, and trialkyl phosphites to the carbonyl oxygen of the α-halo ketones.* The degree of stabilization of the negative charge on the carbonyl carbon in the P–O–C adduct **38** will depend on the kind and number of halogen atoms X at the α carbon. This stabilization should decrease in the order F > Cl > Br >



$$R_3P + O{=}\overset{R'}{C}\underset{|}{C}X \longrightarrow R_3\overset{+}{P}O\overset{R'}{\underset{-}{C}}\underset{|}{C}X$$

I. The lifetime of the 1:1 adduct **38** should depend on (a) the nucleophilicity of the carbanion toward a second carbonyl function, (b) the electrophilicity of that second carbonyl function, (c) the tendency of **38** to eject a halide ion and (d) the tendency of **38** to eject a phosphoryl group.



Operation of factors a and b should lead to the formation of 1,3,2-dioxaphospholane (**42**), as we have observed in *all* the reactions of perfluoro ketones. Operation of factor c will, in extreme cases, render intermediate **38** operationally meaningless; *i.e.*, the formation of the enol-phosphonium ion pair **39** becomes a concerted process. Operation of factor d will lead to the deoxygenations by trivalent phosphorus compounds (**38** → **40** + **41**), about which so much has been written.[26]

The question of whether the P–O–C adduct **38** is formed *directly* by attack of phosphorus on carbonyl oxygen, or *indirectly* by rearrangement of a P–C–O adduct **43**, or in *reversible processes* has not been settled. Again, this matter becomes less operationally significant as the rate of the hypothetical rearrangement **43** → **38** increases and as the position of equilibrium shifts to P–O–C adduct **38**. The probability for the *initial* formation of a P–C–O adduct **43** should be considerably higher for haloaldehydes than for halo ketones. In fact, we have demonstrated[6b] that the *first product* isolated from the reaction of pentafluorobenzaldehyde

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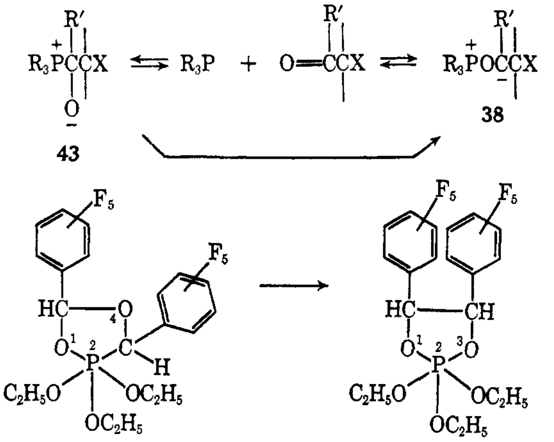
[25] F. Ramirez, C. P. Smith, and S. Meyerson, *Tetrahedron Lett.*, 3651 (1966).

[26] (a) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Amer. Chem. Soc.*, **83**, 173 (1961); (b) F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Org. Chem.*, **31**, 4105 (1966); (c) R. J. Sundberg, *ibid.*, **30**, 3604 (1965); (d) R. J. Sundberg, *J. Amer. Chem. Soc.*, **88**, 3781 (1966); (e) J. I. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Serale, *J. Chem. Soc.*, 4831 (1965); (f) J. I. Cadogan, D. J. Sears, and D. M. Smith, *Chem. Commun.*, 491 (1966); (g) T. Mukaiyama, J. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962); (h) H. Das and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **7**, 965 (1965); (i) A. W. Johnson and R. B. LaCount, *J. Amer. Chem. Soc.*, **83**, 1417 (1961); (j) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962).

with triethyl phosphite was a 1,4,2-dioxaphospholane (**44**) but the final, stable product of the reaction was a 1,3,2-dioxaphospholane (**45**). At some point, still undetermined, a P–C–O bond was transformed into a P–O–C bond.[6b] We have no evidence for or against the operation of this mechanism in the case of ketones.



44, $\delta^{31}P = +37$ ppm (*cis* H/H) $\delta^{31}P = +42$ ppm (*trans* H/H)

45, $\delta^{31}P = +50$ ppm (*cis* H/H) $\delta^{31}P = +54$ ppm (*trans* H/H)

The modes of reaction of many trivalent phosphorus compounds with carbonyl compounds are now fairly well understood. However, the basic factors that tend to direct the phosphorus to oxygen, carbon, or halogen remain to be elucidated. An interesting approach to this problem has been discussed recently.[11c,27]

Experimental Section

The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of Hexafluoroacetone with Trialkylphosphines and with Alkylarylphosphines.—Hexafluoroacetone in excess (over 2 mol equiv of the tertiary phosphine) was collected in a flask cooled by means of a Dry Ice–solvent mixture. The ketone was then allowed to evaporate slowly into a stirred solution of the corresponding tertiary phosphine in hexane (0.5–0.8 *M*) kept at about −70°. There was evidence of reaction at this temperature; in some cases a colorless solid appeared within minutes. The mixture was kept for 15 min at −70° and was then allowed to reach 20°. The hexane was immediately removed under reduced pressure, without the application of heat. The residue was a liquid in the case of the adducts **16**, **17**, and **18**, made from trimethyl-, triethyl-, and tributylphosphines, and crystalline in the case of the adducts **20**, **21**, and **22** made from dimethylphenyl-, diethylphenyl-, and ethyldiphenylphosphines. All the 1,3,2-dioxaphospholanes made in this manner were obtained in nearly quantitative yield, based on the measurements of the ^{31}P, ^{19}F, and ^{1}H nmr spectra and ir spectra which were made on the fresh samples. These data are given in Tables I and II.

The liquid trimethylphosphine adduct **16** solidified at *ca.* 5°. It could be purified by fractional crystallization from hexane at −20°. In one experiment, the crude liquid adduct was filtered through a sintered-glass funnel and submitted to elemental analysis as such. The results agreed with the calculated values.

The liquid triethyl- and tributylphosphine adducts **17** and **18** could not be purified by fractional crystallization and were too unstable for purification by distillation.

The remaining adducts listed in Tables I and II were isolated in *ca.* 90% yield by recrystallizations from pentane. The adducts were stored at −20°, under N_2, for periods of 1 month or less.

High purity of the phosphines and of the ketone is essential for reproducible results. One tank of hexafluoroacetone contained an unknown impurity that resulted in a very complex reaction with trimethylphosphine. When that occurred, white fumes were observed as the ketone became in contact with the phosphine. Removal of the hexane left a solid not observed in other experiments. When the "abnormal" material was treated with $CDCl_3$ a gellike mixture was produced. These phenomena are being studied further.

Reaction of Hexafluoroacetone with Triphenylphosphine.—An excess of hexafluoroacetone was condensed into a solution of 25.8 g (98.3 mmol) of triphenylphosphine dissolved in 80 ml of methylene chloride at −70°. A large amount of a white solid precipitated out after stirring at −70° for 0.5 hr. The mixture was slowly brought to room temperature, giving a clear, pale yellow solution. The mixture was cooled again to −70°, and more hexafluoroacetone was added. After warming to room temperature, the solvent was removed *in vacuo*, leaving behind 54.4 g (93.1%) of the crude adduct, melting at 95–97°. After three recrystallizations from *n*-hexane, 2,2,2-triphenyl-4,4,5,5-tetrakistrifluoromethyl-2,2-dihydro-1,3,2-dioxaphospholane (**24**) was obtained, mp 105–106° with gas evolution. The elemental analysis, the ^{31}P and ^{19}F nmr spectra and the ir spectra are given in Tables I and II.

Pyrolysis of Hexafluoroacetone–Triphenylphosphine Adduct.—The solid adduct (19.24 g, 32.4 mmol) was heated in a bath at 115–120° for 45 min. As the temperature was raised to 100°, the solid adduct began to decompose. At 120° the melt bubbled vigorously. At the end of 45 min, the heating was stopped, and the melt was cooled to 30°; the weight loss was 9.42 g. Hexafluoroacetone was collected in the amount of 5.8 g. (If all the adduct had dissociated into hexafluoroacetone and triphenylphosphine and if all of the former compound had been distilled out, the weight loss would have been 10.7 g.) The residue, on trituration with two 100-ml portions of *n*-hexane, gave a hexane-soluble and a hexane-insoluble portion. Triphenylphosphine was isolated from the hexane-soluble portion in an amount corresponding to 55% based on the adduct decomposing into hexafluoroacetone and triphenylphosphine. The hexane-insoluble portion was subdivided further into a benzene-soluble and a benzene-insoluble portion. Triphenylphosphine oxide was isolated from the benzene-soluble portion in an amount corresponding to 10% based on conversion of all the phosphorus into the oxide. The benzene-insoluble portion gave difluorotriphenylphosphorane in 30% yield based on conversion of the phosphorus of the adduct into the difluorophosphorane. The melting point (157°) and the spectral data were in agreement with those reported in the literature.[19] An authentic sample was made from triphenylphosphine and SF_4 as described.[19]

Reaction of Phenanthrenequinone with Trimethylphosphine. A.—The quinone was added in small portions (20 min) to a solution of trimethylphosphine (1.3 mol equiv) in benzene, at 25°. A clear, pale yellow solution was obtained. The solvent was removed at 20°, first at 20 mm, and then at 0.1 mm, without exposure of the product to moist air. The residue was a yellow solid which was handled in a dry N_2 atmosphere. This adduct, **29**, acquired a greenish color when transferred to an nmr sample tube containing benzene. The ^{31}P nmr spectrum had a major signal at 3.0 ppm (decet, $J = 9$ cps) and a very weak signal at −35.1 ppm [$(CH_3)_3PO$] (6.3:1 proportion).

B.—Although formation of a pale yellow quinone–phosphine adduct, **29**, by the above procedure was reproducible, a slight excess of quinone (over 1 mol equiv) gave a deep brown-green adduct. Apparently, a colored complex between quinone and adduct **29** was formed. Moreover, color was generated by the decomposition of the adduct.

C.—If 1 mol equiv of trimethylphosphine was added, slowly, to a suspension of phenanthrenequinone in benzene at 20°, a brown-red clear solution (0.5 *M* based on quinone) was obtained. The benzene was removed at 20° and 20 mm. The red-brown solid was analyzed by ^{31}P and ^{1}H nmr spectrometry in CH_2Cl_2 solution. The major signals were those corresponding to adduct **29** (*cf.* Table II). There were very weak additional signals, not identified further.

Reaction of Phenanthrenequinone with Alkylarylphosphines and with Triphenylphosphine. Dimethylphenylphosphine.—A 1-mol equiv sample of the phosphine was added dropwise to the quinone in CH_2Cl_2 at −70°. The mixture was brought to 20°, the solvent was removed *in vacuo*, and the yellow adduct **30** was recrystallized from benzene–hexane.

Diethylphenylphosphine.—A 2-mol equiv sample of the phosphine was added to the quinone at 20°. After the exothermic reaction, the mixture became a yellow solid. The adduct **31** was obtained by recrystallization from CH_2Cl_2.

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[27] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

Ethyldiphenylphosphine.—The phosphine (1 mol equiv) was added to the quinone in CH_2Cl_2 at 20°. After 2 hr at 20°, the solvent was removed *in vacuo* and the residue, **32**, was recrystallized from benzene–hexane.

Triphenylphosphine.—Equimolar amounts of the reagents were mixed at 20°. There was no evidence of reaction. The mixture was kept 4 hr at 120°, cooled, and triturated with hexane. The insoluble product, **33**, was recrystallized from benzene. Elemental analyses and spectral data are given in Table I and II.

Registry No.—Hexafluoroacetone, 684-16-2; **1**, 17224-68-7; **2**, 1708-77-6; **3**, 6509-88-2; **4**, 15607-05-3; **5**, 6509-81-5; **6**, 4903-06-4; **17**, 17244-55-2; **18**, 17244-56-3.

Metathesis of 2-Pentene by a Binary Catalyst System of Tungsten Hexachloride and *n*-Butyllithium

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Nearly pure *cis* (94%), pure *trans*, and a mixture of 46% *trans*- and 54% *cis*-2-pentene were metathesized by a catalyst system of tungsten hexachloride and *n*-butyllithium. The reaction with *cis*-2-pentene or mixed 2-pentene reached redistribution equilibrium in 4 hr, where scrambling of the alkylidene groups attained the theoretical maximum, at which 50% of the original olefin was converted. However, conversion of *trans*-2-pentene was only 40% under the same conditions. Regardless of the extent of conversion of 2-pentene, the selectivity to 2-butene and 3-hexene was 100 mol % in experiments at room temperature with ratios of olefin/W = 50, and *n*-BuLi/W = 2. Good results were not obtained at other ratios. A possible mechanism of this metathesis reaction with the *n*-butyllithium catalyst system is proposed. This use of alkyllithium and tungsten hexachloride has not been reported previously.

Recently, a new reaction in olefin chemistry, called "olefin metathesis," has been reported.[1,2] It was found that a ternary catalyst system containing tungsten hexachloride, ethylaluminum dichloride, and ethanol breaks carbon–carbon double bonds in internal olefins and randomly rejoins the fragments.

$$\underset{(50\%)}{2RCH{=}CHR'} \rightleftharpoons \underset{(25\%)}{RCH{=}CHR} + \underset{(25\%)}{R'CH{=}CHR'}$$

A similar reaction, labeled "olefin dismutation" or "olefin disproportionation" by the authors,[3,4] has been described for internal and terminal olefins, which are passed over a solid catalyst of molybdenum or tungsten oxides on alumina. Isomerization and oligomerization were also observed under certain conditions.

To minimize possible cationic reactions due to aluminum compounds, we chose *n*-butyllithium as the reducing agent for tungsten hexachloride, in the absence of ethanol. To the best of our knowledge, alkyllithium and tungsten hexachloride have not been reported previously in this application, although claimed in a patent.[5]

Experimental Section

Materials.—Mixed 2-pentene (*trans/cis* = 0.85), 96% *cis*- and 100% *trans*-2-pentene, and *n*-pentane, from Chemical Samples Co., Columbus, Ohio, were all dried over sodium wire and distilled from sodium bisulfite under nitrogen. The distillates were tested by potassium iodide in acetic acid and found to be free of peroxides. Benzene was distilled and dried with sodium wire. Tungsten hexachloride was purified by sublimation of the more volatile reddish orange tungsten(VI) oxychlorides (WO_2Cl_2 and $WOCl_4$) and nitrogen at about 200°, leaving a residue of pure tungsten hexachloride.

Procedure.—All the reactions were carried out in 4-oz glass bottles at room temperature. Before sealing with rubber and Teflon gaskets, a 4-oz bottle was oven-dried for several hours at 110° and then cooled with nitrogen for about 5 min.

Injections of chemical reagents were done by means of hypodermic syringes from which air and moisture were carefully excluded. The injection order of reactants used in all the experiments was (1) 5 ml of 0.04 *M* WCl_6 in benzene (2×10^{-4} mol), (2) 2.25 ml of 4.5 *M* 2-pentene in *n*-pentane (1×10^{-2} mol), (3) 10 ml of 0.04 *M* *n*-BuLi in benzene (4×10^{-4} mol), and (4) 1 ml of isopropyl alcohol.

Reaction time shown in the tables began from the time of injection of *n*-butyllithium, whereupon the reaction mixture was agitated on a Burrell shaker. It was found that vigorous mixing was necessary for good reproducibility. After a chosen reaction time was reached, reaction was stopped by injecting 1 ml of isopropyl alcohol into the reaction mixture. Then the reaction mixture was cooled in Dry Ice before analysis by vapor phase chromatography (vpc).

Vpc Analysis.—All the analyses were done on a 42 ft × 0.125 in. Tergitol column at a column temperature of 60° and 40 cc/min of helium flow rate. The Aerograph 202 T/C instrument was programmed to 180° after elution of 3-hexene. *n*-Pentane was used as an internal standard to estimate percentage of conversion and selectivity to the products, *trans*- or *cis*-2-butene and 3-hexene. (The isomers of 3-hexene were not resolved by the Tergitol column.) The olefins 2-pentene, 2-butene, and 3-hexene all have the same ratio of vpc area response to *n*-pentane as the weight ratio of each component to *n*-pentane.

Results and Discussion

The terms "conversion" and "selectivity" used here are defined as follows: % conversion = % of initial 2-pentene reacted; mol % selectivity = (moles of 2-butenes or moles of 3-hexenes) × 100/moles of 2-pentene reacted.

The conversion of mixed 2-pentene increased rapidly during the first 60 min and then very slowly until redistribution equilibrium (50% conversion) was reached at 240 min (Figure 1). After that, per cent conversion remained independent of time. *cis*-2-Pentene also attained 50% conversion at 240 min, whereas *trans*-2-pentene reached only 40% conversion after 240 min. The failure of the latter to attain equilibrium

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[1] (a) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, **34**, 3327 (1967); (b) *Chem. Eng. News*, **45** (41), 51 (1967).

[2] N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, in press.

[3] C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, **7**, 269 (1967).

[4] R. L. Banks and G. C. Bailey, *Ind. Eng. Chem.*, *Prod. Res. Develop.*, **3**, 170 (1963).

[5] N. Calderon, Belgian Patent 698,075 (May 5, 1967).