588. *The Reactivity of Organophosphorus Compounds. Part V.*[1] *The Reaction of Trichloromethyl Radicals with Trialkyl Phosphites.*

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From a knowledge of the reactions of benzyl and ββ-dimethylphenethyl radicals, evidence is produced in favour of the radical-induced reaction of carbon tetrachloride with trialkyl phosphites to give dialkyl trichloromethylphosphonates proceeding by a radical-chain reaction involving $[(RO)_3P{\cdot}CCl_3]^+Cl^-$ rather than by decomposition of the phosphoranyl radical $(RO)_3\dot{P}{\cdot}CCl_3$. Evidence concerning the reactivity of phosphoranyl radicals is presented and discussed.

Kamai and Egorava [2] first investigated the reaction between carbon tetrachloride and triethyl phosphite and isolated diethyl trichloromethylphosphonate (II; R = Et) and later [3] Kamai and Kharrasova described it as a radical-chain process. Griffin [4] confirmed the radical nature of this reaction and that with bromotrichloromethane by observing acceleration in the presence of dibenzoyl peroxide and ultraviolet light, findings which have been confirmed in this investigation. On this basis alternative reaction schemes can be formulated.

$$\text{(A)}\left\{\begin{array}{l} {\cdot}CCl_3 + (RO)_3P \longrightarrow (RO)_3\dot{P}{\cdot}CCl_3 \text{ (I)} \\ (RO)_3\dot{P}{\cdot}CCl_3 + CCl_4 \longrightarrow [(RO)_3P{\cdot}CCl_3]^+Cl^- + {\cdot}CCl_3 \\ [(RO)_3P{\cdot}CCl_3]^+Cl^- \longrightarrow (RO)_2P(O){\cdot}CCl_3 \text{ (II)} + RCl \end{array}\right.$$

$$\text{(B)}\left\{\begin{array}{l} {\cdot}CCl_3 + (RO)_3P \longrightarrow (RO)_3\dot{P}{\cdot}CCl_3 \longrightarrow (RO)_2P(O){\cdot}CCl_3 \text{ (II)} + R{\cdot} \\ R{\cdot} + CCl_4 \longrightarrow RCl + {\cdot}CCl_3 \end{array}\right.$$

Scheme A involves chain propagation by the reaction of the phosphoranyl radical (I) with carbon tetrachloride to give a phosphonium salt and a free trichloromethyl radical, the former then undergoing nucleophilic dealkylation to give the observed products and the latter continuing the chain by reaction with another molecule of trialkyl phosphite. Scheme B involves decomposition of the intermediate radical (I) into the trichloromethylphosphonate (II) and an alkyl radical which then continues the chain by attack on the solvent.

Unequivocal evidence in favour of either mechanism has hitherto been lacking. Griffin [4] favours scheme A but, as is admitted, without sufficient evidence. Walling and his co-workers,[5] on the other hand, support scheme B, largely by analogy with their work on a different reaction, that of trialkyl phosphites with thiols. For scheme B to be operative, it is essential that the radical R· should be capable of continuing the chain by attacking carbon tetrachloride. By suitable choice of the initial phosphite and thus of the radical R·, it was our intention to distinguish between the mechanisms.

It is well known [6] that the ββ-dimethylphenethyl radical, $Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}$, when generated in solution, rearranges in part to the more stable αα-dimethylphenethyl radical, $Ph{\cdot}CH_2{\cdot}CMe_2{\cdot}$, and that both radicals can be detected by the products of their dimerisation and disproportionation, *i.e.*, $Ph{\cdot}CMe_3$, $Ph{\cdot}CH_2{\cdot}CHMe_2$, $Ph{\cdot}CH{:}CMe_2$, $Ph{\cdot}CH_2{\cdot}CMe{:}CH_2$, etc. Further, by analogy with related radicals, both radicals would be expected to attack carbon tetrachloride to give the corresponding chlorides. ββ-Dimethylphenethyl diethyl

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[1] Part IV, Cadogan, preceding paper.

[2] Kamai and Egorava, *J. Gen. Chem.* (*U.S.S.R.*), 1946, **16**, 1521.

[3] Kamai and Kharrasova, *Zhur. obshchei Khim.*, 1957, **27**, 953.

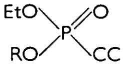
[4] Griffin, *Chem. and Ind.*, 1958, 415; Amer. Chem. Soc. 135th Meeting, 1959, Abs., p. 690.

[5] Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243; Walling, Basedow, and Savas, *ibid.*, 1960, **82**, 2181.

[6] Urry and Kharasch, *J. Amer. Chem. Soc.*, 1944, **66**, 1438; Winstein and Seubold, *ibid.*, 1947, **69**, 2916; Smith and Anderson, *ibid.*, 1960, **82**, 656.

phosphite (III; R = $Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}$) has now been prepared and subjected to peroxide-catalysed reaction with carbon tetrachloride, to give the trichloromethylphosphonate (IV; R = $Ph{\cdot}CMe_2{\cdot}CH_2$). No ββ-dimethylphenethyl chloride or products of rearrangement of the derived radical were detected despite a rigorous search with gas–liquid chromatography.

(III) $(EtO)_2P{\cdot}OR$


(IV)

Strong evidence is thus presented in favour of scheme A. If the reaction had proceeded by way of scheme B, then elimination of both ethyl and ββ-dimethylphenethyl radicals would have probably occurred, since the energy requirements would be similar in each case. Scheme A involves nucleophilic attack (probably S_N2) on the alkyl group by chloride ion and it is known[7] that ββ-dimethylphenethyl compounds will not enter into such reactions whereas ethyl groups readily do; hence exclusive elimination of ethyl chloride, with retention of the dimethylphenethyl group in the phosphorus compound, as observed, is predictable on the basis of scheme A.

It was not found possible to obtain an analytically pure specimen of ethyl ββ-dimethylphenethyl trichloromethylphosphonate from the above reaction. Decomposition readily occurred on heating, to give a mixture (*ca.* 1 : 1) of 2-methyl-1- and 2-methyl-3-phenylpropene. This mixture was similar to that obtained by Heck and Winstein[7] on decomposition of ββ-dimethylphenethyl benzoate, which proceeded by way of the carbonium ion:

$$Ph{\cdot}CMe_2{\cdot}CH_2^+ \longrightarrow Ph{\cdot}CH_2{\cdot}CMe_2^+ \xrightarrow{Ph{\cdot}CO_2^-} Ph{\cdot}CH{:}CMe_2 + Ph{\cdot}CH_2{\cdot}CMe{:}CH_2$$

A similar mechanism probably operates in our reaction.

The results of the peroxide- and light-catalysed reaction of carbon tetrachloride with benzyl diethyl phosphite (III; R = $Ph{\cdot}CH_2{\cdot}$) can also be rationalised by scheme A which predicts, as a result of the extreme lability of benzyl groups towards halide ions,[8] exclusive debenzylation to give diethyl trichloromethylphosphonate (II; R = Et) and benzyl chloride, which were observed. Scheme B alternatively requires the elimination of resonance-stabilised benzyl radicals, some of which would be expected to dimerise to bibenzyl, which was not detected despite a careful search again by gas–liquid chromatography. Such dimerisation constitutes a chain-ending step and the reaction would therefore stop. In this case, however, it could be argued that scheme B was in fact operative and the benzyl radicals, formed exclusively because of the resultant resonance-stabilisation, had reacted entirely by abstraction of chlorine atoms rather than by dimerisation. That this was not the case is shown by the results of the decomposition of di-(9-benzyl-9-fluorenyl) peroxide in carbon tetrachloride and of di-t-butyl peroxide in a mixture of toluene and carbon tetrachloride. The former peroxide has recently been shown[9] to be a good source of free benzyl radicals, as is the decomposition of di-t-butyl peroxide in toluene.[10] These decompositions were carried out under conditions likely to give a concentration of benzyl radicals similar to that expected in the peroxide-catalysed reaction of carbon tetrachloride and benzyl diethyl phosphite if scheme B operates, and in each case benzyl chloride and bibenzyl were isolated. The absence of bibenzyl from the products of the reaction with benzyl diethyl phosphite therefore supports scheme A. It is noteworthy that benzyl chloride is formed in the reactions of di-(9-benzyl-9-fluorenyl) peroxide and of di-t-butyl peroxide and toluene in carbon tetrachloride, thus showing that a benzyl radical will abstract chlorine from carbon tetrachloride, which is at variance with the conclusions of Kharasch, Kane, and Brown[11] and of Leffler and Bartlett.[12]

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[7] Heck and Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 3432.

[8] Clarke and Todd, *J.*, 1950, 2030.

[9] Cadogan, Hey, and Sanderson, *J.*, 1960, 3203.

[10] Beckwith and Waters, *J.*, 1957, 1001; Farmer and Moore, *J.*, 1951, 131.

[11] Kharasch, Kane, and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 1622.

[12] Bartlett and Leffler, *J. Amer. Chem. Soc.*, 1950, **72**, 3030.

It is therefore concluded that the free-radical-induced reaction of carbon tetrachloride with trialkyl phosphites proceeds by a radical-chain mechanism involving $[(RO)_3P\cdot CCl_3]^+Cl^-$ rather than by decomposition of the phosphoranyl radical $(RO)_3\dot{P}\cdot CCl_3$. This is contrary to the suggestion of Walling *et al.*[5] who have proposed the following mechanism for the formation of trialkyl phosphorothionates in the reaction of trialkyl phosphites with thiols:

$$\text{(C)}\left\{\begin{array}{l} (RO)_3P + R'S\cdot \longrightarrow (RO)_3\dot{P}\cdot SR' \longrightarrow (RO)_3PS + R'\cdot \\ R'\cdot + R'SH \longrightarrow R'H + R'S\cdot \end{array}\right.$$

This mechanism corresponds to scheme B above, which Walling favours for the reaction of carbon tetrachloride and trialkyl phosphites. It is now clear that different mechanisms operate in the reactions of phosphites with trichloromethyl radicals on the one hand and with thiyl radicals on the other. This is clearly a function of the properties of the two possible phosphoranyl radicals $(RO)_3\dot{P}\cdot CCl_3$ and $(RO)_3\dot{P}\cdot SR$. It could be argued that the thiophosphoranyl radical was intrinsically less stable than the trichloromethylphosphoranyl radical, thus providing a rationalisation of the difference. That this cannot be so follows from the results of the reaction, initiated by dibenzoyl peroxide, of triethyl phosphite with an equimolar mixture of carbon tetrachloride and butane-1-thiol, which gives diethyl trichloromethylphosphonate (22%), triethyl phosphorothionate (18%), and *S*-butyl diethyl phosphorothioate (60%). The formation of the first two products can be explained on the basis of simultaneous operation of schemes A and C. Much more significant is the formation of the thiolate, which indicates that the thiophosphoranyl radical can also behave like the trichloromethylphosphoranyl radical by readily abstracting a chlorine atom from carbon tetrachloride as follows:

$$\begin{array}{r l} (EtO)_3P + Bu^nS\cdot & \longrightarrow (EtO)_3\dot{P}\cdot SBu^n \\ (EtO)_3\dot{P}\cdot SBu^n + CCl_4 & \longrightarrow [(EtO)_3P\cdot SBu^n]^+Cl^- + \cdot CCl_3 \\ [(EtO)_3P\cdot SBu^n]^+Cl^- & \longrightarrow (EtO)_2P(O)\cdot SBu^n + EtCl \end{array}$$

The thiophosphoranyl radical can also therefore behave according to scheme A, and incidentally provides a new method of preparation of phosphorothiolates. The possibility that the trichloromethylphosphoranyl radical might also react by scheme B under circumstances depending on a suitable choice of substituents cannot be entirely discounted, however, as a result of these experiments.

The propensity of a phosphoranyl radical to abstract a chlorine atom, and thus to react by way of an Arbuzov-type intermediate (scheme A), is probably a result of the favourable energetics of formation of this intermediate. On the other hand, abstraction of a hydrogen atom would presumably give rise to an unstable compound, so decomposition of the phosphoranyl radical is the favoured process. This reluctance to abstract hydrogen is further exemplified by the radical-induced reaction [4] of chloroform with triethyl phosphite to give diethyl dichloromethylphosphonate, thus:

$$\begin{array}{l} \cdot CHCl_2 + (EtO)_3P \longrightarrow (EtO)_3\dot{P}\cdot CHCl_2 \\ (EtO)_3\dot{P}\cdot CHCl_2 + CHCl_3 \longrightarrow [(EtO)_3P\cdot CHCl_2]^+Cl^- + \cdot CHCl_2 \longrightarrow (EtO)_2P(O)\cdot CHCl_2 + EtCl \end{array}$$

whereas it is established [13] that radical-abstraction of hydrogen is usually the preferred reaction, the greater resonance energy of the trichloromethyl radical formed apparently overcoming the greater strength of the C–H bond involved. It is therefore clear that scheme A also obtains in the reaction of chloroform with triethyl phosphite, because scheme B calls for attack on chloroform by an ethyl radical which would extract ***hydrogen*** to give first a trichloromethyl radical and then diethyl trichloromethylphosphonate instead of the observed dichloromethyl compound.

Finally, it should be noted that the above discussion of mechanism is pertinent only

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[13] Hey and Peters, *J.*, 1960, 79; Walling, " Free Radicals in Solution," Wiley & Sons, 1957, p. 255.

to the cases where peroxide and light initiation is known to occur, since experiments with purified triethyl phosphite and carbon tetrachloride in darkened flasks show that formation of diethyl trichloromethylphosphonate is appreciably fast in the absence of peroxidic initiators at 80°, although not as fast as the reaction induced by dibenzoyl peroxide or ultraviolet light. In the formei case the possibility that the peroxide is being partially removed in an ionic reaction with phosphite is a complication which cannot be ignored, however.

EXPERIMENTAL

Gas–liquid chromatography was carried out with a Perkin–Elmer " Fraktometer," model 116, fitted with a high-sensitivity dual thermal-conductivity detector which normally gives a response proportional to molecular weight. This response was tested wherever possible by analysis of mixtures of known composition and was satisfactory.

Benzyl diethyl phosphite, prepared by the method of Hoffman, Ess, and Usinger,[14] who reported b. p. 85—88°/1 mm., n_D^{25} 1·4905, had b. p. 70°/0·1 mm., n_D^{25} 1·4900 (Found: C, 57·9; H, 7·2. Calc. for $C_{11}H_{17}O_3P$: C, 57·9; H, 7·5%).

Preparation of ββ-*Dimethylphenethyl Diethyl Phosphite*.—ββ-Dimethylphenethyl chloride, b. p. 101°/12 mm., n_D^{21} 1·5241, prepared by the method of Smith and Sellas,[15] who reported b. p. 97—98°/10 mm., n_D^{20} 1·5250, was converted into the alcohol as follows: oxygen was passed (3 hr.) through a solution in ether of the Grignard reagent from ββ-dimethylphenethyl chloride (250 g.) at 0°. The mixture was poured into dilute sulphuric acid (2 l.), and the ether solution was washed with water and dried ($MgSO_4$). Distillation gave the alcohol, b. p. 110—112°/12 mm., n_D^{24} 1·5248 (102 g.). The infrared spectrum showed the absence of the chloride. Whitmore, Weisberger, and Shabica [16] reported b. p. 131°/30 mm., n_D^{20} 1·5261.

The alcohol (25 g.) and triethyl phosphite (56·5 g., 1 mol.) were kept at 140° for 4½ hr. and the ethanol (80%) formed was removed through a still-head. The residue, on distillation (twice), gave ββ-*dimethylphenethyl diethyl phosphite* (27 g., 61%), b. p. 98—102°/0·1 mm., n_D^{25} 1·4892 (Found: C, 62·3; H, 8·9. $C_{16}H_{23}O_3P$ requires C, 62·3; H, 8·6%).

Attempts to prepare tris-(ββ-dimethylphenethyl) phosphite by standard reactions gave oils which readily decomposed when heated.

Reaction of Benzyl Diethyl Phosphite with Carbon Tetrachloride in the Presence of Dibenzoyl Peroxide.—Benzyl diethyl phosphite (5·3 g.) and dibenzoyl peroxide (0·3 g., 0·05 mol.) in carbon tetrachloride (15 g.) were boiled under reflux for 18 hr. After removal of the solvent the residue was distilled at 13 mm., giving fractions: (*a*) benzyl chloride, b. p. 40—80°, $n_D^{23.5}$ 1·5240 (1·5 g.), identified by comparison of infrared spectrum and of gas–liquid chromatographic retention time with those of authentic material, (*b*) b. p. 80—90°, $n_D^{23.5}$ 1·5070 (0·8 g.), (*c*) b. p. 90—110°, $n_D^{23.5}$ 1·4770 (0·95 g.), and (*d*) diethyl trichloromethylphosphonate, b. p. 120—130°, $n_D^{23.5}$ 1·4620 (4·2 g.), identified by comparison of infrared spectrum and gas–liquid chromatographic retention time with those of authentic material prepared as described below. Fractions (*b*) and (*c*) were similarly shown to be mixtures of benzyl chloride and diethyl trichloromethylphosphonate. The ester formed 28% of fraction (*b*) and 75% of fraction (*c*). Thus were obtained benzyl chloride (0·86 mol.) and diethyl trichloromethylphosphonate (0·83 mol.). Gas–liquid chromatography of the product before the distillation showed the absence of bibenzyl.

Reaction of ββ-*Dimethylphenethyl Diethyl Phosphite with Carbon Tetrachloride in the Presence of Dibenzoyl Peroxide*.—Dibenzoyl peroxide (0·44 g.) and the ester (10 g.) in carbon tetrachloride (24 g.) were boiled under reflux for 18 hr. After removal of the solvent, the residue was shown by gas–liquid chromatography to contain no ββ-dimethylphenethyl chloride. A portion (50%) of the residue was distilled at 12 mm., decomposition occurring and giving an unsaturated oil, b. p. 90—105°/12 mm., n_D^{20} 1·5208 (2·8 g.), ε 7499 at 244 mμ. Heck and Winstein [7] obtained a product having almost identical properties (n_D^{25} 1·5208, ε 6912 at 244 mμ) from the unimolecular decomposition of ββ-dimethylphenethyl benzoate which proceeded by way of the carbonium ion, and was identified as an equimolar mixture of 2-methyl-1- (n_D^{25} 1·5364; ε 14,000 at 244 mμ) and 2-methyl-3-phenylpropene (n_D^{25} 1·5057; ε 77). The infrared spectrum of our

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[14] Hoffmann, Ess, and Usinger, *J. Amer. Chem. Soc.*, 1956, **78**, 5817.

[15] Smith and Sellas, *Org. Synth.*, 1952, **32**, 90.

[16] Whitmore, Weisberger, and Shabica, *J. Amer. Chem. Soc.*, 1943, **65**, 1469.

product was compatible with a mixture of this type, the composition of which was calculated from a refractive index plot (2-methyl-1-phenylpropene, 53%) and from the absorption at 244 mμ (same ingredient, 56%). This was further confirmed by hydrogenation, the amount of hydrogen corresponding to such a mixture being taken up.

Distillation of a further portion of the residue was attempted at 10^{-4} mm. It gave an oil, b. p. 110°, n_D^{24} 1·5080. Some decomposition occurred even under these conditions and the product is formulated as impure ββ-dimethylphenethyl ethyl trichloromethylphosphonate (Found: C, 47·5; H, 5·5. Calc. for $C_{13}H_{18}Cl_3O_3P$: C, 43·5; H, 5·0%).

Reaction of Triethyl Phosphite with Carbon Tetrachloride.—(i) *In the presence of dibenzoyl peroxide.* Triethyl phosphite (5 g.) and the peroxide (0·05 mol.) in carbon tetrachloride (15 g.) were boiled under reflux for 18 hr. Distillation gave diethyl trichloromethylphosphonate (6·85 g., b. p. 128°/14 mm., n_D^{20} 1·4620. Griffin [4] reported b. p. 137—138°/17 mm., n_D^{20} 1·4612.

(ii) *In the absence of peroxide.* In a similar experiment, in which was used carbon tetrachloride that had been passed through alumina to remove any peroxidic material, the reaction was carried out in the dark and without dibenzoyl peroxide. Diethyl trichloromethylphosphonate (6·94 g., n_D^{25} 1·4597, was again formed.

Triphenyl phosphite did not react with carbon tetrachloride or bromotrichloromethane under either of the above sets of conditions.

Rate of Disappearance of Triethyl Phosphite in its Reactions with Carbon Tetrachloride.—The rate of disappearance of triethyl phosphite on reaction with carbon tetrachloride at 80° was determined by following the reaction by gas–liquid chromatography. Portions (1 ml.) of a standard solution of the ester (8·35 g.) in carbon tetrachloride (24·5 ml.) were immersed in sealed tubes in a thermostat at 80°, removed at intervals (10 min.), and immersed in an ice-salt bath. The amounts of triethyl phosphite remaining were determined by chromatography. The first-order rate constant was found to be $2{\cdot}2 \times 10^{-4}$ sec.$^{-1}$.

The experiment was repeated in the presence of added dibenzoyl peroxide (0·05 mol.), the rate constant being $3{\cdot}5 \times 10^{-4}$ sec.$^{-1}$.

Reaction of Triethyl Phosphite with Carbon Tetrachloride in Ultraviolet Light.—A mixture of the phosphite (5 ml.) and carbon tetrachloride (15 ml.) was degassed by bubbling nitrogen through the solution and then irradiated in a quartz flask under nitrogen from an "Hanovia" source ($\lambda_{min.}$ 2500 Å) at room temperature for 1 hr. Distillation gave diethyl trichloromethylphosphonate (70%).

Triethyl phosphite and carbon tetrachloride had not reacted after 7 hr. in the dark at room temperature.

Decomposition of Di-t-butyl Peroxide in Toluene in the Presence of Carbon Tetrachloride.—Di-t-butyl peroxide (3·7 g.) in toluene (18·4 g.) and carbon tetrachloride (31·1 g.) was heated in a sealed tube at 130° for 48 hr. After removal of the solvents distillation gave fractions (*a*) b. p. 50—85°/13 mm. (2·8 g.) and (*b*) b. p. 50—75°/0·1 mm. (1·2 g.). Fraction (*a*) was shown by gas–liquid chromatography to be largely benzyl chloride (0·66 mole per mole of peroxide) together with an unidentified component. Fraction (*b*) was similarly shown to be bibenzyl (0·12 mol.) with the same unidentified component. Treatment of fraction (*b*) with light petroleum (b. p. 40—60°) gave bibenzyl, m. p. and mixed m. p. 48—50°. The unidentified component may be 2,2,2-trichloroethylbenzene.

Decomposition of Di-(9-benzyl-9-fluorenyl) Peroxide in Carbon Tetrachloride.—The peroxide (0·5 g.), m. p. 170—170·5°, prepared as described by Cadogan, Hey, and Sanderson,[9] was heated in carbon tetrachloride (2·2 ml.) and benzene (2 ml.) in a sealed tube at 130° for 48 hr. After removal of the solvents the residue was examined by gas–liquid chromatography. Bibenzyl and benzyl chloride (0·25 : 1 mol.) were identified by comparison with authentic mixtures. Also present was the unidentified compound found in the previous experiment.

Dibenzoyl Peroxide-initiated Reaction of Triethyl Phosphite with Carbon Tetrachloride and Butane-1-thiol.—A mixture of triethyl phosphite (8·3 g., 0·05 mol.), carbon tetrachloride (15·4 g., 0·1 mol.), butane-1-thiol (9·0 g., 0·1 mol.), and dibenzoyl peroxide (0·61 g., 0·0025 mol.) was refluxed overnight. After removal of the solvents the residue (10·8 g.) was analysed by gas–liquid chromatography in a 1-m. column packed with "Apiezon L" on Celite (545). With a column temperature of 166°, the following components, with relative retention times given in parentheses, were identified by comparison with mixtures of known composition: triethyl phosphorothionate (18%; 1·00), diethyl trichloromethylphosphonate (22%; 2·95), and *S*-butyl diethyl phosphorothioate (60%; 5·29).

Reaction of Benzyl Diethyl Phosphite and Carbon Tetrachloride in Ultraviolet Light.—Irradiation of the phosphite (3·18 g.) in carbon tetrachloride (15 ml.) under nitrogen at room temperature for 4 hr., followed by fractionation, gave benzyl chloride (0·70 g.), b. p. 90°/17 mm., n_D^{25} 1·4995, and diethyl trichloromethylphosphonate (1·27 g.), b. p. 110°/17 mm., n_D^{25} 1·4670, and left a residue (1·8 g.). The nature of these products was confirmed by infrared spectroscopy.

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