methylalloxylhydroxycortisone BMD (XIII) and 30 cc. of 60% aqueous formic acid was heated inside a steam-jacket for 30 minutes. The resulting solution was cooled and extracted with chloroform. The chloroform layer was washed with aqueous sodium bicarbonate solution, dried over sodium sulfate, and concentrated in vacuo. The crude concentrate was dried by azeotropic distillation with benzene. The resulting solution was cooled and extracted with chloroform. The chloroform layer was dried over sodium sulfate, 7:3, to remove an unsaturated fraction, m.p. 170°. The material was acetylated with acetic anhydride in pyridine under standard conditions and chromatographed on silica-gel (Merck). The column was eluted with ether-chloroform, 4:6, afforded 46 mg. of crude 6α-methylalloxylpregnane-11β,16α,20,20,21-bismethylenedioxy-3-ethylenedioxy-allopregnane-11-one.

Another case recently studied is that of the housefly. Musca vicina (R. P. Hobson, Entomol. Rev. 67, 308 (1965)). It cannot itself synthesize the sterols they require but must rely on their food for the supply of these essential factors. According to Bloch and co-workers, larvae of the beetle Dermestes vulpinus transform acetate normally to squalene but cannot cyclize the latter to lanosterol (and cholesterol).

In the case of the housefly Musca vicina Macq., 4-cholesterol and sitosterol, and to a lesser extent ergosterol and stigmasterol, were found effective in promoting larval growth and pupation. Also a number of minor changes of the molecular structure of cholesterol was found compatible with the biological functions of the compound, while more drastic changes destroyed its ability to regulate growth and pupation and produced either biologically inactive substances or even antagonists of the natural sterols. In particular, the removal of the sterol side chain of the compound, in which the side-chains are similar to those of cholesterol in which the side-chains are similar to those of cholesterol, as growth promoters of housefly larvae. No pupation occurred when these "unnatural" sterols were added to the sterile medium on which the larvae were reared.

The synthesis and Biological Availability of Some Lower Homologs of Cholesterol

BY ERNST D. BERGMANN, MORDECAI RABINOVITZ AND ZWI H. LEVINSON

RECEIVED JULY 10, 1958

Several analogs of cholesterol containing shorter side-chains have been synthesized from the chloride of 3-acetoxy-etiochol-5-enic acid (II) and dibutyl-, di-n-pentyl- and diphenylacm and from pregnenolone acetate (III) and n-butyl-, n-pentyl- and phenylmagnesium bromide. In the former case, the ketones obtained were reduced, in the latter the tertiary carbonols dehydrated and subsequently hydrogenated. The structure of these dehydration products and the configuration of the hydroxylation products has been established, the latter by the observation that the analogous series of reactions with 4-methylpentylmagnesium bromide leads to cholesterol acetate. These "unnatural" sterols show an effectiveness of at least 40% of that of cholesterol, as growth promoters of housefly larvae. No pupation occurred when these "unnatural" sterols were added to the sterile medium on which the larvae were reared.

It has been known for some time that insect larvae cannot themselves synthesize the sterols they require but have to rely on their food for the supply of these essential factors. According to Bloch and co-workers, larvae of the beetle Dermestes vulpinus transform acetate normally to squalene but cannot cyclize the latter to lanosterol (and cholesterol).

In the case of the housefly Musca vicina Macq., 4-cholesterol and sitosterol, and to a lesser extent ergosterol and stigmasterol, were found effective in promoting larval growth and pupation. Also a number of minor changes of the molecular structure of cholesterol was found compatible with the biological functions of the compound, while more drastic changes destroyed its ability to regulate growth and pupation and produced either biologically inactive substances or even antagonists of the natural sterols. In particular, the removal of the sterol side chain of the compound, in which the side-chains are similar to those of cholesterol, as growth promoters of housefly larvae. No pupation occurred when these "unnatural" sterols were added to the sterile medium on which the larvae were reared.

(5) Ergosterol is also less active than cholesterol in promoting larval growth of the flies Musca domestica L. (C. S. Hammes, Ann. Entomol. Soc. Am., 65, 254 (1962)).
A few syntheses of such "unnatural" sterols have been reported before. Mitui\(^6\) has prepared 33-hydroxy-20-\(n\)-butyl-pregnan-5-ene (norcholesterol) (I, \(R = \text{CH}_3\)) by Clemmensen reduction of 33-hydroxy-20-\(3\prime\)-oxobutyl/pregnan-5-ene, and de Vries and Backer\(^8\) have synthesized a number of sterols by condensation with 3-acetoxycyclopent-5-enic acid chloride and dialkyl cadmium compounds and subsequent reduction of the ketone formed, either by the method of Wolff–Kishner or by catalytic hydrogenolysis of their thioketals. The compounds these authors describe have formula I, with \(R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9\). Kazuno synthesized 20\(^\prime\)-(3\'-oxopentyl)-pregnane (II) from cholanic acid amide and ethylmagnesium chloride and used the ketone for some further transformations.

In the present study, 3-acetoxycyclopent-5-enic acid (II) and pregnenolone acetate (III)\(^11\) were used as starting materials. The chloride of I was condensed with cadmium di-\(n\)-butyl, di-\(n\)-pentyl and diphenyl and the ketone formed (IV, \(R = \text{n-C}_4\text{H}_{11}, \text{n-C}_5\text{H}_{11}, \text{C}_6\text{H}_5\)) reduced by the method of Huang–Minlon. Thus, we obtained the sterols

\[ V (R = \text{n-C}_4\text{H}_{11}, \text{n-C}_5\text{H}_{11}, \text{C}_6\text{H}_5) \]  

A second series of unnatural sterols was prepared by the reaction of III with the Grignard compounds from \(n\)-butyl bromide, \(n\)-pentyl bromide and bromo-benzene, dehydration of the carbinols formed (VI, \(R = \text{C}_4\text{H}_{11}, \text{C}_5\text{H}_{11}, \text{C}_6\text{H}_5\)) to the dienes VII (\(R' = \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_5\text{H}_{11}\)) and VIII, respectively, and catalytic hydrogenation of the dienes with platinum oxide in the presence of glacial acetic acid under conditions which do not involve the \(\Delta^\delta\)-double bond.\(^1\) We thus obtained I (\(R = \text{CH}_3, \text{C}_2\text{H}_5\)) and IX.\(^13\)

The Grignard reactions with pregnenolone acetate (III) were preferred to those with pregnenolone itself, as the latter formed an insoluble magnesyl derivative and, therefore, the reaction remained incomplete. The products of the Grignard reactions with III appear, of course, in deacetylated form and were re-acetylated in their crude state. The compounds were homogeneous in all cases; of the possible epimers at \(C_3\) only one was formed. This is at variance with the observations of Woodward\(^6\) in his synthesis of the saturated cholestanol.

Two questions arose in the course of these experiments, viz., (1) the structure of the dienes formed by dehydration of the carbinols VI and (2) the configuration at \(C_4\) resulting from the catalytic hydrogenation of these dienes. While in VIII, the dehydration product of VII, the question does not arise (indeed, the infrared spectrum shows the C–H bending bands at 910 and 990 cm\(^{-1}\), characteristic for terminal methylene groups in olefins),\(^14\) the formula of the dienes VII is not per se unambiguous; they may be the isomers with terminal methylene groups (as VIII). The fact that in neither case (\(R' = \text{C}_3\text{H}_7, \text{C}_4\text{H}_9\)) infrared bands were observed at 910 and 990 cm\(^{-1}\) indicates the correctness of formula VII. This was proven unambiguously by ozonization of VII (\(R' = \text{C}_3\text{H}_7\)) which gave in quantitative yield butyraldehyde, identified as 2,4-dinitrophenylhydrazone. Woodward\(^6\) in the synthesis of cholesterol has not isolated the intermediate product.

As to the configuration at \(C_4\) in I (\(R = \text{CH}_3, \text{C}_2\text{H}_5\)) and in IX, we satisfied ourselves that it is identical with the configuration in the natural

\[ (1) \text{We are deeply indebted to Messrs. Syntex, Mexico, for a most generous gift of pregnenolone.} \]

\[ (2) \text{The configuration at } C_1 \text{ resulting from the catalytic hydrogenation of VIII is unambiguous; indeed, the infrared spectrum shows the C–H bending bands at } 910 \text{ and } 990 \text{ cm}^{-1}, \text{ characteristic for terminal methylene groups in olefins.} \]

\[ (3) \text{The formula of the dienes VII is not per se unambiguous; they may be the isomers with terminal methylene groups (as VIII).} \]

\[ (4) \text{Two questions arose in the course of these experiments, viz., (1) the structure of the dienes formed by dehydration of the carbinols VI and (2) the configuration at } C_4 \text{ resulting from the catalytic hydrogenation of these dienes.} \]

\[ (5) \text{The Grignard reactions with pregnenolone acetate (III) were preferred to those with pregnenolone itself, as the latter formed an insoluble magnesyl derivative and, therefore, the reaction remained incomplete.} \]

\[ (6) \text{The compounds were homogeneous in all cases; of the possible epimers at } C_3 \text{ only one was formed. This is at variance with the observations of Woodward (6) in his synthesis of the saturated cholestanol.} \]

\[ (7) \text{We have shown that under these conditions of hydrogenation, cholestanol acetate does not absorb hydrogen.} \]

\[ (8) \text{The Grignard reactions with pregnenolone acetate (III) were preferred to those with pregnenolone itself, as the latter formed an insoluble magnesyl derivative and, therefore, the reaction remained incomplete.} \]
sterols by showing that the application of the above synthesis to the preparation of cholesterol yielded cholesteryl acetate, identical in melting point (and mixed melting point), rotation and infrared spectrum with the natural product. For this purpose, III was treated with the magnesium derivative of 4-methylpentyl bromide (X); thus 33-acetoxy-20-hydroxy-20-(4'-methylpentyl)-pregn-5-ene (VI, \( R = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)) was obtained; it was dehydrated to 38-acetoxy-17-(a-methyl-3-(3'-methylbutyl)-vinyl)-pregn-5-ene (VII, \( R = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)) and the latter was hydrogenated. Two similar syntheses of cholesterol have been reported recently, the one based on the reaction between 38-acetoxy-norchol-5-enic acid chloride and diisobutylcadmium, the other (leading to cholesteryl methyl ether) starting from 3P-methoxy-bisnorchol-5-enic acid chloride and diisomylcadmium.

The utilizable sterol by 40-50%. The introduction of a hydroxyl group in the 20-position (VI) seems to affect the utilizability of the compound more than a shortening of its side chain. Replacement of the aliphatic side chain of cholesterol by an aromatic hydrocarbon radical destroys the biological availibility of the resulting compounds (V, VIII, IX). No pupation occurred in the presence of the unnatural sterols. This could be due largely to the retarded growth rate which would prevent the larvae from attaining a body weight sufficient for pupation. If such an analog is fed to the larvae simultaneously with a minute amount of cholesterol (in itself insufficient for normal growth and pupation), it greatly accelerates growth and makes pupation possible. Further experiments in this direction are under way.

### Experimental

All optical rotations have been determined in chloroform solution at \( c = 1.0 \).

Pregnenolone was converted into its acetate III, m.p. 146-147° (from ethanol), according to Butenandt and co-workers. For the preparation of 38-acetoxy-etiochol-5-enyl butyrate (IV) we employed the method of King with some modifications. The solution of 15.6 g. of pregnenolone in 75 ml. of warm dry pyridine was cooled, 12.8 g. of iodine added and the mixture heated, with stirring, for 1 hr. on the water-bath. The stirring was continued for 12 hr. at room temperature and the precipitate collected, washed with methanol and heated at 100° for 1.5 hr. with a solution of 7.5 g. of sodium hydride in 250 ml. of 80% ethanol. The clear solution then was cooled and acidified and the crude acid obtained dried at 90°. It was then acetylated at room temperature (12 hr.) with 75 ml. of acetic anhydride in 75 ml. of pyridine. The solution obtained was poured onto ice and the product filtered, dried, extracted with ether (Soxhlet) and the ether solution concentrated. The residue was recrystallized from a mixture of petroleum ether and benzene and melted at 247°; yield 12 g. The chloride of the acid was prepared according to Steiger and Reichstein.

38-Acetoxy-etiochol-5-enyl Butyl Ketone (IV, \( R = \text{C}_6\text{H}_5 \)). To a solution of di-n-butylcadmium (from 0.5 g. of magnesium, 2.8 g. of butyl bromide, 1.6 g. of cadmium chloride), 3 g. of the acid chloride in 30 ml. of benzene was added and the mixture refluxed for 1 hr. Then the ether was driven off and the benzene solution heated for another 3 hr., cooled and decomposed with ice. The benzene was removed by steam distillation, the residue acetylated and the product filtered. After chromatography on alumina from its benzene-petroleum ether solution, the ketone was recrystallized from methanol; needles, m.p. 100°; yield 2.5 g. (80 %); [\( a \] = 25.2°.

*Anal.* Calcd. for \( \text{C}_30\text{H}_40\text{O}_2 \): C, 78.0; H, 10.0. Found: C, 78.3; H, 10.1.

In the same manner, we prepared these compounds.

38-Acetoxy-etiochol-5-enyl methyl ketone (IV, \( R = \text{CH}_3 \)). From methanol, leaflets of m.p. 107°; [\( a \] = 25.4°; yield 75%.

*Anal.* Calcd. for \( \text{C}_30\text{H}_38\text{O}_2 \): C, 78.2; H, 9.1. Found: C, 77.9; H, 9.8.

### Table I

<table>
<thead>
<tr>
<th>Sterol added</th>
<th>Utilization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cholesterol</td>
<td>100.0</td>
</tr>
<tr>
<td>Cholesteryl acetate</td>
<td>84.5</td>
</tr>
<tr>
<td>38-Hydroxy-20-n-amy1-pregn-5-ene (I, ( R = \text{CH}_3 ))</td>
<td>42.7</td>
</tr>
<tr>
<td>17-n-Hexyl-androst-5-ene-30-ol (as V, ( R = \text{CH}_3 ))</td>
<td>42.7</td>
</tr>
<tr>
<td>33-Acetoxy-20-n-butyl-pregn-5-ene (as I, ( R = \text{CH}_3 ))</td>
<td>74.4</td>
</tr>
<tr>
<td>38-Acetoxy-17-n-pentyl-androst-5-ene (V, ( R = \text{C}_6\text{H}_5 ))</td>
<td>30.7</td>
</tr>
<tr>
<td>33-Acetoxy-20-hydroxy-20-n-amy1-pregn-5-ene (VI, ( R = \text{CH}_3 ))</td>
<td>24.1</td>
</tr>
<tr>
<td>33-Acetoxy-17-(a-methyl-3-buty1-vinyl)-pregn-5-ene (VII, ( R' = \text{CH}_3 ))</td>
<td>22.2</td>
</tr>
<tr>
<td>33-Acetoxy-17-(a-methyl-3-propyl-vinyl)-pregn-5-ene (VII, ( R' = \text{CH}_3 ))</td>
<td>15.6</td>
</tr>
<tr>
<td>38-Acetoxy-20-phenyl-pregn-5-ene (IX)</td>
<td>5.1</td>
</tr>
<tr>
<td>33-Acetoxy-17-(a-phenylvinyl)-pregn-5-ene (VIII)</td>
<td>3.8</td>
</tr>
<tr>
<td>17-Benzyl-androst-5-ene-30-ol (as V, ( R = \text{CH}_3 ))</td>
<td>None</td>
</tr>
</tbody>
</table>

### Notes

1. In this case, too, the infrared spectrum was used to establish the position of the double bond in the side chain.


3. A. Romeo and R. Villotti, *Ann. chim.* (Rome), 47, 618 (1957); (C, 81, 1069/69 (1957)).

4. The sterol acetates and the free sterols were assumed to be equivalent, since cholesteryl acetate is known to be utilized only an unnatural sterol resembles that of cholesterol, the more readily the sterol appears to be utilized. A comparison of the utilization of the unsaturated sterols VII with that of their saturated homologs I shows that the presence of the double bond in the side chain reduces the biological availability of the sterol by 40-50%.

5. Pregnenolone was converted into its acetate III, m.p. 146-147° (from ethanol), according to Butenandt and co-workers. For the preparation of 38-acetoxy-etiochol-5-enyl butyrate (IV) we employed the method of King with some modifications. The solution of 15.6 g. of pregnenolone in 75 ml. of warm dry pyridine was cooled, 12.8 g. of iodine added and the mixture heated, with stirring, for 1 hr. on the water-bath. The stirring was continued for 12 hr. at room temperature and the precipitate collected, washed with methanol and heated at 100° for 1.5 hr. with a solution of 7.5 g. of sodium hydride in 250 ml. of 80% ethanol. The clear solution then was cooled and acidified and the crude acid obtained dried at 90°. It was then acetylated at room temperature (12 hr.) with 75 ml. of acetic anhydride in 75 ml. of pyridine. The solution obtained was poured onto ice and the product filtered, dried, extracted with ether (Soxhlet) and the ether solution concentrated. The residue was recrystallized from a mixture of petroleum ether and benzene and melted at 247°; yield 12 g. The chloride of the acid was prepared according to Steiger and Reichstein.

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*Anal.* Calcd. for \( \text{C}_30\text{H}_38\text{O}_2 \): C, 78.2; H, 9.1. Found: C, 77.9; H, 9.8.
heating 2 g. of it with 30 ml. of pyridine and converted into a crystalline compound by trituration with petroleum ether, 9:1, and recrystallized from acetone; needles of m.p. 176°; [\(\alpha\])\(_D\) -52.5°.

Anal. Caled. for C\(_{12}\)H\(_{19}\)O: C, 81.1; H, 10.9. Found: C, 81.1; H, 10.7.

17-\(\alpha\)-Hexyl-androst-5-ene-3,5-diol (V, \(R = CH_3\)).—The reduction of IV (\(R = CH_3\)) was carried out in the preceding case, but the reaction product was not acetylated. From methanol, m.p. 125-126°; [\(\alpha\])\(_D\) -50.0°; yield 70%.

Anal. Caled. for C\(_{12}\)H\(_{20}\): C, 83.3; H, 9.0.

Analogously, we prepared 17-benzyl-androst-5-en-3,5-diol (V, \(R = C_6H_5\)), from methanol; m.p. 105°; [\(\alpha\])\(_D\) +87.0°; yield 90%.

Anal. Caled. for C\(_{15}\)H\(_{22}\): C, 84.9; H, 9.8.

35-Acetoxy-20-\(\alpha\)-butyl-pregn-5-ene (V, \(R = CH_3\)).—Following the method of Petrov and Stuart-Webb, 10 g. of pregnenolone acetate (I) in 50 ml. of benzene was added to a solution of butylmagnesium bromide, prepared from 1 g. of magnesium and 5.5 g. of butyl bromide in 100 ml. of ether. The mixture was refluxed with stirring for 1 hr., the ether distilled off and the benzene solution refluxed for 4 more hr. Decomposition with ice and hydrochloric acid, extraction with benzene and concentration of the dried benzene solution gave an oil, which could be converted into a crystalline compound by crystallization with petroleum ether but was directly re-acetylated with 30 ml. of acetic anhydride in 30 ml. of pyridine at room temperature (12 hr.). The solution was poured into cold dilute hydrochloric acid and the product chromatographed (benzene) and recrystallized from methanol; m.p. 83°; yield 1.2 g. (60%); [\(\alpha\])\(_D\) +54.8°; yield 80%.

Anal. Caled. for C\(_{10}\)H\(_{18}\)O: C, 81.3; H, 10.8.

Cholesteryl acetate, from methanol; m.p. and mixed m.p. with an authentic specimen, 115°; [\(\alpha\])\(_D\) +43.5°; yield 85%.

36-Hydroxy-20-\(\alpha\)-methyl-pregn-5-ene (I, \(R = CH_3\)) from acetone. Double melting points 87 and 124-125°; [\(\alpha\])\(_D\) +47.6°; yield 70%.

Anal. Caled. for C\(_{12}\)H\(_{20}\): C, 81.1; H, 11.0.

Analogously, we prepared 35-acetoxy-20-\(\alpha\)-methyl-pregn-5-ene (I, \(R = CH_3\)) from acetone. Double melting points 87 and 124-125°; [\(\alpha\])\(_D\) +47.6°; yield 70%.

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Cholesteryl acetate, m.p. and mixed m.p. with an authentic specimen, 115°; [\(\alpha\])\(_D\) +43.5°; yield 85%.

36-Hydroxy-20-\(\alpha\)-methyl-pregn-5-ene (IA, \(R = CH_3\)).—A solution of 2.0 g. of the acetate (I, \(R = CH_3\)) in 10 ml. of


The solution obtained was poured into a mixture of ice and hydrochloric acid and the product extracted with ether. The etheral solution then was washed with sodium bicarbonate solution and water, dried and concentrated and the residue chromatographed (ether—petroleum ether) and recrystallized from methanol; m.p. 80°; [\(\alpha\])\(_D\) +54.8°; yield 1.5 g. (83%).

Anal. Caled. for C\(_{10}\)H\(_{18}\): C, 81.0; H, 9.5.

Cholesteryl acetate, m.p. and mixed m.p. with an authentic specimen, 115°; [\(\alpha\])\(_D\) +43.5°; yield 85%.

36-Hydroxy-20-\(\alpha\)-methyl-pregn-5-ene (I, \(R = CH_3\)).—A solution of 2.0 g. of the acetate (I, \(R = CH_3\)) in 10 ml. of


Trialkyl Phosphites with Thiyl and Alkoxy Radicals

BY CHEVES WALLING AND ROBERT RABINOWITZ

Trialkyl Phosphite-Mercaptan Reactions.- 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 trialklyphosphorothionates 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 reported a remarkable reaction occurring between trialkyl phosphites and mercaptans at elevated temperatures or in the presence of light.

\[ RSH + P(\text{OE})_3 \rightarrow RH + SP(\text{OE})_3 \] (1)

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

\[ RSSR + P(\text{OE})_3 \rightarrow RSR + SP(\text{OE})_3 \] (2)

and proposed that both involve radical chains with the propagation steps

\[ R \cdots + P(\text{OE})_3 \rightarrow R \cdots + P(\text{OE})_3 \] (3)

\[ R \cdots + P(\text{OE})_3 \rightarrow R \cdots + SP(\text{OE})_3 \] (4)

\[ R^* + HSR \rightarrow RH \rightarrow RS^* \] (5a)

or

\[ R^* + RSSR \rightarrow RSR + RS^* \] (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, 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) 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 40–50% efficient. 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 transfer constants of styrene with n-alkyl mercaptans being approximately 20 and with a variety of dialkyl disulfides, 0.005–0.03. Nevertheless it seemed possible that reaction 2 could be realized...