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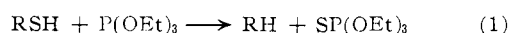
Some Radical Reactions of Trivalent Phosphorus Derivatives with Mercaptans, Peroxides, and Olefins. A New Radical Cyclization¹

BY CHEVES WALLING AND MYRNA SCHMIDT PEARSON²

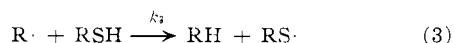
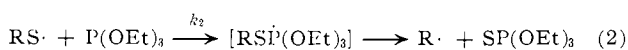
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In the radical reaction between *n*-butyl mercaptan and triethyl phosphite, thiyl radicals are shown to react with phosphite at rates intermediate between their addition to styrene and cyclohexene. By suitable adjustment of reagent concentrations the *n*-butyl radicals formed may be caused to alkylate styrene and methyl acrylate in low yield. Reaction of 6-mercapto-1-hexene with triethyl phosphite produces the 6-hexen-1-yl radical which cyclizes chiefly to methylcyclopentane. This "unexpected" direction of radical ring closure and the failure of the 5-penten-1-yl radical to cyclize is suggested to have a steric origin. By competitive reactions it is shown that *t*-butoxy radicals attack triethyl phosphite 500–1000 times as rapidly as they abstract hydrogen from typical hydrocarbons, and some 82 times as rapidly as they attack triphenylphosphine. Relative reactivities of thiyl radicals toward trivalent phosphorus give an order of reactivity $P(n-C_4H_9)_3 > P(OC_2H_5)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$.

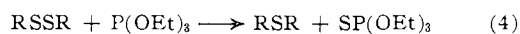
Previous work from these laboratories³ has shown that the reaction between trialkyl phosphites and mercaptans



first described by Hoffmann, *et al.*,⁴ is a radical chain process involving the propagating steps



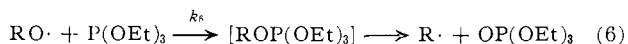
It was also found that a comparable reaction occurs between disulfides and trialkyl phosphites (again using triethyl phosphite as an example)



in which reaction 3 is replaced by



and that alkoxy radicals from *t*-butyl and cumyl peroxides are rapidly deoxygenated by phosphites to

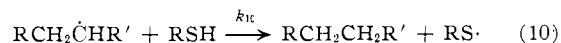
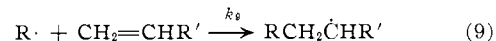
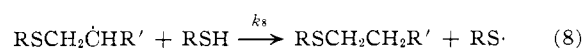
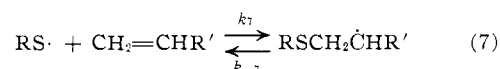


give phosphate and hydrocarbon by coupling or disproportionation of $R\cdot$ radicals. Similar reactions were also found to take place with trialkyl- or triarylphosphines.⁵

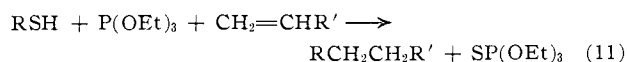
These processes are interesting, both as among the first examples of radical addition to phosphorus to yield the phosphoranyl radical with a valence shell expanded to nine electrons,⁶ and because they provide a method of generating carbon radicals of known structure from the corresponding mercaptan, disulfide, or peroxide. The work described here was undertaken to determine the relative rates of the intermediate steps involved and to see whether carbon radical additions to olefins could be introduced into the chain sequence to yield over-all reactions of synthetic utility.

Mercaptan-Phosphite-Olefin Reactions.—If an olefin is introduced into a mercaptan-phosphite system, four

additional elementary steps are possible in the chain sequence leading to two additional products



Sequence 7 and 8 amounts simply to the radical addition of a mercaptan to a double bond to give a sulfide but 2, 9, and 10 gives the over-all reaction



a possible technique for free radical alkylation.

We have investigated the relative rates of these processes by treating *n*-butyl mercaptan with triethyl phosphite in the presence of styrene and cyclohexene at 70° using azobisisobutyronitrile (AIBN) as initiator. Results are shown in Table I. In all reactions, sulfide

TABLE I
REACTIONS OF TRIETHYL PHOSPHITE, *n*-BUTYL MERCAPTAN,
AND OLEFINS
Quantities in millimoles, all at 70°, 1–24 hr. reaction in the presence of AIBN unless indicated^a

	[Olefin] ₀	[RSH] ₀	[P-(OEt) ₃] ₀	[SP-(OEt) ₃] _f	[Sulfide] _f	k_7/k_2
Styrene	2.1	4.5	4.5	1.9	1.5	2.3
	3.5	4.3	4.5	1.3	1.9	2.3
	4.3	4.1	4.3	1.6	2.5	1.9
	17.4	9.5	29.2	0.52	1.37	4.4
	26.2	9.5	29.2	0.43	1.02	4.9
Cyclohexene	100	100	100	73	18	0.15 ^b
	19.0	9.5	29.2	4.05	0.66	.26
	28.5	9.5	29.2	3.14	0.87	.26

^a Subscript 0 and f indicate initial and final concentration, respectively. ^b At 60°.

was a conspicuous product, but no alkylated olefin could be detected. Under these circumstances, yields of sulfide and phosphorothionate, $SP(OEt)_3$, should be given by the relation

$$\frac{d[\text{olefin}]}{d[P(OEt)_3]} = \frac{d[\text{sulfide}]}{d[SP(OEt)_3]} = \frac{k_7[\text{olefin}]}{k_2[P(OEt)_3]} \quad (12)$$

providing the reversibility⁷ of 7 can be neglected.

(7) C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).

(1) Taken from the Ph.D. Thesis of M. S. Pearson, Columbia University, 1963. Partial support of this work by grants from the National Science Foundation is gratefully acknowledged.

(2) Du Pont teaching fellow 1960–1961; Esso Fellow, 1961–1962.

(3) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957); **81**, 1243 (1959).

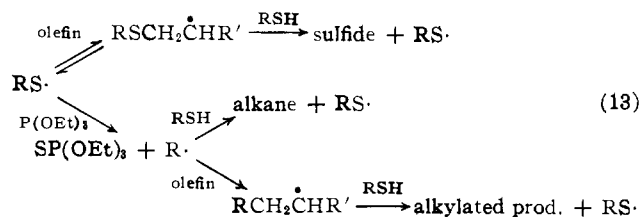
(4) F. W. Hoffmann, R. J. Ess, T. C. Simmons, and R. S. Hanzel, *ibid.*, **64**, 14 (1956).

(5) C. Walling, O. H. Basedow, and E. S. Savas, *ibid.*, **82**, 2181 (1960).

(6) F. Ramirez and N. McKelvie, *ibid.*, **79**, 5829 (1957).

Values of k_7/k_2 for styrene have been calculated from the integrated form of 12 and show some scatter with an average value of 3.2. If 7 is significantly reversible, the true value would be somewhat larger and observed ratios would vary with mercaptan concentration, and it may be noted that the lowest value calculated, 1.9, is in fact from an experiment in which mercaptan was completely consumed. The absolute value of k_7 has been calculated by Sivertz⁸ as 8×10^8 at 25° and, as a very low activation energy process, should be quite temperature insensitive. Thus k_2 must be approximately 2.5×10^8 , indicating that thiyl radical attack on phosphite is an extremely rapid, low activation energy process. For cyclohexene at 70°, $k_7/k_2 = 0.26$. Qualitatively such a smaller ratio is expected since cyclohexene is in general less reactive toward radical addition than is styrene. However, comparison of the two values gives a relative reactivity styrene:cyclohexene of 12.3, significantly lower than the results of direct competition toward the structurally similar dodecanethyl radical at 60° for which a ratio of 68 has been reported.⁷

Since no alkylated olefin was detected in the experiments of Table I, it was evident that a change in reaction conditions would be required to suppress the competing formation of sulfide and alkane. Taking into account the possible reversibility of 7 the competitions involved become



Sulfide formation should be reduced by decreasing olefin and mercaptan concentration and by raising temperature which increases the reversibility of the thiyl radical addition.⁷ In the competition between conversion of $\text{R}\cdot$ to alkane and its addition to olefin to give alkylation, alkylation will also be favored by low mercaptan concentration. This analysis suggests that slow addition of an olefin-mercaptan mixture to phosphite at a higher temperature should favor the alkylation reaction. Results of a series of experiments with cyclohexene, styrene, and methyl acrylate are given in Table II. Although no alkylation was detected with cyclohexene, low yields of *n*-hexylbenzene and methyl heptanoate were obtained from styrene and methyl acrylate at 120–130° in the presence of di-*t*-butyl peroxide (DTBP). In all experiments mercaptan conversion was essentially complete. Volatile material assumed to be butane was also produced, and *n*-pentane was isolated and identified in comparable experiments with styrene and *n*-pentyl mercaptan. The order of yields observed also appears reasonable. With cyclohexene the alkylation presumably fails because of the low rate of $\text{R}\cdot$ addition to an unactivated sterically hindered bond. With methyl acrylate polar factors favor $\text{R}\cdot$ addition, but decrease reactivity toward $\text{RS}\cdot$.

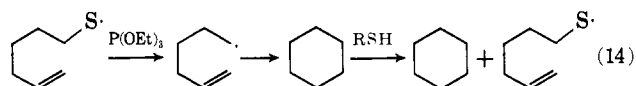
(8) Cf. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 322.

TABLE II
ALKYLATION YIELDS^a IN SLOW ADDITION EXPERIMENTS

Olefin	Conditions ^b	Sulfide, %	Alkylated olefin, %
Cyclohexene	A	25	0
	B	<1–2	0
Styrene	A	156	0
	B	22	7
Methyl acrylate	B	20–22	10–15

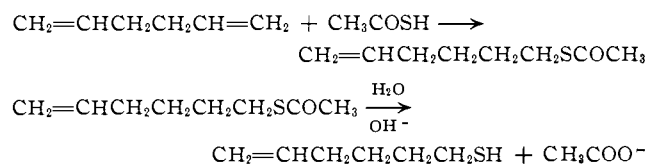
^a All yields relative to SP(OEt)_3 produced. ^b A, equimolecular quantities of reagents, 60–70°, AIBN initiator; B, 50% excess phosphite, 120–130°, DTBP initiator.

Radical Cyclizations.—The results of the previous section demonstrate that alkyl radicals produced in the reaction of mercaptans with phosphites can be trapped by olefins, although yields of alkylated products are small. The fact that alkylation could occur at all suggested the possibility that cyclic hydrocarbons could be synthesized from unsaturated mercaptans with structures conducive to ring formation and that, in fact, such processes should be aided by the well recognized tendency of radicals to undergo facile intramolecular reactions.⁹ Thus, for example, 6-mercapto-1-hexene might be expected to undergo the sequence



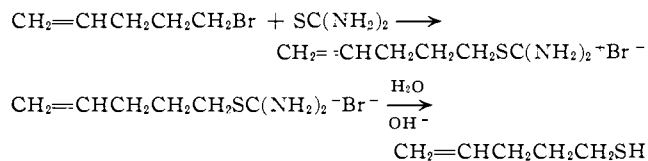
6-Mercapto-1-hexene and 5-mercapto-1-pentene were chosen for study. Their synthesis from available starting material involved straightforward reactions, but, as might be expected, they proved to polymerize readily and were best kept at a low temperature in the dark under nitrogen and in the presence of an inhibitor such as 4-*t*-butylcatechol.

6-Mercapto-1-hexene was prepared by radical addition of thiolacetic acid to 1,5-hexadiene using AIBN as initiator, followed by hydrolysis



Physical constants, spectra, and gas chromatographic analysis (g.l.c.) were consistent with a single pure product.

5-Mercapto-1-pentene was prepared from commercially available 5-bromo-1-pentene by reaction with thiourea followed by hydrolysis



Product analysis by g.l.c. revealed a major peak and two contaminants. The latter were collected and identified as 2-methyltetrahydrothiophene (I) and thiacyclohexane (II). The major product could not be obtained in pure form since on collection and reanalysis additional I and II were generated. Never-

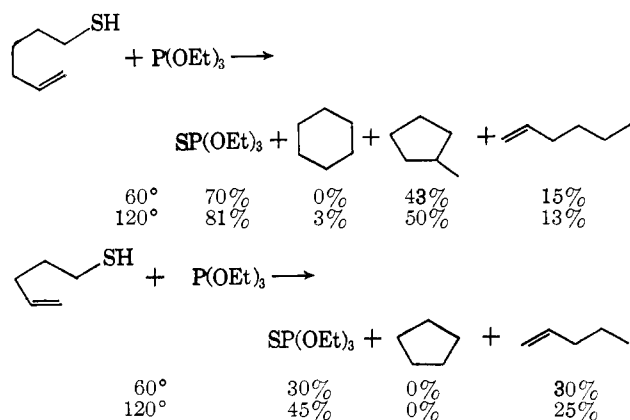
(9) C. Walling, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 7.

theless it was identified as the desired 5-mercapto-1-pentene on the basis of spectra, reaction with AgNO_3 , and ready reaction with triethyl phosphite. The cyclic sulfides evidently arise from intramolecular radical



addition and, since they are inert toward phosphite, the crude unsaturated mercaptan was used in subsequent experiments without further purification.

Cyclizations were investigated by slowly adding the unsaturated mercaptans to excess triethyl phosphite containing initiator (AIBN at 60° , DTBP at 120°) with results shown below. Yields of phosphorothionate are based on mercaptan added, and of hydrocarbon on phosphorothionate produced, on the assumption that each phosphorothionate molecule formed yields one alkyl radical for further reaction.

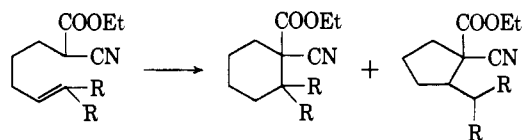


At first these findings appear incongruous, since the six-carbon system preferentially cyclizes to a five-membered ring, while the five-carbon system fails to cyclize at all. However, inspection of models suggests that results are consistent with steric restrictions placed on the systems. In the five-membered case, if one assumes that the carbon radical will attack the terminal double bond by a path affording maximum overlap with the π -orbital, the transition state is highly strained, so ring closure competes poorly with intermolecular reactions. In the six-carbon system, overlap is not sterically hindered, and ring closure can occur at either carbon 5 or 6. This leaves unexplained, however, why the preferred path leads to methylcyclopentane, since it is not only the less stable product thermodynamically, but also the consequence of radical addition in the "unexpected" direction to the more substituted end of the double bond. Classically, radical additions to double bonds have been interpreted by the rule that addition occurs in that direction which yields the most stable radical product. However, copolymerization results suggest that, except when the formation of highly resonance-stabilized radicals is involved, the predominant directive effect is probably steric,¹⁰ and recently examples have been described where directive effects are relatively small and vary with the attacking radical.¹¹ In an intramolecular reaction such as this, steric hindrance to

(10) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 266 (1950).

(11) J. F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961).

addition to the nonterminal end of the double bond is apparently unimportant. Admittedly this does not explain why it becomes the preferred reaction,¹² but our case of five-membered ring formation is not unique. In our preparation of 5-mercapto-1-pentene, compound I arises from a similar "unexpected" ring closure, and recently Julia, *et al.*,¹³ have reported both five- and six-membered ring formation in the radical cyclization of unsaturated α -cyanoesters of the type



although only the cyclohexane derivative is formed when R's are both hydrogen. Here a highly resonance-stabilized radical must attack the double bond, and energy considerations may become more important.

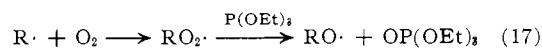
Competing Hydrogen Abstraction in Alkoxy Radical Reactions.—As seen above, thiyl radical attack on triethyl phosphite occurs at a rate comparable to thiyl radical addition to double bonds. We have also investigated the competition between alkoxy radical attack on triethyl phosphite, reaction 6, with hydrogen abstraction



To do this we have decomposed small amounts of *t*-butyl peroxide in the presence of triethyl phosphite and five hydrocarbons and analyzed the products for *t*-butyl alcohol and triethyl phosphate. Under these conditions, reactions 6 and 15 compete, so k_6/k_{15} may be obtained from the relation

$$d[\text{OP}(\text{OEt})_3]/d[\text{C}_4\text{H}_9\text{OH}] = k_6[\text{P}(\text{OEt})_3]/k_{15}[\text{R}'\text{H}] \quad (16)$$

Only small amounts of alcohol were detected (<1%), but results proved to be quite reproducible providing systems were adequately degassed. In the presence of oxygen, phosphate:alcohol ratios were higher, presumably *via* incursion of the process



A similar series of experiments was carried out with triphenylphosphine which also deoxygenates *t*-butoxy radicals, and results are summarized in Table III.

Two conclusions may be drawn from the rate ratios observed: triethyl phosphite reacts with *t*-butoxy radicals approximately 82 ± 20 times as rapidly as does triphenylphosphine, and both reactions are extremely rapid, faster even than hydrogen abstraction.¹⁴

The data of Table III also provide an indirect measurement of hydrocarbon reactivities toward *t*-butoxy

(12) In internal $\text{S}_{\text{N}}2$ displacements, five-membered ring formation appears to be the most facile cyclization, *e.g.*, in the cyclization of ω -haloamines: *cf.* M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 116.

(13) M. Julia, J. M. Surzur, and L. Katz, *Compt. rend.*, **251**, 1030 (1960); M. Julia and F. LeGoffic, *ibid.*, **255**, 714 (1962). Since this work was finished, predominant cyclization of the 5-hexenyl radical (derived from 6-heptenyl peroxide) to methylcyclopentane has also been described by R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963). More recently additional examples of preferential five-membered ring formation have been reported: N. O. Brace, *ibid.*, **86**, 523 (1964).

(14) The gas phase reaction of *t*-butoxy radicals with typical hydrocarbons appears to have an activation energy of only about 3 kcal. [P. Gray and A. Williams, *Chem. Rev.*, **59**, 230 (1959)] although it may be higher in solution due to radical solvation; *cf.* ref. 15 and 16.

TABLE III
RELATIVE REACTIVITY RATIOS IN REACTION OF DTBP WITH
HYDROCARBONS AND PHOSPHORUS DERIVATIVES AT 130°^a

Hydrocarbon	k_8/k_{15}	
	P(OEt) ₃	P(C ₆ H ₅) ₃
Cyclohexane	610 ± 10 (2)	7.02 ± 0.21 (4)
	770 ± 10 (4) ^b	
Cyclohexene	440 ± 10 (2)	7.37 ± .24 (4)
	690 ± 20 (4) ^b	
Cyclopentene	610 ± 10 (2)	7.42 ± .17 (3)
	700 ± 20 (3) ^b	
Cumene	730 ± 10 (2)	10.3 ± .5 (3)
	1200 ± 30 (3) ^b	
2,3-Dimethylbutane	1100 ± 100 (3)	9.8 ± .7 (3)
	2000 ± 100 (3) ^b	

^a De gassed systems unless indicated. Numbers in parentheses indicate number of experiments carried out. ^b Under N₂. ^c Difficulties noted in degassing these samples.

radicals, since the reciprocals of k_8/k_{15} 's are proportional to relative hydrocarbon reactivities. Such relative reactivities, expressed per reactive hydrogen and taking cyclohexane as standard, are calculated in Table IV and compared with other values from the literature. While agreement between the two phosphorus systems is good, correspondence with direct competitions using *t*-butyl hypochlorite is only qualitative. While in part this may be due to differences in temperature, it may also indicate either that our reactions here are actually more complicated than indicated, or that the sort of transition state solvation effects which have recently been found to be so important in other alkoxy radical reactions^{15,16} perturb the results.

TABLE IV
RELATIVE REACTIVITIES OF HYDROCARBONS TOWARD
t-BUTOXY RADICALS BY VARIOUS TECHNIQUES

Hydrocarbon	ROCl ^a	Relative reactivities (per H)		
		DTBP ^b	P(OEt) ₃	P(C ₆ H ₅) ₃
Cyclohexane (std.)	1.00	1.00	1.00	1.00
Cyclohexene	24.4	..	4.2	3.8
Cyclopentene	24.4	..	3.0	3.8
Cumene	4.55	2.5 ^c	10.0	8.3
		4.8		
2,3-Dimethylbutane	2.81	4.3	3.7	4.3

^a Competitive chlorination of hydrocarbons at 40° using *t*-butyl hypochlorite; C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961). ^b Indirect determination from *t*-C₄H₉OH/acetone ratios at 135°; J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957). ^c Similar to *b*; G. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956).

Competitive Reactions between Phosphorus Compounds.—Results of the last sections yielded an indirect measurement of the relative reactivities of triethyl phosphite and triphenylphosphine. We have also carried out direct competitions of several phosphorus derivatives by treating *n*-butyl mercaptan or di-*t*-butyl peroxide with mixtures of two phosphorus compounds and following either their disappearance or the appearance of products. Toward the thiyl radical from *n*-butyl mercaptan three pairs gave the following reactivities: triethyl phosphite–triphenyl phosphite, 20.8 ± 0.6; tri-*n*-butylphosphine–triphenylphosphine, 8.89 ± 0.23; triethyl phosphite–tri-*n*-butyl phosphine, 0.173 ± 0.015. Toward the *t*-

(15) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **84**, 2854 (1962); **85**, 1593 (1963).

(16) C. Walling and P. Wagner, *ibid.*, **85**, 2333 (1963).

butoxy radical from di-*t*-butyl peroxide, the same pairs gave relative reactivities of 1.6 ± 0.2, 2.46 ± 0.25, and 0.83 ± 0.07, respectively. However, material balances in this case for the two systems containing triethyl phosphite showed that approximately twice as much of the phosphorus derivatives was consumed as anticipated from the amount of peroxide used, that only 50–65% of the peroxide oxygen appeared as triethyl phosphate, and that additional unidentified products were produced.

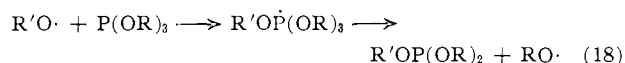
In Table V, relative reactivities are listed calculated from the above data. Because of the complications just mentioned, the *t*-butoxy radical data are probably of only qualitative significance, although they parallel the autoxidation results of Floyd and Boozer.

TABLE V
RELATIVE REACTIVITIES OF PHOSPHORUS DERIVATIVES
TOWARD THIYL AND ALKOXY RADICALS

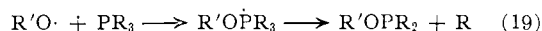
Compound	<i>n</i> -C ₄ H ₉ S (70°)	<i>t</i> -C ₄ H ₉ O (130°)	Autox. ^b
P(OEt) ₃ (std.)	1.0	1.0	1.0
P(OC ₆ H ₅) ₃	0.048	0.63	
P(C ₄ H ₉) ₃	5.8	1.2	1.53
		0.03 ^a	
P(C ₆ H ₅) ₃	0.65	.49	0.61
		.012 ^a	

^a Calculated from indirect data of Table III, P(OEt)₃/P(C₆H₅)₃ = 82. ^b Relative rates of autoxidation, calculated from data of M. B. Floyd and C. E. Boozer, *J. Am. Chem. Soc.*, **85**, 984 (1963), and assuming similar reactivities for P(OEt)₃ and P(OBu)₃.

A few experiments were carried out to determine the nature of the additional reactions occurring in the *t*-butoxy radical systems, and it was shown that two phosphorus compounds and DTBP were required for the process. Starting materials were recovered unchanged on heating triethyl phosphite with either triphenyl phosphite or tributylphosphine in the absence of DTBP, while triethyl phosphite or tributylphosphine plus DTBP showed a consumption of phosphorus compound equivalent to 90–100% of the DTBP used. A plausible hypothesis would be a radical exchange



which here would generate the resonance-stabilized phenoxy radical. Consistent with this suggestion, in the P(OEt)₃–P(OC₆H₅)₃ system two unidentified peaks were indeed noted on g.l.c. analysis with retention times between the two starting materials. In the P(OEt)₃–P(C₄H₉)₃ system one additional peak was noted and assumed to be *t*-butyl-di-*n*-butyl phosphinite, the consequence of a similar exchange already reported by Buckler.¹⁷



Reaction 19 and the more hypothetical 18 point up the fact that at least two modes of decomposition of phosphoranyl radicals are available: β-scission as in reactions 2 and 6 and an α-scission which amounts to the reversible addition of a radical to trivalent phosphorus (although the leaving radical may be different from that which adds). Buckler has noted that the competition between the two modes is quite solvent dependent, and additional examples of α-scission

(17) S. A. Buckler, *ibid.*, **84**, 3093 (1962).

have been noted in the electrolytic reduction of R_4P^+ to R_3P and $R\cdot$,¹⁸ and as a step in the cooxidation of PCl_3 and hydrocarbons.¹⁹

The possibility that β -scission may involve one of the groups initially attached to phosphorus rather than the attacking radical has been shown by the isolation of 3% toluene from the reaction of *n*-butyl mercaptan with benzyl diethyl phosphite.⁵ The use of thiophenol provides a better case, since cleavage of the phenyl-sulfur bond should be relatively difficult. In this system we now find 10% toluene and only 4% benzene among the products obtained with AIBN at 60°.

Experimental

Materials except as indicated were commercial reagents, fractionally distilled before use when appropriate and purity checked by g.l.c. or physical constants.

Sulfides.—Authentic samples of *n*-butyl cyclohexyl sulfide and *n*-butyl β -phenylethyl sulfide were prepared by heating equimolar quantities of cyclohexene and styrene, respectively, with *n*-butyl mercaptan at 60° in the presence of AIBN.

6-Mercapto-1-hexene.—Thiolacetic acid (0.40 mole) was added dropwise with stirring to 0.60 mole of 1,5-hexadiene²⁰ containing 1–2% AIBN in a stirred flask under nitrogen at room temperature, and the mixture held at 50° overnight. Distillation yielded 20% 6-hexen-1-yl thiolacetate, b.p. 85–90° (7 mm.), n_D^{20} 1.4792, together with unreacted diene and a high boiling residue. The material had an infrared spectrum consistent with the expected structure and was used without further purification. For hydrolysis, 13 g. of the thiolacetate was refluxed under nitrogen for 2.5 hr. with 30 ml. of water and 60 ml. of 20% methanolic KOH. After distillation of the methanol, additional water was added and the mercaptan extracted with ether, washed, dried, and distilled. The product, 6-mercapto-1-hexene, b.p. 45–50° (14 mm.), $n_D^{22.5}$ 1.4694, was obtained in 50% yield. It showed a single peak on g.l.c. analysis and an infrared spectrum consistent with an –SH group and a terminal double bond. Due to its facile polymerization it was stored at –25° in the dark under N_2 .

5-Mercapto-1-pentene.—5-Bromo-1-pentene (10 g.), thiourea (5 g.), and 40 ml. of absolute ethanol containing 0.1 g. of 4-*t*-butylcatechol were refluxed under N_2 . Addition of ether and cooling to –25° gave 11.39 g. (71%) of the isothiuronium hydrobromide as white needle-like crystals, m.p. 91–93°. Hydrolysis of 10 g. of the salt was accomplished by stirring under nitrogen in the dark at room temperature with 5 ml. of 50% aqueous NH_4OH containing 0.1 g. of hydroquinone. At the end of 2 hr. two layers of liquid were visible. The lower aqueous layer was acidified with dilute HCl, and extracted with ether. The upper layer was washed with water, dried, and distilled together with the ether extract to give 2.5 g. of crude mercaptan, b.p. 37–39° (11 mm.), which was stored under N_2 at –25°. Although both infrared and n.m.r. spectra showed the expected –SH and vinyl groups, g.l.c. analysis indicated two contaminants I and II and a purity of about 80%. The three components could be separated by g.l.c., but reanalysis of the collected major peak showed that the two impurities were reformed during collection. Heating the crude mercaptan or exposing it to air also led to conversion to I, II, and polymer. Compound I was

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(19) F. R. Mayo, L. Durham, and K. S. Griggs, *J. Am. Chem. Soc.*, **85**, 3156 (1963).

(20) "Organic Syntheses," Coll. Vol. 111, H. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 121.

separated by g.l.c. and identified as 2-methyltetrahydrothiophene on the basis of infrared and n.m.r. spectra and analysis; n.m.r.: doublet 8.7 (–CH₃); multiplet 7.75–8.30 (β -CH₂); multiplet 7.00–7.30 (α -CH₂); quartet 6.6 τ (α -CH); relative areas 3:4:2:1. Anal. Calcd. for C₅H₁₀S: C, 58.76; H, 9.86; S, 31.38. Found: C, 58.75; H, 9.69; S, 31.66.

Compound II had a similar analysis: C, 59.07; H, 9.80; S, 31.57, and infrared and n.m.r. spectra consistent with thiacyclohexane; n.m.r.: multiplet 8.00–8.45 (β, γ CH₂), multiplet 7.35–7.60 τ (α -CH₂), relative areas 3:2.

Phosphite-Mercaptan-Olefin Reactions.—Experiments listed in Table I were carried out in sealed degassed tubes, and analyzed by g.l.c. using cyclohexylbenzene (added after reaction) as an internal standard. Slow addition experiments (Table II) were carried out under N_2 in a small stirred flask equipped with a dropping funnel and condenser attached to a cold trap. Products were analyzed by g.l.c. using cyclohexylbenzene as an internal standard and identified both by retention time and by collection and comparison of infrared spectra with authentic samples.

Cyclization experiments were carried out essentially as above. Analysis was again by g.l.c. and the hydrocarbons were identified both by retention time and by collection and comparison of infrared spectra.

Phosphite-Hydrocarbon DTBP Competitions.—Reactions were carried out in sealed tubes which had been degassed or flushed with N_2 as indicated in Table III using 2–3 moles of both phosphite and hydrocarbon per mole of DTBP. After reaction, the contents of a tube was transferred to a small flask and distilled into a cold trap at 8 mm. pressure, while slowly warming the flask to 50°. The distillate was analyzed for *t*-butyl alcohol and acetone by g.l.c. using 1,2-dichloroethane as an internal standard, and the residue was analyzed for triethyl phosphite using *o*-dichlorobenzene as standard. Relative yields of *t*-butyl alcohol and phosphite were then used to calculate the relative reactivities given.

Triphenylphosphine-hydrocarbon-DTBP reactions were carried out similarly, except that here unreacted phosphine was determined by dissolving the residue in alcohol-benzene and titration of aliquots with alcoholic I₂ as described by Bartlett and Meguerian.²¹

Competitive reactions of phosphorus compounds listed in Table V were carried out in sealed degassed tubes using approximately 1–3 moles of each phosphorus compound per mole of mercaptan or peroxide and analyzed essentially as above except for any modifications noted below. In triethyl phosphite-*n*-butyl phosphite-*n*-butyl mercaptan runs, consumption of phosphine and phosphite were determined, and the latter checked against phosphorothionate produced, giving agreement within 2%. With triethyl phosphite-triphenyl phosphite-*n*-butyl mercaptan, consumption of both phosphites was again determined and checked against triethyl phosphorothionate formed. In tributylphosphine-triphenylphosphine-*n*-butyl mercaptan experiments, products boiling below 110° (0.5 mm.) were separated adding dibutyl phthalate as a "chaser," the tributylphosphine in the distillate determined by g.l.c., and the triphenylphosphine remaining by titration. The same analytical methods were used in the DTBP experiments. However, since in experiments containing triethyl phosphite more than stoichiometric quantities of reagents were consumed, the yield of triethyl phosphite was measured directly, and consumption of the other reagent taken as [initial concentration] + [OP(OEt)₃]_f – 2[DTBP]_o. As noted in the Discussion, this makes the values reported of rather qualitative significance.

(21) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).