ethanol was refluxed for 3 hr. with a solution of 1 g. of sodium hydroxide in 2 ml. of water. The product, which crystallized upon cooling, was recrystallized from ethanol and melted at 132°; yield 0.3 g: $[\alpha]^{25}_{D}$ −38.9°.

Anal. Calcd. for $C_{26}H_{44}O$: C, 83.7; H, 11.8. Found: C, 83.2; H, 11.3.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Reaction of Trialkyl Phosphites with Thiyl and Alkoxy Radicals[1]

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The reaction between mercaptans and trialkyl phosphites yielding hydrocarbons and trialkyl phosphorothionates is shown to be a free radical chain process, initiated by azobisisobutyronitrile. An analogous reaction between disulfides and trialkyl phosphites to give sulfides and trialkylphosphorothionates also occurs, induced by light and organic peroxides. Free radical chain mechanisms are proposed for both reactions involving thiyl radical attack on the phosphite to yield an intermediate phosphorus radical with an expanded valence shell. At higher temperatures the non-radical Arbuzov type reaction between phosphites and disulfides (to yield phosphorothiolates) apparently occurs as well. When di-*t*-butyl peroxide and dicumyl peroxide are allowed to react with triethyl phosphite (either thermally or photochemically) the products are triethyl phosphate and hydrocarbon mixtures arising from alkyl radical dimerization and disproportionation. The utility of these reactions for producing complex organic hydrocarbon radicals of known structure is suggested, and the extension of our observations to the interpretation of other organophosphorus reactions pointed out.

In 1956, Hoffman and co-workers[2] reported a remarkable reaction occurring between trialkyl phosphites and mercaptans at elevated temperatures or in the presence of light.

$$RSH + P(OEt)_3 \longrightarrow RH + SP(OEt)_3 \quad (1)$$

Although no suggestion was made as to mechanism, the light catalysis suggested a radical process. In a preliminary communication[3] we showed that an analogous reaction may be induced between trialkyl phosphites and alkyl disulfides

$$RSSR + P(OEt)_3 \longrightarrow RSR + SP(OEt)_3 \quad (2)$$

and proposed that both involve radical chains with the propagation steps

$$RS\cdot + P(OEt)_3 \longrightarrow RS—\dot{P}(OEt)_3 \quad (3)$$

$$RS—\dot{P}(OEt)_3 \longrightarrow R\cdot + SP(OEt)_3 \quad (4)$$

$$R\cdot + HSR \longrightarrow RH \longrightarrow RS\cdot \quad (5a)$$

or

$$R\cdot + RSSR \longrightarrow RSR + RS\cdot \quad (5b)$$

This paper describes our experimental results in more detail and also some observations on a quite analogous (but non-chain) reaction which occurs between dialkyl peroxides and triethyl phosphite to yield hydrocarbons and triethyl phosphate. In the light of our findings we have also suggested the utility of these reactions for generating complex hydrocarbon radicals of known structure, and the possible radical nature of several other reactions of trivalent phosphorus.

Results

Trialkyl Phosphite—Mercaptan Reactions.—The strongest evidence for the proposed radical chain mechanism for reaction (1) would be the demonstration that it is brought about by typical radical chain initiators. This was investigated by comparing the reaction of triethyl phosphite and isobutyl mercaptan at 69° in the presence and absence of azobisisobutyronitrile (AIBN). Using a slight excess of phosphite and no AIBN, no detectable reaction was noted in 30 minutes. In the presence of 1.84 mole % AIBN, gas evolution (isobutane) was noted in 2 minutes. Gas chromatographic analysis of the reaction mixture cooled after 2 minutes showed no mercaptan, disappearance of the expected amount of phosphite, and strong peaks of isobutane and triethyl phosphorothionate. A *minimum* kinetic chain length for reaction (1) could be calculated. From the data of Lewis and Matheson,[4] AIBN decomposes to the extent of 0.5% in 2 minutes at 69°. Assuming complete reaction and that each decomposition starts two chains, the average chain length is 100/0.0184 = 5400. This value (which is larger than that reported earlier[3]) necessarily represents a minimum since (a) the system did not reach bath temperature immediately, (b) the reaction may have been essentially complete in less than 2 minutes, and (c) chain initiation by AIBN is usually not more than 40–80% efficient.[5] Nevertheless, the very long chain nature of the reaction is clearly evident.

Photochemical Reaction of Triethyl Phosphite with Disulfides.—An important step in our formulation of the trialkyl phosphite-mercaptan reaction is (5a), attack of an alkyl radical upon the S–H bond, a process which is well established in the free radical addition of mercaptans to olefins. The analogous attack on disulfides (5b) is also known, and accounts for the appreciable transfer constants of disulfides in vinyl polymerization. In general, (5b) occurs less readily than (5a), the tranfer constants of styrene with *n*-alkyl mercaptans[6] being approximately 20 and with a variety of dialkyl disulfides, 0.005–0.03.[7] Nevertheless it seemed possible that reaction 2 could be realized

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[1] Taken from the Ph.D. Dissertation of Robert Rabinowitz. Support of this work by the National Science Foundation is gratefully acknowledged.

[2] F. W. Hoffman, R. J. Ess, T. C. Simmons and R. S. Hanzel, THIS JOURNAL, **78**, 6414 (1956).

[3] C. Walling and R. Rabinowitz, *ibid.*, **79**, 5326 (1957).

[4] F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

[5] G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

[6] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 319.

[7] R. M. Pierson, A. J. Costanza and A. H. Weinstein, *J. Polymer Sci.*, **17**, 221 (1955).

via the sequence of steps 3, 4, 5b with disulfides yielding reactive alkyl radicals. To test this hypothesis a mixture of 0.27 mole of isobutyl disulfide and 0.27 mole of triethyl phosphite was irradiated in Pyrex with ultraviolet light at 60°. Gas chromatographic analysis indicated significant reaction in 4 hours and complete disappearance of disulfide in 27 hours. Fractional distillation of the product yielded isobutyl sulfide (92%) and triethyl phosphorothionate (106% based upon disulfide). The only other product isolated was approximately 0.75 cc. of an 8:1 mixture of isobutane and isobutylene. No detectable reaction was noted when a similar mixture was heated in the dark for several hours at 140°. The small amount of C_4-hydrocarbons may be accounted for as the result of chain termination between *t*-butyl radicals, or possibly as a consequence of a small amount of photolysis of isobutyl sulfide.

$$C_4H_9—S—C_4H_9 \xrightarrow{h\nu} C_4H_9S\cdot \qquad (6)$$

Since the resulting thiyl radical would react with additional phosphite, the excess yield of phosphorothionate would also be accounted for. However, there is evidently no fast chain process involving monosulfides and trialkyl phosphites, since a 5-hour irradiation of a mixture of *n*-butyl sulfide and triethyl phosphite gave only recovered starting materials.

Comparable reactions occur between ethyl disulfide and triethyl phosphite and between *n*-butyl disulfide and both trimethyl and triethyl phosphites, while in a competitive reaction in which both were present, triethyl phosphite appeared to be approximately twice as reactive as trimethyl phosphite.

An attempted reaction of benzyl disulfide and triethyl phosphite proceeded only sluggishly and yielded rather different products. After 14 hours irradiation little reaction was observed, but a mixture of 0.20 mole of benzyl disulfide and 0.58 mole of triethyl phosphite after 3 weeks irradiation at 60° gave 5% benzyl sulfide, 19% toluene, 26% bibenzyl and 82% triethyl phosphorothionate (based on total sulfur available). Here apparently kinetic chains are very short, and the relatively stable benzyl radicals produced in (4) largely dimerize or abstract hydrogen rather than attacking the disulfide, a plausible result in view of the low transfer constants of the analogous styrene radical with disulfides[7] cited above.

The high conversion of phosphite to phosphorothionate indicates that step 3 occurs readily enough, and in addition such benzyl sulfide as is formed may be further photolyzed as in reaction 6 since previous work[8] has shown that benzyl-type sulfides undergo rather ready photolytic decomposition.

Radical Initiation of the Disulfide–Phosphite Reaction.—Suitable radical initiators are also capable of bringing about the reaction of disulfides and trialkyl phosphites. When 0.051 mole of isobutyl disulfide containing 1.1 mole % di-*t*-butyl peroxide (DTBP) and 0.058 mole of triethyl phosphite were heated, first for 1 hour at 120° and then for 2 hours at 125°, 60–70% reaction occurred. From the data of Raley, Rust and Vaughan,[9] 17.5% decomposition of the peroxide would occur in this time, indicating a minimum kinetic chain length of 350. While this again represents a minimum value, it is only 1/17 that observed in the mercaptan experiment above. Again, this is consistent with the expected slower attack of an alkyl radical on a disulfide (5b) compared with a mercaptan (5a), and with the idea that chain termination in these systems involves interaction of two alkyl radicals.

The reactions of *n*-butyl disulfide and of ethyl disulfide with triethyl phosphite are also readily initiated by DTBP, but α,α-dimethylbenzyl peroxide (dicumyl peroxide, DCP) is rather less effective, giving only 50% conversion of *n*-butyl disulfide in 6.5 hours at 130°, conditions under which DTBP gives complete reaction in 4.3 hours. This difference, and the mechanism of peroxide initiation are discussed further below.

In contrast to the peroxides, AIBN is ineffective as an initiator, isobutyl disulfide plus 1.56 mole % AIBN, heated for 12 hours at 50° and 40 minutes at 100° with a slight excess of triethyl phosphite, giving only starting materials. Since AIBN readily initiates the mercaptan–phosphite reaction and since the disulfide–phosphite reaction occurs photochemically at this temperature, we may conclude that AIBN initiation must involve attack on the sulfur species rather than the phosphite; and that this process fails in the case of disulfides, *i.e.*

$$\text{AIBN} \longrightarrow N_2 + 2(CH_3)_2\dot{C}—CN \xrightarrow{\text{RSSR}} \text{no reaction} \qquad (7)$$

The result is certainly plausible since the cyanoisopropyl radical is highly resonance stabilized and also contains a strongly electron-withdrawing group. Electron-withdrawing groups on radicals are known to reduce their rate of reaction with mercaptans,[6] and would be expected to do the same for their (already slower) reaction with disulfides.

High Temperature Disulfide–Phosphite Reactions.—Jacobson, Harvey and Jensen[10] have reported that ethyl disulfide and triethyl phosphite, on refluxing together, yield ethyl sulfide and triethyl phosphorothiolate (isomeric with the product of our lower temperature reactions)

$$\text{EtSSEt} + \text{P(OEt)}_3 \longrightarrow \text{EtSEt} + \text{EtSPO(OEt)}_2 \qquad (8)$$

while Poshkus and Herweh[11] observe reaction (9) on refluxing the components in benzene

$$C_6H_5SSC_6H_5 + P(OEt)_3 \longrightarrow C_6H_5SC_2H_5 + C_6H_5SPO(OEt)_2 \qquad (9)$$

Both groups of authors propose ionic Arbuzov-type paths for their reactions, but it seemed possible[3] in light of our own results that both could be radical chains. Thus (8) might be interpreted as our sequence followed by the known[12] isomerization of phosphorothionate to phosphorothiolate

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[8] C. Walling and R. Rabinowitz, THIS JOURNAL, **81**, 1137 (1959).

[9] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 1336 (1948). The data used were those for decomposition in tributylamine in which rates are slightly higher than in most solvents.

[10] H. I. Jacobson, R. G. Harvey and E. V. Jensen, *ibid.* **77**, 6064 (1955).

[11] A. C. Poshkus and J. E. Herweh, *ibid.*, **79**, 4245 (1957).

[12] W. G. Emmett and H. O. Jones, *J. Chem. Soc.*, **99**, 713 (1911).

$$\mathrm{SP(OR)_3 \longrightarrow RSPO(OR)_2} \qquad (10)$$

Reaction 9 in turn could involve the sequence

$$\mathrm{C_6H_5S\cdot + P(OEt)_3 \longrightarrow C_6H_5\dot{S}P(OEt)_3} \qquad (11)$$

$$\mathrm{C_6H_5S\dot{P}(OEt)_3 \longrightarrow C_6H_5SPO(OEt)_2 + \cdot C_2H_5} \qquad (12)$$

$$\mathrm{C_2H_5\cdot + C_6H_5SSC_6H_5 \longrightarrow C_2H_5SC_6H_5 + C_6H_5S\cdot} \qquad (13)$$

the alternate cleavage in (12) arising because of the strong C_6H_5–S bond.[13]

We have reinvestigated the thermal reaction of ethyl disulfide and triethyl phosphite at 180–185° and find that the products after 23 hours are ethyl sulfide and approximately an equal mixture of phosphorothionate and phosphorothiolate, both in the presence and absence of 0.5 mole % trinitrobenzene which might be expected to act as an inhibitor for the radical process. Treated under the same conditions, pure triethyl phosphorothionate is largely converted to the phosphorothiolate. Better evidence for the actual independent existence of the Arbuzov-type process was obtained by treating *n*-butyl disulfide with triethyl phosphite for 23 hours at 195–200° in the presence of 0.5 mole % hydroquinone. The products determined were O,O-diethyl-S-*n*-butyl phosphorothiolate (50%), *n*-butyl ethyl sulfide (49%), ethyl sulfide (16%) and *n*-butyl sulfide (9%). The major sulfide observed is that anticipated from the Arbuzov process

$$\mathrm{BuSSBu + P(OEt)_3 \longrightarrow BuS\overset{+}{P}(OEt)_3(BuS^-) \longrightarrow BuPO(OEt)_2 + EtSBu} \qquad (14)$$

while the radical formulation should have yielded *n*-butyl sulfide.

Reaction of Triethyl Phosphite with Dialkyl Peroxides.—Our results on the reactions between phosphites and mercaptans and disulfides suggested that analogous reactions might occur between trialkyl phosphites and alkoxy radicals derived from dialkyl peroxides. When DCP and excess triethyl phosphite were heated together at 125°, the products obtained were triethyl phosphate (93.5%) and 2,3-diphenyl-2,3-dimethylbutane (dicumene, 70.6%) on the basis of the equation

$$\mathrm{ROOR + 2P(OEt)_3 \longrightarrow R{-}R + 2OP(OEt)_3} \qquad (15)$$

The same reaction carried out photochemically at 25° again gave triethyl phosphate (98.5%) and dicumene (45.5%), the obvious reaction sequence being

$$\mathrm{ROOR \xrightarrow[\text{or } h\nu]{\Delta} 2RO\cdot} \qquad (16)$$

$$\mathrm{RO\cdot + P(OEt)_3 \longrightarrow R\dot{P}O(OEt)_3} \qquad (17)$$

$$\mathrm{R\dot{P}O(OEt)_3 \longrightarrow R\cdot + OP(OEt)_3} \qquad (18)$$

$$\mathrm{2R\cdot \longrightarrow R{-}R} \qquad (19)$$

Dimerization is certainly the expected fate of cumyl (α,α-dimethylbenzyl) radicals,[14] and, since we were unable to detect either acetophenone or α,α-dimethylbenzyl alcohol (the usual decomposition products of α,α-dimethylbenzyloxy radicals[15]) in our reaction mixtures, reaction 17 must be a very rapid process indeed.

The reaction of triethyl phosphite and DTBP follows a similar course, but the hydrocarbon products are more complex. Results are listed in Table I.

TABLE I

REACTION PRODUCTS OF DTBP AND TRIETHYL PHOSPHITE

Products	Yield, % 25°, light	Yield, % 125°[a]
Triethyl phosphate	106	110
Isobutane	30.7	+
Isobutylene	19.9	+
2,2,3,3-Tetramethylbutane	8.0	+
2,2,4-Trimethylpentane	3.5	
2,4,4-Trimethyl-1-pentene	1.8	
2,4,4-Trimethyl-2-pentene	...	+

[a] Hydrocarbons identified but not determined quantitatively.

The tetramethylbutane is evidently a dimerization product of *t*-butyl radocals,[16] while the isobutane and isobutylene must arise from disproportionation which appears to be the preferred reaction of these species.[17] The other C_8-hydrocarbons can be accounted for by the addition of *t*-butyl radicals to isobutylene (the yield of which is correspondingly reduced) followed by subsequent disproportionation. Again, only traces of acetone or *t*-butyl alcohol were detected nor could we detect any *t*-butyl ether, a reported product of reaction of DTBP and triphenylphosphine.[18]

The very rapid reaction of alkoxy radicals with trialkyl phosphites, which is here able to swamp out their known rapid conversion to alcohols or ketones, clearly indicates the course of peroxide initiation of the phosphite–disulfide reactions discussed earlier, and also accounts satisfactorily for the low efficiency of DCP as an initiator. Alkoxy radicals produced by peroxide cleavage are first converted to alkyl radicals, and these in turn attack the disulfide to start reaction chains. In the case of DCP the resulting benzyl radicals are relatively unreactive (as in the case of benzyl disulfide) and largely dimerize and are thus lost.

Discussion

Heretofore most known free radical reactions involving compounds of phosphorus have involved radical attack on P–H bonds as in the addition of phosphines and dialkyl phosphites to olefins.[19] Our results on the reaction of thiyl and alkoxy radicals with trialkyl phosphites point to the importance of another type of process, the direct attack of a free radical upon the phosphorus atom to yield, as a transient intermediate, the tetracovalent *phosphoranyl*[20] radical in which the phosphorus has undergone an expansion of its outer valence shell to accommodate nine electrons. Since the reaction occurs very rapidly with strongly electron-accepting thiyl and alkoxy radicals, but

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[13] Bond dissociation energies indicated that $D(C_6H_5{-}H)$ is approximately the same as $D(CH_3{-}H)$, and in addition there should be overlap between the *p*-orbitals of S and the orbitals of the benzene ring; *cf.* ref. 6, Chapter 2.

[14] M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

[15] M. S. Kharasch, A. Fono and W. Nudenberg, *ibid.*, **16**, 113 (1951).

[16] A. V. Grosse, THIS JOURNAL, **75**, 1261 (1952); B. deB. Darwent and C. A. Winkler, *J. Phys. Chem.*, **49**, 150 (1945).

[17] M. S. Kharasch, D. W. Lewis and W. B. Reynolds, THIS JOURNAL, **65**, 493 (1943); J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957).

[18] L. Horner and W. Jurgeleit, *Ann.*, **591**, 139 (1955); in view of our results, it seems likely that this reaction should be reinvestigated.

[19] *Cf.* reference 6, pp. 341–343.

[20] F. Ramirez and N. McKelvie, THIS JOURNAL, **79**, 5829 (1957).

we find no products corresponding to the attack of the simple alkyl radicals present on the phosphite, it seems plausible that the reaction derives considerable driving force from the contribution of polar structures to the transition state. The

$$\mathrm{RS\cdot\ P(OEt)_3 \longrightarrow RS^{-}\cdot\overset{+}{P}(OEt)_3} \qquad (20)$$

subsequent breakdown of the phosphoranyl radical in turn must owe its driving force to the very strong semi-covalent PO (or PS) bonds in the resulting phosphate. While the energetics of the two steps cannot be separated, that for the overall process can be estimated taking $D(t\text{-}C_4H_9\text{–}O)$

$$t\text{-}\mathrm{C_4H_9O\cdot + P(OEt)_3 \longrightarrow R\cdot + OP(OEt)_3}\ \Delta H = -30\ \text{kcal.} \qquad (21)$$

= 92 kcal.[21] and $D(O\text{–}P(OEt)_3)$ = 122 kcal. the same as $D(O\text{–}PCl_3)$.[22]

This ability of trialkyl phosphites to convert alkoxy and thiyl radicals to the corresponding alkyl radicals should be of considerable value in the further study of radical reactions since it should permit the preparation of a wide variety of alkyl radicals of known structure from the corresponding mercaptans, disulfides or peroxides, and we are investigating the use of the sort of reactions described here for this purpose.

The extent to which free radical, rather than Arbuzov-type, processes may account for other reactions of trivalent phosphorus still constitutes an important problem. In the case of disulfides and trialkyl phosphites, as we have seen, both processes may occur. When triethyl phosphite is treated with t-butyl hydroperoxide we find that a rapid reaction occurs even at 0° in the presence of trinitrobenzene, but the products are exclusively t-butyl alcohol and triethyl phosphate presumably *via* the polar sequence.

$$\mathrm{ROOH + P(OEt)_3 \longrightarrow RO\overset{+}{P}(OEt)_3OH^{-} \longrightarrow ROH + OP(OEt)_3} \qquad (22)$$

On the other hand, Ramirez and Dershowitz[23] have detected a radical intermediate in the reaction of triphenylphosphine and trialkyl phosphites with chloranil, and Ramirez and McKelvie have shown that triphenylphosphine and bromoform react to give triphenyl-(dibromomethyl)-phosphonium bromide under conditions which clearly indicate a chain process.[20] The reaction of CCl_4 with triethyl phosphite to yield diethyl trichloromethanephosphonate has been studied by Kamai[24] who suggested[25] a series of steps

$$\mathrm{CCl_3\cdot + P(OEt)_3 \longrightarrow CCl_3\dot{P}(OEt)_3} \qquad (23)$$

$$\mathrm{CCl_3\dot{P}(OEt)_3 + CCl_4 \longrightarrow CCl_3PCl(OEt)_3 + \cdot CCl_3} \qquad (24)$$

$$\mathrm{CCl_3PCl(OEt)_3 \longrightarrow CCl_3PO(OEt)_2 + EtCl} \qquad (25)$$

which clearly should constitute a radical chain. More recently Griffin[26] has shown that the reaction is indeed light and peroxide catalyzed. In view of our results, we would suggest that (24-25) should be replaced by

$$\mathrm{CCl_3\dot{P}(OEt)_3 \longrightarrow CCl_3PO(OEt)_2 + \cdot Et} \qquad (26)$$

$$\mathrm{Et\cdot + CCl_4 \longrightarrow EtCl + CCl_3\cdot} \qquad (27)$$

an alternative considered but discounted by Griffin since no hydrocarbon was detected among the volatile fractions. In view of the very rapid known reaction of ethyl radicals with CCl_4,[27] this hardly seems a valid objection.

Finally, we have observed that, when triethyl phosphite is treated with peroxides without the careful exclusion of air, much additional phosphite is oxidized to phosphate. Here we would suggest the sequence

$$\mathrm{R\cdot + O_2 \longrightarrow RO_2\cdot} \qquad (28)$$

$$\mathrm{RO_2\cdot + P(OEt)_3 \longrightarrow ROO\dot{P}(OEt)_3} \qquad (29)$$

$$\mathrm{ROO\dot{P}(OEt)_3 \longrightarrow RO\cdot + OP(OEt)_3} \qquad (30)$$

followed by (17–18), *i.e.*, an autoxidation of phosphite involving a continued recycling of alkyl radicals. It seems possible that similar phosphoranyl radicals may be involved in two other, at present rather obscure, radical reactions of oxygen with hydrocarbons and phosphorus derivatives: that with PCl_3 and hydrocarbons to give alkane phosphonyl chlorides[28] and with white phosphorus and olefins to give complex oxygen-containing products.[29]

Experimental

Materials.—Reagents were in general commercial materials, further purified by conventional methods if required. **Triethyl phosphite** was obtained from the Virginia Carolina Corp. and further purified by fractional distillation through an 40-cm. helix packed column, b.p. 155°. **Disulfides** were Eastman Kodak Co. white label material, usually redistilled. **Di-*t*-butyl peroxide** from the Lucidol Co. was used without further purification. **Dicumyl peroxide** (Borden) was recrystallized from 95% ethanol with the aid of Norite, m.p. 39–40°.

O,O-Diethyl-S-*n*-butyl phosphorothiolate was prepared by refluxing 247 g. of n-butyl iodide and 48.4 g. of triethyl phosphorothionate for 43 hours.[30]. Fractional distillation yielded ethyl iodide (88%) and the phosphorothiolate, n-$C_4H_9SPO(OEt)_2$, b.p. 102.5–103.0° (1.5 mm.), $n^{25}\text{D}$ 1.4561.

Benzyl 1,1,3,3-Tetramethylbutyl Sulfone.—Sulfuric acid (25 drops) was added to 0.70 g. (6.1 mmoles) of 2,2,4-trimethyl-1-pentene and 0.64 g. (5.1 mmoles) of benzyl mercaptan in 20 ml. of glacial acetic acid. After an hour the mixture was diluted with 20 ml. of water and extracted with 20-ml. portions of CCl_4. The CCl_4 extract was dried and CCl_4 removed at 100° and 10 mm. pressure. The oily residue was treated dropwise with 10 ml. of 40% peracetic acid. The oxidation was highly exothermic. After 10 min., addition of water precipitated 0.50 g. (30%) of white solid, m.p. 120.4–121.1° after 3 recrystallizations from 95% ethanol. *Anal.* Calcd. for $C_{15}H_{24}O_2S$: C, 67.16; H, 8.96; S, 11.94. Found: C, 67.23, 67.38; H, 9.02, 9.10; S, 11.86, 11.72.

Photochemical Experiments.—Disulfide experiments were carried out in Pyrex flasks or tubes irradiated by a General Electric RS sun lamp. The distance from the lamp was varied (10–18 cm.) to maintain a reaction temperature of 60 ± 5°. The peroxide–triethyl phosphite experiments were carried out with the low pressure mercury arc system described previously.[8]

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[21] P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956).

[22] T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth, London, 1954.

[23] F. Ramirez and S. Dershowitz, THIS JOURNAL, **73**, 5614 (1956); *J. Org. Chem.*, **22**, 856 (1957).

[24] G. Kamai and L. P. Egoroda, *Zhur. Obshchei Khim.*, **16**, 1521 (1946).

[25] G. Kamai and Z. Kbarrasova, *ibid.*, **27**, 953 (1957).

[26] C. E. Griffin, *Chemistry & Industry*, 415 (1958).

[27] *Cf.* reference 6, Sect. 6.2.

[28] J. O. Clayton and W. L. Jensen, THIS JOURNAL, **70**, 3880 (1948); *cf.* ref. 6, pp. 452–453.

[29] R. Willstätter and E. Sonnenfeld, *Ber.*, **47**, 2801 (1914); C. Walling, F. W. Stacey, S. E. Jamison and E. S. Huyser, THIS JOURNAL, 4543, 4546 (1958).

[30] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 234.

Product Analysis.—Extensive use was made of gas chromatography, both in following reactions and identifying products. Instruments employed were a Perkin-Elmer model 154 vapor fractometer and a Wilkens Instrument Co. aerograph A-100. Peaks were identified by comparison with runs on known materials and, when necessary, by actual collection of the effluent material. Details of specific experiments are given below.

Isobutyl Mercaptan–Triethyl Phosphite.—Two 10.00-ml. aliquots of a solution of 10.00 ml. of bromobenzene (standard for gas chromatographic analysis), 10.00 ml. of triethyl phosphite (0.0584 mole), and 5.00 ml. of isobutyl mercaptan (0.0455 mole) were placed in separate aluminum foil covered flasks, A and B. After the addition of 0.0055 g. of AIBN (0.000335 mole) to flask A, both were stoppered and placed in a 69° thermostat. Flask A was removed after 2 minutes when it was noted that gas was leaking past the stopper (isobutane); B, which never appeared to have gas leaking from it, was removed after 30 minutes. Results were:

Mixture	Peak heights *i*-BuSH	 P-(OEt)$_3$	 C_6H_5Br
A	1	8	92
B	128	55	80
Original	144	53	92

The gas chromatographic pattern of A also showed a very high peak in the low boiling region (104 units, isobutane) as well as a high boiling component (25 units and broad, triethyl phosphorothionate).

Isobutyl Disulfide–Triethyl Phosphite (Photochemical).—Triethyl phosphite (44.94 g., 0.271 mole) and 37.18 g. of isobutyl disulfide were irradiated at 60° for 72 hours. Gas chromatographic analysis indicated, by the absence of any isobutyl disulfide peak, that complete reaction had occurred. The reaction mixture was fractionally distilled through a one-foot vacuum-jacketed silvered Vigreux column at 15 mm. The first fraction was collected by bubbling air through the capillary in the reaction mixture, without heating the pot. Thus 0.75 ml. was collected in a −80° trap. Gas chromatographic analysis of this material, which was gaseous at room temperature, showed only 2 components, identified as isobutane and isobutylene in a ratio of 8:1. Further distillation yielded 28 g. of isobutyl sulfide (92%), $n^{25}\mathrm{D}$ 1.4437, infrared spectrum identical with that of Eastman Kodak Co. white label grade isobutyl sulfide, $n^{25}\mathrm{D}$ 1.4444. In addition, 44.0 g. of triethyl phosphorothionate (106% based on isobutyl disulfide going to isobutyl sulfide) was isolated, $n^{25}\mathrm{D}$ 1.4459. Its infrared spectrum was identical with that of Virginia-Carolina triethyl phosphorothionate, $n^{25}\mathrm{D}$ 1.4462.

Isobutyl Disulfide–Triethyl Phosphite (Radical Initiators).—A solution of 9.0 g. of isobutyl disulfide (0.0580 mole) was degassed 3 times at −80°. After heating this solution for 36 hours at 100° and 2.75 hours at 140°, gas chromatography showed only a trace of reaction. When 0.158 g. of DTBP (0.0011 mole) was added to the solution and it was heated for 2 hours at 135–140°, analysis indicated complete conversion to isobutyl sulfide and triethyl phosphorothionate.

In a second experiment a solution of 9.03 g. of isobutyl disulfide (0.0509 mole) and 9.58 g. of triethyl phosphite (0.057 mole) was degassed 3 times at −80°. After heating for 2.25 hours at 120°, gas chromatographic analysis showed that no reaction had taken place. After the addition of 0.079 g. of DTBP (0.00055 mole), the mixture was heated at 120° for 1 hour and 125° for 2 hours. Analysis at this point indicated 60–70% reaction.

A mixture of 9.495 g. of triethyl phosphite (0.057 mole), 6.861 g. of isobutyl disulfide (0.039 mole), and 0.100 g. of AIBN (0.00061 mole) was degassed 3 times at −80° and then heated for 12 hours at 50° and 40 minutes at 100°. Gas chromatographic analysis showed only a trace of reaction. The solution then was irradiated with a General Electric RS sun lamp for 3.75 hours at 60°. Gas chromatographic analysis at this point showed almost complete conversion to sulfide and phosphorothionate.

Ethyl Disulfide–Triethyl Phosphite (DTBP Initiated).—A mixture of 5.0 g. of ethyl disulfide (0.041 mole) and 9.7 g. of triethyl phosphite (0.059 mole) showed negligible reaction when heated for 185 minutes at 140°. The addition of 0.079 g. of DTBP (0.00055 mole) and subsequent heating for 53 minutes led to almost complete disappearance of the ethyl disulfide. A similar mixture of 49.7 g. of ethyl disulfide (0.0407 mole), 101.5 g. of triethyl phosphite (0.56 mole) and 1.04 g. of DTBP (0.0072 mole) was heated at 140° for 5 hours. The mixture was fractionally distilled through a 36-inch glass helix-packed column, 26.1 g. (74%) of ethyl sulfide was obtained, b.p. 91.2°. This was identified by oxidation to the sulfone with excess peracetic acid. The sulfone, m.p. 70.9–72.2°, did not depress the melting point of an authentic sample of ethyl sulfone. In addition, 77.9 g. of triethyl phosphorothionate (100% based on disulfide going to sulfide) was obtained, b.p. 103° (11 mm.), $n^{25}\mathrm{D}$ 1.4455; infrared spectrum identical with commercial triethyl phosphorothionate, $n^{25}\mathrm{D}$ 1.4462.

Ethyl Disulfide-Triethyl Phosphite (Thermal Reaction).—Ethyl disulfide (34.8 g., 0.29 mole) and 48.5 g. of triethyl phosphite were heated for 41 hours at 160°. Gas chromatographic analysis indicated that significant reaction had taken place, leading to one low boiling component, ethyl sulfide, and two high boiling products. The high boiling components, which were present in approximately equal amounts, were separated by distillation on the Aerograph gas chromatography apparatus into two pure substances. The lower boiling of the two, $n^{25}\mathrm{D}$ 1.4450, was identified as triethyl phosphorothionate by comparison of its elution time and its infrared spectrum with that of an authentic sample. The other component, $n^{25}\mathrm{D}$ 1.4544, was identified as triethyl phosphorothiolate. Its infrared spectrum was identical with that of the major product found in the thermal isomerization of triethyl phosphorothionate, $n^{25}\mathrm{D}$ 1.4541. A similar mixture of products was formed when the reaction was carried out in the presence of 0.5 mole % of trinitrobenzene.

***n*-Butyl Disulfide–Triethyl Phosphite (Radical Initiators).**—Triethyl phosphite 82.5 g., (0.50 mole), 56.2 g. of *n*-butyl disulfide and 1.58 g. of DTBP (0.011 mole) were heated below a reflux condenser for 2.75 hours at 140°. Nitrogen was bubbled through continuously and the gaseous stream passed through a trap at −80°; 4.0 g. of material was found in the trap, and was identified by gas chromatographic techniques as 3.7 g. of *n*-butane (0.064 mole) and 0.3 g. of isobutane (0.0054 mole). Gas chromatographic analysis of the reaction mixture revealed that the reaction was complete. It was therefore fractionally distilled through a 36-inch, glass helix packed column at reduced pressure; 32.8 g. of *n*-butyl sulfide (71%), b.p. 100° (30 mm.), was obtained. This was identified by oxidation to the sulfone in 95% yield, m.p. 44.7–45.4°, no depression in melting point upon mixing with an authentic sample. Also isolated was 61.0 g. of triethyl phosphorothionate (98% based on disulfide going to sulfide), b.p. 103° (12 mm.), $n^{25}\mathrm{D}$ 1.4455, infrared spectrum identical with that of commercial triethyl phosphorothionate, $n^{25}\mathrm{D}$ 1.4462.

The relative efficiencies of DTBP and DCP as initiators were compared by heating mixtures of 6.5 g. of triethyl phosphite and 3.2 g. of *n*-butyl disulfide at 130° with the results.

Initiator	Time, hr.	Reacn., %
None	17	0
79 mg. DTBP	4.3	100
107.6 mg. DCP	6.5	50
	26.5	62

***n*-Butyl Disulfide–Triethyl Phosphite (Thermal Reaction).**—Triethyl phosphite (122 g., 0.74 mole), 93.7 g. of *n*-butyl disulfide (0.53 mole), and 0.250 g. of hydroquinone (0.0023 mole) were heated at 195–200° in an aluminum foil covered flask for 38 hours. Fractional distillation of the reaction mixture through a 36-inch, glass helix packed

TABLE II

IDENTIFICATION OF THE SULFIDES OBTAINED IN THE THERMAL REACTION OF *n*-BUTYL DISULFIDE WITH TRIETHYL PHOSPHITE

Sulfide	B.p., °C.	M.p. of sulfone, °C.	M.p. of authentic sulfone, °C.	Mixed, m.p.
EtSEt	91.2	71.0–72.2	70.9–72.2	Same
EtS-*n*-Bu	143.0	49.5–50.2	49.5–50.2	Same
n-BuS-*n*-Bu	95 (25 mm.)	44.5–45.2	44.5–45.3	Same

column gave 7.6 g. of ethyl sulfide (16%), 6.9 g. of *n*-butyl sulfide (9%) and 30.0 g. of *n*-butyl ethyl sulfide (49%). Each was identified by oxidation with peracetic acid to the corresponding sulfone. The main high boiling component of this reaction was identified as O,O-diethyl-S-*n*-butyl phosphorothiolate, 54.7 g. (50%), b.p. 104° (1.5 mm.), $n^{25}D$ 1.4561, by comparing its infrared spectrum with that of an authentic sample, b.p. 103° (1.5 mm.), $n^{25}D$ 1.4561.

Isobutyl Disulfide–Trimethyl Phosphite.—A mixture of equal volumes of isobutyl disulfide and trimethyl phosphite was heated for 40 min. at 100°. Analysis of an aliquot indicated no reaction. The mixture was next irradiated for 30 minutes at 60°. It now showed strong peaks corresponding to isobutyl sulfide and trimethyl phosphorothionate. On longer irradiation the reaction was essentially complete.

A series of experiments were also run to determine the relative reactivities of trimethyl and triethyl phosphites toward isobutyl disulfide by irradiating a mixture of the three components (containing insufficient disulfide for complete consumption of the phosphites and also bromobenzene as an internal standard), and determining the relative amounts of the two phosphites consumed. Results appear in Table III.

TABLE III

RELATIVE REACTIVITIES OF TRIETHYL AND TRIMETHYL PHOSPHITES IN REACTION WITH ISOBUTYL DISULFIDE

Concentration, millimoles				Rel.
$[P(OEt)_3]_0$	$[P(OEt)_3]$	$[P(OMe)_3]_0$	$[P(OMe)_3]$	react.^{a}
93	72.8	94	82.8	0.64
93	66.5	94	75.2	.67
116	66.0	40.4	30.2	.51
116	76.8	40.4	32.8	.51
116	53.2	40.4	28.6	.44

^{a} Calculated from d ln $[P(OMe)_3]$/d ln $[P(OEt)_3]$ = relative reactivity.

While they indicate that triethyl phosphite is approximately twice as reactive as trimethyl phosphite, there appears to be a significant difference in reactivity for different phosphite ratios which needs further study.

Thermal Isomerization of Triethyl Phosphorothionate.—Triethyl phosphorothionate (64.2 g., 0.32 mole) was heated at 180–185° below a reflux condenser for 23 hours. Gas chromatographic analysis at this point indicated that most of the triethyl phosphorothionate had been converted to a higher boiling material. The reaction mixture was fractionally distilled through an 18-inch, glass helix packed, silvered, vacuum jacketed column and 34 g. of triethyl phosphorothiolate (70% based on reacted triethyl phosphorothionate), was found, b.p. 138° (28 mm.), $n^{25}D$ 1.4541; reported[31] b.p. 110° (11 mm.), $n^{25}D$ 1.4552. The infrared spectrum showed a very strong band at 8.0 μ (the P→O bond) absent in the starting material.

***n*-Butyl Sulfide–Triethyl Phosphite.**—A mixture of 1.70 g. of *n*-butyl sulfide (0.012 mole) and 2.90 g. of triethyl phosphite (0.017 mole) was irradiated for 5 hours at 50° with a General Electric RS sun lamp. Gas chromatographic analysis showed only starting materials.

Benzyl Disulfide–Triethyl Phosphite.—Benzyl disulfide (10.0 g., 0.040 mole) and 34 g. of triethyl phosphite (0.20 mole) were irradiated for 14 hours at 60°. Fractional distillation of the reaction mixture revealed that the major portion of the benzyl disulfide had not reacted. A similar mixture, containing 50.0 g. of benzyl disulfide (0.20 mole) and 97 g. of triethyl phosphite (0.58 mole) was irradiated for 3 weeks at approximately 60°. Fractional distillation of the reaction mixture yielded 7.3 g. (19%) of toluene, $n^{25}D$ 1.4930, infrared spectrum identical with authentic toluene, $n^{25}D$ 1.4927, as well as 65 g. of triethyl phosphorothionate, b.p. 106° (25 mm.), $n^{25}D$ 1.4456, infrared spectrum identical with that of an authentic sample, $n^{25}D$ 1.4462. In addition 2.7 g. (26%) of bibenzyl, b.p. 126° (0.1 mm.), m.p. 51.1–52.5°, and 2.1 g. (5%) of benzyl sulfide, b.p. 130° (0.1 mm.), were isolated. The bibenzyl was identified by comparison of its infrared spectrum with that of an authentic sample and the fact that it did not depress the melting point of the authentic sample. The benzyl sulfide was identified as the sulfone as follows: 3.5 g. of the final distillation fraction, b.p. 130° (0.1 mm.), was refluxed in 12 ml. of 36% hydrochloric acid for 20 hours. This mixture was extracted with ether, the ether dried over $MgSO_4$ and evaporated, leaving a 1.553-g. liquid residue (of disagreeable odor). This residue was oxidized with 10 ml. of 40% peracetic acid and upon addition of water to the oxidation mixture, a white precipitate formed, 0.825 g. This material melted at 151–152° after 2 recrystallizations from 30% ethanol. A mixed melting point with authentic benzyl sulfone showed no depression.

Photolysis of DCP in Triethyl Phosphite.—DCP (40.0 g., 0.148 mole) dissolved very easily in 131 g. of triethyl phosphite (0.79 mole). This mixture was irradiated with a high intensity, low pressure mercury arc for 122 hours at 25°. Nitrogen was bubbled through the reaction mixture continuously and the gaseous steam passed through a trap at −80°. Investigation of the contents of the trap revealed 2.0 g. liquid, which was identified as chiefly triethyl phosphite. The reaction mixture was chilled to −20° and 12.0 g. of a crystalline solid precipitated, m.p. 116.8–118.0° after 4 recrystallizations from 95% ethanol. A mixed melting point with an authentic sample of dicumene showed no depression. Fractional distillation of the reaction mixture gave 58.2 g. of triethyl phosphate (98% based on oxygen available from the peroxide), b.p. 115° (25 mm.), $n^{25}D$ 1.4037. The 23.7-g. distillation residue appeared to be a mixture of a solid and an oil. The solid, 3.1 g., was separated and recrystallized 3 times from 95% ethanol, m.p. 117–118°. It did not depress the melting point of an authentic sample of dicumene; total dicumene, 16.1 g. (46%).

Reaction of DCP with Triethyl Phosphite.—DCP (20.0 g., 0.074 mole) and 65.5 g. of triethyl phosphite (0.40 mole) were heated below a reflux condenser in an aluminum foil covered system for 100 hours at 125°. Nitrogen was bubbled through continuously. The reaction mixture was cooled to 20° and 12.42 g. of a crystalline solid (dicumene 70.6%) precipitated, m.p. 117–118° after one recrystallization from 95% ethanol. A mixed melting point with an authentic sample of dicumene showed no depression. Fractional distillation of the reaction mixture gave 25.1 g. of triethyl phosphate (93% based on oxygen available from the peroxide), b.p. 110° (20 mm.), $n^{25}D$ 1.4032.

Photolysis of DTBP in Triethyl Phosphite.—DTBP (31.6 g., 0.216 mole) and 131 g. of triethyl phosphite (0.78 mole) were irradiated for 32 hours at 25°. Nitrogen was bubbled through the reaction mixture continuously and the gaseous stream passed through a trap at −80°. At the end of the reaction the trap contained 11.4 g. of liquid. Mass spectrometric and gas chromatographic[32] analysis of this material revealed 63.8% isobutane, 27.6% isobutylene, 5.7% *n*-butane, 0.8% ethane and 0.3% ethylene. Fractional distillation of the reaction mixture revealed a mixture of hydrocarbon material, b.p. 95–105°, which contained a very volatile solid (2,2,3,3-tetramethylbutane). Only a negligible amount of *t*-butyl alcohol and acetone was found. In addition, 81.8 g. of triethyl phosphate (106% based on oxygen available from the peroxide) was obtained, b.p. 131° (50 mm.), $n^{25}D$ 1.4037; reported[33] 1.4039. Only 4.3 g. of material boiling above triethyl phosphate was found. Six more reactions of 0.216 mole of DTBP and 0.78 mole of triethyl phosphite each were carried out. They were worked up simultaneously, in an effort to establish the identity of the hydrocarbon that formed. Analysis of the combined trap materials revealed 45.6 g. of isobutane and 19.2 g. of isobutylene. Fractional distillation of the reaction mixtures resulted in the identification of these several components: 0.7 g. of isobutane (total therefore 46.3 g., 30.7%), 9.7 g. of isobutylene (total therefore 28.9 g., 19.9%), 5.19 g. of 2,2,4-trimethylpentane (3.5%), 11.43 g. of 2,2,3,3-tetramethylbutane (8%) and 2.50 g. of 2,4,4-trimethyl-1-pentene (1.8%). The latter three hydrocarbons were identified:

2,2,4-Trimethylpentane was separated from a mixture of the above C_8-hydrocarbons by fractional distillation of the Aerograph gas chromatography apparatus, $n^{25}D$ 1.3383. Its

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[31] H. I. Jacobson, R. G. Harvey and E. V. Jensen, THIS JOURNAL, **77**, 6064 (1955).

[32] This analysis was arranged for by Dr. P. D. Caesar and performed by Mr. P. Hochgesang, both of the Socony Mobil Oil Co.

[33] D. P. Evans, W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 1310 (1930).

infrared spectrum was identical with that of Eastman Kodak Co. spectral grade isoöctane, $n^{25}D$ 1.3380.

2,2,3,3-Tetramethylbutane which solidified in the distilling head during the distillation of the reaction mixture, was recrystallized once from methanol, m.p. 100–101°, reported[34] m.p. 100.6°. The infrared spectrum was identical with that of 2,2,3,3-tetramethylbutane reported by the American Petroleum Institute Project 44 (Spectrum 444).

2,4,4-Trimethyl-1-pentene occurred in a mixture containing the other C_8-hydrocarbon as well as ethanol. It could not be separated from the 2,2,3,3-tetramethylbutane, even by gas chromatographic techniques. Therefore, 11 ml. of the distillate in which the 2,4,4-trimethyl-1-pentene was present was diluted with 30 ml. of ether, washed 7 times with 25-ml. portions of water (to remove the ethanol), and twice with saturated salt solution. The ether layer was dried over sodium sulfate and the ether then slowly evaporated. To the residue, in 25 ml. of glacial acetic acid, was added 1.06 g. of benzyl mercaptan (0.0086 mole), 10 mg. of hydroquinone and finally 50 drops of 18 *M* sulfuric acid. After standing 16 hours at room temperature, the reaction mixture was diluted with an equal volume of water and extracted with two 35-ml. portions of CCl_4. After drying the extract over sodium sulfate, the CCl_4, as well as anything else volatile at 100° (10 mm.), was removed by distillation. The oily residue, which was void of any mercaptan odor, was oxidized with 10 ml. of peracetic acid. The addition of water to this oxidation mixture resulted in a white precipitate, 0.425 g., m.p. 120.3–121.0°, after 3 recrystallizations from 30% ethanol. This was identified as benzyl 1,1,3,3-tetramethylbutyl sulfone, since it did not depress the melting point of known material (see above).

Thermal Reaction of DTBP with Triethyl Phosphite—DTBP (31.6 g., 0.216 mole) and 121 g. of triethyl phosphite (0.73 mole) were heated below a reflux condenser for 42 hours at 120°. Nitrogen was bubbled through the reaction mixture continuously, and the gaseous stream passed through a trap at −80°. Gas chromatographic examination of the contents of the trap revealed a mixture of low (C_4) and high (C_8) boiling hydrocarbons, very similar to the mixture obtained in the photolysis of DTBP in triethyl phosphite, with the exception that apparently no 2,4,4-trimethyl-1-pentene formed, but instead a peak corresponding to authentic 2,2,4-trimethyl-2-pentene. A white crystalline solid, 0.53 g., whose infrared spectrum was identical with that of 2,2,3,3-tetramethylbutane, except for medium sized peaks at 9.7 and 10.9 μ (where triethyl phosphite has very strong bands) was found at the inlet to the trap. After 2 sublimations (atmospheric pressure, 50°) a product, m.p. 93–97°, was obtained. The infrared spectrum was again identical with that of 2,2,3,3-tetramethylbutane; however, the peaks at 9.7 and 10.9 μ were still present, although greatly reduced in relative size. Fractional distillation of the reaction mixture revealed 86.4 g. of triethyl phosphate (110% based on oxygen available from the peroxide), b.p. 126° (40 mm.), $n^{25}D$ 1.4048; 16 g. of material boiling above the triethyl phosphate was found, but not identified.

Reaction of *t*-Butyl Hydroperoxide with Triethyl Phosphite.—*t*-Butyl hydroperoxide was added dropwise to 9.7 g. of triethyl phosphite at 0°. Reaction was instantaneous and exothermic and addition was continued until no further heat was produced. Gas chromatographic analysis of the reaction mixture revealed that only two products formed, *t*-butyl alcohol and triethyl phosphate. When the reaction was repeated in the presence of 0.100 g. of trinitrobenzene (a pink solution with triethyl phosphite), an exactly analogous instantaneous and exothermic reaction occurred.

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[34] S. W. Ferris, "Handbook of Hydrocarbons," Academic Press, Inc., New York, N. Y., 1955, pp. 25–256.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY AND THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Conformational Analysis. VII. Reaction of Alkylcyclohexyl Bromides with Thiophenolate. The Conformational Equilibrium Constant of Bromine[1]

BY ERNEST L. ELIEL[2] AND RALPH G. HABER

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The bimolecular substitution and elimination rates of cyclohexyl bromide (k), *cis*-4-*t*-butylcyclohexyl bromide (k_a) and *trans*-4-*t*-butylcyclohexyl bromide (k_e) with thiophenolate have been measured. The over-all rate for the (axial) *cis* isomer is about 61 times as large as that for the (equatorial) *trans* isomer, the ratio for the corresponding tosylates (ref. 8) being 36, The equilibrium constant: axial cyclohexyl bromide $\rightleftarrows$ equatorial cyclohexyl bromide, calculated by the previously presented (ref. 3) equation $K = (k_a - k)/(k - k_e)$ is 3.4, corresponding to a difference of 0.73 kcal./mole between equatorial and axial bromine. This difference, which is supported by data in the literature, is considerably smaller than the accepted difference of 1.6–1.8 kcal./mole between equatorial and axial methyl. It is suggested that the difference is due largely to London forces which, at the inter-atomic distance between axial positions in cyclohexane, are of similar order of magnitude as the repulsive van der Waals forces. Contrary to an earlier report (ref. 8), elimination occurs in the reaction of *trans*-4-*t*-butylcyclohexyl tosylate as well as *trans*-4-*t*-butylcyclohexyl bromide with thiophenolate. This observation supports the "merged mechanism" of Winstein, Darwish and Holness (ref. 36) for the thiophenolate displacement.

In a previous paper[3,4] we have proposed the relationship $K = (k_a - k)/(k_a - k_e)$ (i) where K is the conformational equilibrium constant for the atom or group X (Fig. 1), k_a and k_e are specific rates of a suitable reaction[5] for the axial and equatorial isomer, respectively, and k is the experimental rate constant of the naturally occurring equilibrium mixture of the two conformational isomers for the reaction in question. The constants k_a and k_e are measured experimentally by studying the reaction in question with 4-*t*-butylsubstituted compounds.[4] Because of the large bulk of the 4-*t*-butyl group,[4] this group will tend to occupy exclusively the equatorial position. Therefore, in *cis*-4-*t*-butylcyclohexyl-X, X will occupy the axial position[6] and the compound will react at the specific rate k_a, whereas in *trans*-4-*t*-butylcyclohexyl-X, X will occupy the equatorial position

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[1] (a) Presented, in part, before the Division of Organic Chemistry, San Francisco Meeting, Am. Chem. Soc., April 15, 1958; (b) Paper VI, *J. Org. Chem.*, in press.

[2] National Science Foundation Senior Postdoctoral Fellow 1958–1959.

[3] E. L. Eliel and C. A. Lukach, THIS JOURNAL, **79**, 5986 (1957).

[4] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955), have earlier proposed an equivalent relationship $k = N_e k_e + N_a k_a$ where N_e and N_a are the mole fractions of substrate in the equatorial and axial conformation, respectively.

[5] The nature of the reaction chosen is immaterial.

[6] Provided X is substantially smaller than *t*-butyl.