The Reaction of Triphenylmethyl Halides with Tributylphosphine and Tributylamine in Apolar Solvents†

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Triphenylmethyl bromide (**1a**) and chloride (**1b**) react with tributylphosphine and tributylamine in aromatic hydrocarbons by single electron transfer. The triphenylmethyl radicals produced (which may be detected by e.s.r. spectroscopy) abstract hydrogen from the solvent or the radical cations of the reagents to give triphenylmethane (**1c**), and are trapped by oxygen to give triphenylmethylperoxy radicals and subsequently [*via* triphenylmethyl hydroperoxide (**1e**)] benzophenone, triphenylmethanol (**1d**), and phenol. Tributylphosphine and tributylamine may act as hydrogen donors in the hydrogen-transfer processes involved in the formation of these oxygenation products. The halides (**1a**, **b**) and tributylphosphine furnish, in the absence of oxygen, in addition to triphenylmethane (**1c**) the *tele* substitution products (**2a**) and (**2b**), respectively. There is some evidence that the phosphonium salt (**2a**) is formed by an S_{ET}' process, *i.e.* out-of-cage recombination of triphenylmethyl radicals and tributylphosphine radical cations or tributylphosphine.

Further to our studies[1] of single-electron-transfer (SET) initiated thermal reactions of triarylmethyl halides and related substances with nucleophiles, the reactions of triphenylmethyl-bromide (**1a**) and -chloride (**1b**) with tributylphosphine and tributylamine in aromatic hydrocarbons have now been studied. While anionic *O*-,[2] *S*-,[3] and *N*-,[2c] as well as neutral *N*-nucleophiles[1,4] are known to be able to transfer, under appropriate conditions, single electrons to triarylmethyl and related halides, SET from *P*-nucleophiles to such halides has, to our knowledge, never been described.

Results

When heated with tributylphosphine (1.1 mol equiv.) in dry cumene for 6.5 h to 153 °C under argon, bromide (**1a**) gave 66–82% of the reduction product (**1c**), along with *ca.* 28% of the *tele* substitution product (**2a**) and some ($\leqslant 3\%$) of the hydrolysis product (**1d**), probably formed during work-up from the unchanged starting bromide. The chloride (**1b**) reacted similarly but at a much lower rate. After 50 h (under otherwise identical conditions) *ca.* half of the starting compound was still unchanged [as shown by the isolation of 43% of the hydrolysis product (**1d**)], and only after being heated for *ca.* 150 h were the reduction product (**1c**) (53%) and of the *tele* substitution product (**2b**) (32%) isolated.

When heated with tributylphosphine (1.1 mol equiv.) in dry t-butylbenzene for 6.5–16 h to 153 or 169 °C under oxygen, bromide (**1a**) gave benzophenone (83–90%) as the main product. Triphenylmethanol (**1d**) (8–11%) was also produced, part of which may have formed (during work-up) from the unchanged starting bromide (see below); phenol (17–22%, isolated in the form of its benzoate) was also produced. Chloride (**1b**), when heated for 14 h to 153 °C under otherwise identical conditions, gave the same products (in 68, 12, and 3% yields, respectively).

The reactions of halides (**1a**) and (**1b**) with tributylamine were rather similar. Thus, when the reactions were carried out at 153 °C under argon, triphenylmethane (**1c**) was the only product formed in appreciable amounts (60–74%) irrespective of which of the two halides was used, whether 1 or 2 mol equiv. of tributylamine was added, and irrespective of whether cumene or t-butylbenzene was used as solvent. (In addition, one or more unidentified products were isolated in trace amounts from several of the reaction mixtures.) At 80 °C bromide (**1a**) reacted considerably more slowly and the yield of (**1c**) was substantially lower (*ca.* 45%); triphenylmethanol (**1d**) was isolated as a further product (34 and 13% after a reaction time of 120 and 180 h, respectively). In contrast with the reactions with tributylphosphine, no *tele* substitution products (**2c**) were obtained with tributylamine, nor was the dimeric product (**3a**) detected in any of the resulting mixtures.

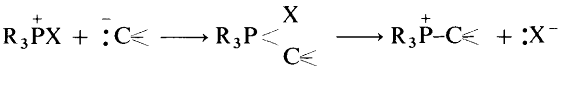
When refluxed with tributylamine (1 mol equiv.) in dry t-butylbenzene for 7–19 h under oxygen, neither of the halides gave triphenylmethane (**1c**); instead, benzophenone (60–76%) and phenol (22–42%) were isolated as the main products, along with some triphenylmethanol (**1d**).

Discussion

Reactions with Tributylphosphine.—Phosphines react with alkyl halides as nucleophiles, attacking either the α-carbon or the halogen atom [equations (1) and (2)].[5] For the attack at

$$R_3P\!: + \geqslant C{-}X \longrightarrow R_3\overset{+}{P}{-}C\leqslant \; + :X^- \tag{1}$$

$$R_3P\!: + X{-}C\leqslant \longrightarrow R_3\overset{+}{P}X + \overset{-}{:}C{-} \tag{2}$$



$$R_3\overset{+}{P}X + \overset{-}{:}C\leqslant \longrightarrow R_3P{<}\begin{matrix}X\\ C\leqslant\end{matrix} \longrightarrow R_3\overset{+}{P}{-}C\leqslant \; + :X^- \tag{3}$$

(intermediate
or TS)

$$\overset{-}{:}C\leqslant \xrightarrow{+H^+} H{-}C\leqslant \tag{4}$$

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† Single electron transfer initiated thermal reactions of arylmethyl halides, part 14; for part 13, see ref. 1.

Ph_2CRX
(1)
a; $R = Ph, X = Br$
b; $R = Ph, X = Cl$
c; $R = Ph, X = H$
d; $R = Ph, X = OH$
e; $R = Ph, X = OOH$
f; $R = Ph, X = OOCPh_3$
g; $R = CONMe_2, X = Br$
h; $R = CONMe_2, X = H$

$4\text{-}(R_3\overset{+}{Q})C_6H_4CHPh_2X^-$
(2)
a; $R = Bu, Q = P, X = Br$
b; $R = Bu, Q = P, X = Cl$
c; $R = Bu, Q = N, X = Br, Cl$
d; $R = Ph, Q = P, X = Cl$
e; $R = Ph, Q = P, X = PF_6$
f; $R = Ph, Q = P, X = BF_4$

$4\text{-}(Ph_2RC)C_6H_4CHPhR$
(3)
a; $R = Ph$
b; $R = CONMe_2$

halogen to be feasible, the resulting carbanion must be stabilized either by inductive effects (*e.g.* as in the case of the trichloro- and tribromo-methanide anion; this is the initial step of the Appel reaction[6]) or by resonance (*e.g.* as in the case of α-halo ketones[7]). The carbanion may subsequently attack the halophosphonium cation to give, either in a concerted manner or in two steps [equation (3)], the same phosphonium salt as is obtained directly according to reaction (1),[5] or it may abstract a proton either from the solvent or from a reagent added during work-up to form the product of reductive dehalogenation [equation (4)].[*]

When allowed to react with tributylphosphine in cumene at elevated temperatures under argon, both triphenylmethyl halides (**1a**) and (**1b**) were smoothly converted into their common reductive dehalogenation product triphenylmethane (**1c**). Although the triphenylmethanide anion resulting from attack by the phosphine at the halogen atom [equation (2)] would be stabilized by resonance, *i.e.* the reductive dehalogenation could, in principle, take place *via* reactions (2) and (4), a further mechanism has to be considered for this reaction. According to this mechanism, the reaction would be initiated by an SET from the phosphine to the halide, leading either *via* the radical anion of the halide or by dissociative electron transfer to the formation of the triphenylmethyl radical [equation (6)][†]

$$\begin{array}{lc} & Ph_3CX^{-\bullet} + Bu_3P^{+\bullet} \\ Ph_3CX + Bu_3P & \downarrow \\ (\mathbf{1a,b}) & Ph_3C\bullet + X^- + Bu_3P^{+\bullet} \end{array} \qquad (6)$$

which, subsequently, would abstract a hydrogen atom either from the solvent cumene[‡] or from the tributylphosphine radical cation to give the reductive dehalogenation product (**1c**) [equations (7*a*) and (7*b*)]. While, in principle, tributylphosphine could also serve as the hydrogen donor,[‡] reaction (7*c*) probably does not contribute significantly to the formation of (**1c**) in the present case because the phosphine used is in slight excess.

$$\begin{array}{l} Ph_3C\bullet + Me_2CHPh \longrightarrow Ph_3CH + Me_2\dot{C}Ph \qquad (7a) \\ \qquad\qquad\qquad\qquad\quad (\mathbf{1c}) \qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{products} \end{array}$$

$$\begin{array}{l} Ph_3C\bullet + Bu_3P^{+\bullet} \longrightarrow Ph_3CH + PrCH{=}P^+Bu_2 \qquad (7b) \\ \qquad\qquad\qquad\qquad\quad (\mathbf{1c}) \qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{products} \end{array}$$

$$\begin{array}{l} Ph_3C\bullet + Bu_3P \longrightarrow Ph_3CH + Pr\dot{C}HPBu_2 \qquad (7c) \\ \qquad\qquad\qquad\qquad\quad (\mathbf{1c}) \qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{products} \end{array}$$

The SET initiated mechanism for the conversion of (**1a**) and (**1b**) into (**1c**) appeared feasible since (*i*) SET to triphenylmethyl (and related) halides had been observed previously,[2–4] (*ii*) the triphenylmethyl radical is, similarly to the corresponding carbanion, stabilized by resonance, and (*iii*) formation of the triphenylmethanide anion in aromatic hydrocarbons appears, because of the low polarity of the solvent, less likely than formation of the triphenylmethyl radical.

The operation of the SET initiated mechanism of the reductive dehalogenation of halides (**1a**) and (**1b**) by tributylphosphine was proved by e.s.r. spectroscopy and trapping studies. Mixtures of triphenylmethyl bromide (**1a**), tributylphosphine, and cumene (of the same composition as used in the thermolyses) sealed under argon exhibited, even at room temperature, the characteristic e.s.r. spectrum[2c,3b] of the triphenylmethyl radical.[§] This observation, by itself, does not prove that triphenylmethyl radicals are actually the intermediates of the reductive dehalogenation. However, the reaction of the halides (**1a**) and (**1b**) with tributylphosphine could be diverted to yield various oxygenation products rather than triphenylmethane (**1c**) by running it at elevated temperatures in t-butylbenzene (which is known to have extremely poor hydrogen-atom donating ability) under oxygen. This strongly suggests the intermediacy of triphenylmethyl radicals which, in the absence of oxygen, are converted into triphenylmethane (**1c**) by hydrogen abstraction but, in the presence of oxygen, are trapped to yield, ultimately, the oxygenation products.[¶] Control experiments have shown that triphenylmethane (**1c**) is, under identical conditions, oxidized by molecular oxygen both in the presence and absence of tributylphosphine to a negligible extent only. Therefore, triphenylmethane (**1c**) is not an intermediate of the tributylphosphine-mediated conversion of triphenylmethyl halides (**1a**) and (**1b**) by molecular oxygen into their various oxidation products (see below).

On the other hand, the observation that refluxing of bromide

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[*] Trialkyl phosphites and organic halides react analogously but the product of nucleophilic attack at carbon is unstable and becomes stabilized by loss of an *O*-alkyl group [Arbuzov reaction,[8] equation (5)].

$$(RO)_3P + \gt C{-}X \longrightarrow \overset{-}{X}\!: + R{-}O{-}\overset{+}{P}(OR)_2{-}C\lt \longrightarrow XR + O{=}P(OR)_2{-}C\lt \qquad (5)$$

The formation of 2,3,5,6-tetrachloropyridine from 2,3,4,5,6-pentachloropyridine and trialkyl phosphites, on the other hand, has been explained by assuming the successive operation of equations (2) and (4)[9] (with RO replacing the R groups).

[†] The fate of the resulting radical cations has not been studied. In addition to undergoing reaction (7*b*), the cations could react with the solvent cumene, see *e.g.* ref. 10.

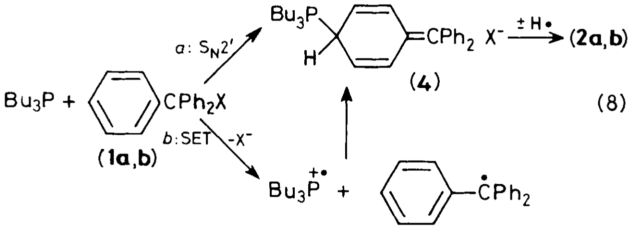
[‡] The dimer (**12**)[11] of triphenylmethyl (which easily dissociates thermally into triphenylmethyl radicals), when heated either with cumene or with tributylphosphine (or tributylamine) in t-butylbenzene under argon, was found to be partly converted into triphenylmethane (**1c**).

[§] Also mixtures of halide (**1a**), triphenylphosphine, and cumene or t-butylbenzene, sealed under argon, exhibited the e.s.r. spectrum of the triphenylmethyl radical.

[¶] Our observations do not rule out the simultaneous operation of the non-SET mechanism [equations (1)–(4)] for the formation of triphenylmethane, but they do establish the operation of the SET pathway [equations (6)–(7*c*)] for the formation of this product, either alone or in competition with the non-SET pathway. However, the high combined yields of triphenylmethanol (**1d**) and benzophenone (94–98%) in the reactions of the bromide (**1a**) and tributylphosphine in Bu^tOH under oxygen, appear to indicate that the contribution of the non-SET pathway is, at most, slight.

(**1a**) in t-butylbenzene for 16 h under oxygen in the absence of tributylphosphine resulted in the formation of 90% of benzophenone (while in the presence of the phosphine but under otherwise identical conditions 83–85% of benzophenone was obtained) demonstrates that, under these conditions, oxidation of bromide (**1a**) does not necessarily involve SET from the phosphine to the bromide. However, at the slightly lower temperature of 153 °C, oxidation of bromide (**1a**) is considerably faster in the presence of the phosphine [90% of benzophenone and 8% of triphenylmethanol (**1d**) were obtained within 6.5 h] than in its absence [*ca.* 50% unchanged bromide was present after 6.5 h]. The rate of oxidation of chloride (**1b**) was similarly enhanced by the addition of tributylphosphine. These observations indicate that, at least at or below 153 °C, the SET reaction of the phosphine with halides (**1a**) and (**1b**) is not completely suppressed because of consumption of the phosphine by its reaction with oxygen; and, therefore, that oxidation of the halides by molecular oxygen in the presence of tributylphosphine involves formation of triphenylmethyl radicals either *via* the halide radical anions or by dissociative electron transfer, and trapping of these radicals by oxygen.

The conversion of both halides, (**1a**) and (**1b**) into the reduction product (**1c**) is accompanied by their conversion into the *tele* substitution products (**2a**) and (**2b**),* respectively, both reactions being significantly slower for the chloride (**1b**) than for the bromide (**1a**). Since the reduction product (**1c**) is assumed to be formed by an SET initiated process, and SET to chlorides is known to be much less efficient than to the corresponding bromides,[2e,15] the observed trend of the rates of formation of this product is as expected. For the formation of the *tele* substitution products (**2a, b**) the picture is less clear because two mechanisms [equation (8), paths *a* and *b*] are conceivable and the chloride should, according to both mechanisms, react more slowly than the bromide. Path *a* is an S_N2' process. Because of steric crowding around the central carbon atoms of the starting halides one of their *para* carbon atoms is attacked by the phosphine (which is a manifestation of the well-known ambident reactivity of triphenylmethyl systems[16]) to yield the semibenzene-type intermediate (**4**) which, at the elevated reaction temperature, rearranges to form the final product. Because of the absence of a strong base and the low polarity of the solvent the final rearrangement is thought to take place by successive loss and uptake of a hydrogen atom, rather than by deprotonation–protonation. The SET initiated path *b* would lead, by reaction of the resulting triphenylmethyl radicals either with tributylphosphine radical cations or with tributylphosphine (with subsequent electron loss in the second case), *via* the same semibenzene (**4**) to the same products. For some evidence in favour of the operation of the latter process in the bromide series, see below.

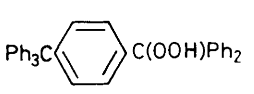


(8)

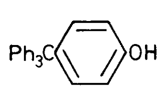
Benzophenone (main product), triphenylmethanol (**1d**), and phenol were obtained as the oxygenation products when the reaction of halides (**1a**) and (**1b**) with tributylphosphine were carried out in the presence of oxygen. Triphenylmethanol (**1d**) was shown not to be, in our experiments, an intermediate on the pathway leading to benzophenone and phenol because, when a solution of (**1d**) in t-butylbenzene was refluxed for 12 h in a stream of oxygen, 97% of unchanged starting material was recovered and, at best, only traces of benzophenone were detected. The formation of all oxygenation products may be rationalized by assuming that the triphenylmethyl radicals are trapped by molecular oxygen. Because of the high combined yields of benzophenone and triphenylmethanol (individual yields 83–90 and 8–11%, respectively) isolated in the reactions starting with bromide (**1a**), hardly any *tele* substitution product (**2a**) could have been formed. This appears to indicate that the *tele* substitution product (**2a**) is formed *via* the S_{ET}' process from bromide (**1a**) [equation (8), path *b*] with out-of-cage recombination of triphenylmethyl radicals and tributylphosphine radical cations.

The triphenylmethylperoxy radicals, resulting from the reaction of triphenylmethyl radicals with oxygen could either abstract a hydrogen atom to yield triphenylmethyl hydroperoxide (**1e**) (for the discussion of the origin of the hydrogen atom, see below), or react with a second triphenylmethyl radical to yield bis(triphenylmethyl) peroxide (**1f**). Thus, the hydroperoxide (**1e**) and the peroxide (**1f**) appear to be likely intermediates of the reactions leading to the oxygenation products.

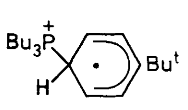
Triphenylmethyl hydroperoxide (**1e**) is known to yield mixtures of benzophenone, triphenylmethanol (**1d**), and phenol on thermolysis,[17] *i.e.* mixtures of the same compounds which were obtained by us from halides (**1a**) and (**1b**) with tributylphosphine in the presence of oxygen. An analogous thermal cleavage of diphenyl(4-triphenylmethylphenyl)methyl hydroperoxide (**5**) to give benzophenone and 4-(triphenylmethyl)phenol (**6**) has also been described.[18] In agreement herewith, thermolysis of triphenylmethyl hydroperoxide (**1e**)[19] in t-butylbenzene furnished mixtures of benzophenone, triphenylmethanol (**1d**), and phenol, the product ratios being strongly dependent on the reaction conditions. When *e.g.* hydroperoxide (**1e**) was refluxed for 4 h with t-butylbenzene under oxygen, 62% of benzophenone, 14% of triphenylmethanol (**1d**), and 7% of phenol were isolated;† these figures compare quite well with the amounts of the same products (68–90, 8–12, and 17–22%, respectively) isolated from the reactions of halides (**1a**) and (**1b**) with tributylphosphine in the presence of oxygen. We believe, therefore, that formation of the oxygenation products in the latter reactions involves the intermediacy of hydroperoxide (**1e**).



(**5**)



(**6**)



(**7**)

The O–O bonds of hydroperoxides are known[20] to be weak. Therefore, it appears reasonable to assume that the conversion of hydroperoxide (**1e**) into the oxygenation products is initiated by homolysis of the O–O bond [equation (9)]. An analogous initiation step has been assumed for the thermolysis of cumenyl hydroperoxide in hydrocarbon solvents by Kharasch and coworkers.[21] The triphenylmethoxy radical formed according to equation (9) either abstracts a hydrogen atom from a suitable source (see below) to give triphenylmethanol (**1d**) or rearranges by phenyl migration to yield the phenoxydiphenylmethyl

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* Related *tele* substitution products (**2d–f**) have been obtained by the reaction of triphenylphosphine with triphenylmethyl chloride (**1b**) [prepared either in a separate step or, *in situ*, from triphenylmethanol (**1d**) and conc. hydrochloric acid] in chloroform[12] and with triphenylcarbenium hexafluorophosphate, and tetrafluoroborate in CH_2Cl_2.[13] See also ref. 14.

† For the neat thermolysis of hydroperoxide (**1e**) and the decomposition of insufficiently purified samples of (**1e**) at room temperature, see ref. 19.

radical[19,21b,22] [equation (10)]. Recombination of the latter with a hydroxyl radical, formed according to equation (9), furnishes the phenyl hemiacetal of benzophenone which is subsequently cleaved to yield benzophenone and phenol [equation (11)]. A chain mechanism for the same transformation with reaction (9) as the initiation, and reactions (10) and (12) as the propagation steps may also be considered.

$$Ph_3CO\text{–}OH \underset{?}{\overset{\Delta}{\rightleftharpoons}} Ph_3CO\cdot + \cdot OH \qquad (9)$$

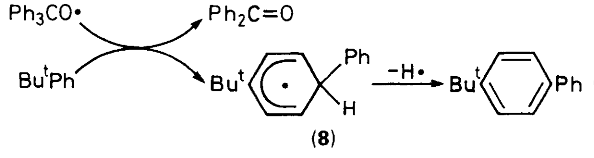
$$Ph_3CO\cdot \longrightarrow Ph_2\dot{C}(OPh) \qquad (10)$$

$$Ph_2\dot{C}(OPh) + \cdot OH \longrightarrow Ph_2C(OPh)(OH) \longrightarrow Ph_2C{=}O + PhOH \qquad (11)$$

$$Ph_3CO\text{–}OH + Ph_2\dot{C}(OPh) \longrightarrow Ph_3CO\cdot + Ph_2C(OPh)(OH) \qquad (12)$$

Tributylphosphine radical cations and the excess phosphine may be considered as the sources of hydrogen atoms [*cf.* equations (7b) and (7c)] for the conversion of triphenylmethylperoxy and triphenylmethoxy radicals into triphenylmethyl hydroperoxide (**1e**) and triphenylmethanol (**1d**), respectively.* The ability of tributylphosphine (and tributylamine) to transfer hydrogen atoms to triphenylmethoxy radicals is indicated by the increased yields of triphenylmethanol (**1d**) when the hydroperoxide (**1e**) is thermolysed in the presence of added tributylphosphine or tributylamine in t-butylbenzene at 153 °C under argon (26–50% in the absence of other reagents, 88 and 80% in the presence of 1 mol equiv. of added tributylphosphine and tributylamine, respectively).

The observation that the ratios of the phenol and benzophenone isolated both from the reactions of halides (**1a**) and (**1b**) with tributylphosphine in the presence of oxygen, and from the thermolyses of the hydroperoxide (**1e**) were invariably less than 0.5:1, although a 1:1 ratio would be expected according to equation (11), appears to indicate that the phenol resulting from reaction (11) could be an additional hydrogen donor† to the oxygen containing radicals in question. However, when solutions of phenol in t-butylbenzene were heated to 153 or 169 °C, 41–54% of the phenol were consumed within 6 h both under oxygen and under argon (and both in the absence and presence of added tributylphosphine or tributylamine) which suggests that additional pathways for the consumption of phenol are available, (the nature of these processes has not been studied). A further process which reduces the relative amount of phenol in the product mixture could be the direct conversion of triphenylmethoxy radicals into benzophenone, accompanied by conversion of an equivalent amount of the solvent into 4-(t-butyl)biphenyl [equation (13)]. Small amounts of 4-(t-butyl)biphenyl were present among the thermolysis products of the hydroperoxide (**1e**). The intermediate (**8**) of reaction (13)



(13)

could serve as an additional hydrogen-atom source for the triphenylmethylperoxy and triphenylmethyl radicals.

Tervalent phosphorus compounds are known to reduce hydroperoxides to the corresponding alcohols [equation (14)].[24] Whether this pathway operates in the present case is not

$$\geqslant CO\text{–}OH + {:}PR_3 \longrightarrow \geqslant C\text{–}O\overset{+}{P}R_3 + {}^{-}OH \longrightarrow HO\text{–}C\leqslant + O{=}PR_3 \qquad (14)$$

known but, if it operates, the second step of sequence (14) should, because of steric crowding at the central carbon atom of the phosphonium intermediate (**9**), be rather inefficient.

$Ph_3CO\overset{+}{P}Bu_3$

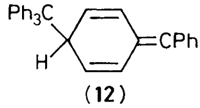
(9)

$[Ph_2(PhO)C\text{–}]_2$

(10)

$Ph_2C(OPh)_2$

(11)



(12)

We have also tested whether bis(triphenylmethyl) peroxide (**1f**), too, could be an intermediate in the conversion of triphenylmethyl radicals into benzophenone, triphenylmethanol (**1d**), and phenol; it appears not to be so. Bis(triphenylmethyl) peroxide (**1f**) had been known[22a] to rearrange in *ca.* 70% yield into compound (**10**) when refluxed for 10 min in xylene;‡ the product, on prolonged thermolysis, is converted into a mixture of ketal (**11**) and tetraphenylethylene as the main products (75% combined yield). The same compounds were now found to be the main products (22–37 and 31–40% individual yields, respectively) when peroxide (**1f**) was thermolysed in t-butylbenzene under various conditions. Since neither of these compounds was formed in the reaction of halides (**1a**) and (**1b**) with tributylphosphine under oxygen, not only the intermediacy of bis(triphenylmethyl) peroxide (**1f**) is definitely ruled out but the peroxide is even shown not to be formed under these conditions. It is known, however, that the dimer (**12**)[11] of triphenylmethyl (the so-called 'hexaphenylethane') is easily autoxidized to give the peroxide (**1f**) in a non-chain process.[25] The explanation of this apparent contradiction is probably that dissociation of dimer (**12**) yields triphenylmethyl radical pairs; reaction with a molecule of oxygen then results in formation of triphenylmethylperoxy–triphenylmethyl radical pairs which easily recombine to give product (**1f**). The conditions for the reaction of halides (**1a**) and (**1b**) with tributylphosphine, on the other hand, are such that they do not favour formation of triphenylmethyl radical pairs.

Establishment of the possibility of SET from tervalent phosphorus compounds to halides has enabled us to rationalize some early observations concerning the formation of 'anomalous' products resulting from the reactions of phosphorous acid derivatives and alkyl halides. Arbuzov and Arbuzov have, *e.g.*, observed the formation of either bis(triphenylmethyl) peroxide (**1f**) or of the dimer (**12**) when triphenylmethyl bromide (**1a**) is allowed to react with sodium diethyl phosphite in air and under nitrogen, respectively; characteristically, the corresponding chloride (**1b**) gave only the normal product (**13**).[26] Similarly, Pudovik and Tarasova have obtained mixtures containing bis(triphenylmethyl) peroxide (**1f**), triphenylmethane (**1c**), and triphenylmethanol (**1d**)§ in various relative concentrations

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* The intermediate distonic radical cations (**7**) formed by attack of the $Bu_3P^{+\cdot}$ radical cation on the solvent, *cf.* second footnote on p. 1514, as well as the radicals (**8**) could act as further hydrogen-atom donors to triphenylmethylperoxy and triphenylmethoxy radicals.

† For reactions in which phenols act as hydrogen-atom donors, see ref. 23.

‡ The obvious intermediates of this rearrangement are triphenylmethoxy radical pairs which rearrange to phenoxydiphenylmethyl radical pairs [equation (10)]; the latter, subsequently, recombine to product (**10**).

§ This product could have been formed during work-up from unchanged halide, although the original authors have suggested another mechanism for its formation, see ref. 27.

when sodium *O,O'*-dialkyl thiophosphites are allowed to react with halides (**1a**) and (**1b**); in some of their experiments normal products analogous to compound (**13**) were also obtained.[27] The isolation of peroxide (**1f**) and of triphenylmethane (**1c**) has been considered by these authors as a clear indication of the intermediacy of triphenylmethyl radicals but no mechanism for their formation has been suggested. The operation of a SET initiated process now appears to be clear. The relative propensities of bromide (**1a**) and chloride (**1b**) to act as electron acceptors is the explanation for the contrasting results of the reactions studied by the Arbuzovs[26] and mentioned above, depending on whether bromide (**1a**) or chloride (**1b**) was used as the starting material. For further 'anomalous' products resulting from similar experiments, see refs. 28 and 29.

Reactions with Tributylamine.—Since, under similar conditions, identical products were obtained in the reactions with tributylphosphine and tributylamine, and replacement of argon by oxygen resulted in the same change of the nature of the product in both series, the mechanisms of the reactions leading to the products may be assumed to be identical, save for the replacement of phosphorus by nitrogen. The most conspicuous difference between the two series of experiments, especially between those conducted under argon, is that considerably longer reaction times were necessary for the reactions to proceed to (near) completion in those experiments in which tributylamine was used as the nucleophile. This possibly reflects the superior single-electron donating ability of tributylphosphine.

$$\mathrm{Ph_3CP({=}S)(OEt)_2}$$

(13)

Heating bromide (**1a**) in t-butylbenzene for *ca.* 40 h to 153 °C under argon in the presence of 1 or 2 mol equiv. of tributylamine led to the formation of the reduction product (**1c**) in 61 and 62% isolated yield. This observation appears to prove that the tributylaminium radical cation (**14**), formed according to equation (15), is able to transfer a hydrogen atom to the triphenylmethyl radical [equation (16)] since, after consumption of the tributylamine in the experiment carried out in the presence of 1 mol equiv. of the amine, no other hydrogen donor is present in the reaction mixture.

$$\underset{\textbf{(1a)}}{\mathrm{Ph_3CBr}} + \mathrm{:NBu_3} \xrightarrow[\text{steps}]{\text{1 or 2}} \mathrm{Ph_3C\cdot} + \underset{\textbf{(14)}}{\overset{+\bullet}{\mathrm{N}}\mathrm{Bu_3}} + \mathrm{Br^-} \qquad (15)$$

$$\mathrm{Ph_3C\cdot} + \underset{\textbf{(14)}}{\mathrm{PrCH_2}\overset{+\bullet}{\mathrm{N}}\mathrm{Bu_2}} \longrightarrow \underset{\textbf{(1c)}}{\mathrm{Ph_3CH}} + \mathrm{PrCH{=}}\overset{+}{\mathrm{N}}\mathrm{Bu_2} \qquad (16)$$

To our knowledge, the only analogous reaction in which an α-hydrogen atom is *directly* transferred from an aminium radical cation to a suitable acceptor has been observed by our group;[1] indirect α-hydrogen atom transfers (*i.e.* successive proton and electron transfers) from aminium radical cations are, however, known (see the discussion in ref. 1).

The non-formation of the dimeric product (**3a**) in the reactions of halides (**1a**) and (**1b**) with tributylamine conducted under argon, not even at 80 °C in the presence of 2.3 mol equiv. of tributylamine, is somewhat surprising because the related compound (**1g**) had been found to yield 41–48% of the dimeric product (**3b**) and at most traces of the reductive dehalogenation product (**1h**) when allowed to react with 2.3 mol equiv. of triethylamine in refluxing benzene under nitrogen, *i.e.* under essentially identical conditions.[4] The reason for this discrepancy is not known at present.

Experimental

Purifications by t.l.c. were performed on 20 × 20 cm plates coated with Kieselgel 60 $\mathrm{PF_{254+366}}$ as the adsorbent. Most of the products described in the present paper were known compounds. They were identified by m.p. and mixed m.p. determinations, and by comparison of their i.r. spectra and R_f values with those of authentic samples. M.p.s are uncorrected. The ^{1}H and ^{13}C n.m.r. spectra of compounds (**2a**) and (**2b**) were recorded with a Varian XL-400 spectrometer with $\mathrm{SiMe_4}$ as the internal reference. A JEOL JES-FE/3X spectrometer (100 kHz, field 3 233 ± 50 G, mod. 0.26 G) was used for the e.s.r. studies. I.r. and mass spectra were recorded with Zeiss Specord 75 and an AEI-MS-902 (70 eV, direct insertion) spectrometers, respectively.

Starting Materials and Solvents.—Triphenylmethyl bromide (**1a**) (Merck, Darmstadt), contaminated by traces of benzophenone, was recrystallized from acetic acid–acetic anhydride–phosphorus tribromide 9:1:0.2 (v/v), triphenylmethyl chloride (**1b**) (EGA) from heptane–thionyl chloride 98:2 (v/v). Tributylphosphine (EGA) and tributylamine (Fluka) were freshly distilled at reduced pressure under argon. Cumene (BDH) and t-butylbenzene[30] were distilled at normal pressure and stored over sodium wire. Bis(triphenylmethyl) peroxide (**1f**) was obtained by literature methods.[31]

Reactions of the Triphenylmethyl Halides (**1a**) *and* (**1b**) *with Tributylphosphine and Tributylamine Under Argon.*—(*a*) Mixtures of halides (**1a**) (3 experiments) or (**1b**) (2 experiments) (*ca.* 1 g), tributylphosphine (1.1 mol equiv.), and dry cumene [8.5 and 10 cm^3 per gram of (**1a**) and (**1b**), respectively] were placed into thick-wall tubes, flushed with and sealed under argon as described in ref. 1 for the reaction of (4-chlorophenyl)di(4-t-butylphenyl)methyl chloride with tributylamine. The mixtures containing bromide (**1a**) were then heated for 6.5 h, those containing chloride (**1b**) for 50–150 h to 153 °C, allowed to cool, and worked up according to method A or, if isolation of the *tele* substitution products (**2a**) and (**2b**), respectively, was also desired, method B.

Method A. The mixtures were evaporated to dryness at reduced pressure and the residues worked up by t.l.c. (benzene–hexane 1:1; eluant: methanol–$\mathrm{CH_2Cl_2}$ 1:1) to give 67–82% of triphenylmethane (**1c**) from bromide (**1a**), and 26% of (**1c**) and 43% of triphenylmethanol (**1d**) after 50 h from chloride (**1b**).

Method B. Three volumes of ether were added to the reaction mixture to precipitate an oily product which was thoroughly triturated with the supernatant. The latter was decanted and the oily product washed with ether (2 × 10 cm^3). The combined supernatant and washings were evaporated to dryness and the residue worked up according to method A to give 66% of triphenylmethane (**1c**) and 3% of triphenylmethanol (**1d**) from bromide (**1a**), and, after a reaction time of 150 h, 53% of (**1c**) and 8% of (**1d**) from chloride (**1b**).

The oily precipitates proved to contain mainly the phosphonium salts (**2a**) and (**2b**), respectively, and were purified by t.l.c. (methanol–$\mathrm{CH_2Cl_2}$, 1:3; elution: methanol–$\mathrm{CH_2Cl_2}$, 1:1). Yields of 28 and 32% for the *tele* substitution products (**2a**) and (**2b**), respectively, were obtained; both compounds were formed as oils which resisted all attempts to crystallize them.

Compound (**2b**), purity *ca.* 95% (according to its ^{1}H n.m.r. spectrum) (Found: C, 77.35; H, 8.85; Cl, 7.25. $\mathrm{C_{31}H_{42}ClP}$ requires C, 77.4; H, 8.8; Cl 7.35%); δ_H($\mathrm{CDCl_3}$) 0.94 (t *J* 7.4 Hz) 1.4–1.6 and 2.80 (2 × m) ($^2J_{PH}$ *ca.* 14 Hz) (3 × Bu), 5.61 (s $\mathrm{Ar_3C}$*H*), 7.10 (d J_{ortho} 7.6 Hz; 2 × Ph, *ortho* Hs), 7.26 (t J_{ortho} 7.2 Hz; 2 × Ph, *para*-H), 7.32 (dd J_{ortho} 7.6 and 7.2 Hz; 2 × Ph, *meta*-Hs), 7.43 and 7.87 (AA'BB', J_{ortho} 8.3 Hz; with additional splitting due to P–H coupling, $^4J_{PH}$ 2.6 and $^3J_{PH}$ 11.3 Hz, respectively; *para* disubstituted benzene ring. δ_C($\mathrm{CDCl_3}$): 13.53 and 23.81 ($^3J_{CP}$ 15.5 Hz) and 23.82 ($^2J_{CP}$ 4.6 Hz) and 19.76 ($^1J_{CP}$

48.6 Hz) (Bu), 56.80 (*C*H), 115.48 ($^1J_{CP}$ 80.1 Hz) and 132.00 ($^2J_{CP}$ 9.0 Hz) and 131.30 ($^3J_{CP}$ 11.9 Hz) and 151.24 ($^4J_{CP}$ 3.0 Hz) (disubstituted benzene ring), 126.98, and 128.69, 129.31, and 142.08 (*para*, *meta*, *ortho*, and *ipso* carbon atoms, respectively, of the Ph groups).

Compound (**2a**): hygroscopic oil (Found: C, 63.9; H, 8.1. $C_{31}H_{42}BrP{\cdot}3H_2O$ requires C, 64.24; H, 8.34%).

The ^{1}H n.m.r. spectrum of compound (**2a**) was identical with that of compound (**2b**) except for a slight difference in the chemical shift (δ 7.98) of the signal of the proton in the *ortho* position relative to the phosphonium group.

(*b*) Mixtures of halides (**1a**) or (**1b**) (3 experiments each) (*ca.* 0.8 g), tributylamine (2, in one case 1 mol equiv.), and dry cumene or t-butylbenzene (4.3 cm^3 per gram of halide) were similarly sealed into thick-wall tubes under argon, heated, in the case of bromide (**1a**), for *ca.* 40 h and, in the case of chloride (**1b**), for *ca.* 65 h to 153 °C, allowed to cool, and worked up by method A [using in some cases hexane or benzene–hexane (1:3) as the solvent] to give 60–74% of triphenylmethane (**1c**).

(*c*) Mixtures (2 experiments) of bromide (**1a**) (0.6 g), tributylamine (2.3 mol equiv.), and t-butylbenzene (4.3 cm^3 per gram of bromide) were sealed in thick-walled tubes under argon and heated for 120 and 180 h, respectively, to 153 °C. Work-up as described in (*b*) furnished 44–45% of triphenylmethane (**1c**), and 34 and 13% of triphenylmethanol (**1d**) after heating for 120 and 180 h, respectively.

Reactions of the Dimer (**12**)[11] *of Triphenylmethyl with Hydrogen-atom Donors* (*Cumene, Tributylphosphine, and Tributylamine*) *Under Argon.*—(*a*) Compound (**12**) (0.44 g, 0.9 mmol) was heated with dry cumene (5 cm^3) in a sealed tube for 3 and 10 h, respectively, to 80 °C under argon. Chromatographic work-up afforded 23 and 45%, respectively, of triphenylmethane (**1c**). Significant amounts of the starting dimer remained unchanged, but the rearrangement product (**3a**) of the starting compound was not formed.

When a similar mixture was heated for 5 h to 153 °C under argon, 59% of triphenylmethane (**1c**) and 27% of the rearrangement product (**3a**) were obtained.

(*b*) A mixture of compound (**12**) (0.87 g, 1.8 mmol), tributylphosphine (0.81 g, 4 mmol), and Bu^{t}Ph (10 cm^3) was heated in a sealed tube for 6.5 h to 153 °C under argon. Chromatographic work-up furnished 39% of triphenylmethane (**1c**) and 35% of the rearrangement product (**3a**).

(*c*) When a mixture of compound (**12**) (0.87 g, 1.8 mmol), tributylamine (0.74 g, 4 mmol), and Bu^{t}Ph (10 cm^3) was heated in a sealed tube for 20 h to 153 °C under argon, 60% of triphenylmethane (**1c**) and 28% of the rearrangement product (**3a**) were obtained.

When this experiment was carried out at 80 °C, only 8% of compound (**1c**) and none of compound (**3a**) were obtained. The unchanged starting compound (**12**) was recovered in the form of bis(triphenylmethyl) peroxide (**1f**).

Reaction of the Triphenylmethyl Halides (**1a**) *and* (**1b**) *with Tributylphosphine and Tributylamine in the Presence of Oxygen.*—(*a*) Mixtures of bromide (**1a**) (*ca.* 1 g), tributylphosphine (1.1 mol equiv.), and t-butylbenzene [8.6 cm^3 per gram of bromide (**1a**)] were refluxed (b.p. 169 °C) for 16 h under oxygen (2 experiments), allowed to cool, and extracted with 10% aqueous NaOH. The alkaline solutions were washed with ether (20 cm^3), the combined t-butylbenzene solutions and ethereal washings evaporated to dryness and worked up by t.l.c. (dioxane–hexane 1:4 or 2:5; elution: methanol–CH_2Cl_2, 1:1) to give 83–85% of benzophenone and 10–11% of triphenylmethanol (**1d**).

The aqueous-alkaline solutions were treated with benzoyl chloride, the mixtures vigorously stirred for 1.5 h, and kept in a refrigerator until the phenyl benzoate crystallized. A second crop was obtained by extraction of the aqueous filtrate with ether; total yield 17%.

When similar mixtures of the halides (**1a**) and (**1b**) (*ca.* 1 g), tributylphosphine (1.1 mol equiv.) and t-butylbenzene [8.6 cm^3 per gram of (**1a**) and 10 cm^3 per gram (**1b**), respectively] were heated for 6.5 and 14 h, respectively, to 153 °C under oxygen, 90 and 68%, respectively, of benzophenone, 8 and 12%, respectively, of triphenylmethanol (**1d**), and 22 and <3%, respectively, of phenyl benzoate were obtained by similar work-up.

(*b*) Mixtures of bromide (**1a**) and chloride (**1b**) (*ca.* 0.7 g) (1 and 2 experiments respectively), tributylamine (1 mol equiv.), and t-butylbenzene (4.3 cm^3 per gram of halide) were refluxed, in the case of the bromide, for 7 and, in the case of the chloride, for 19 h under oxygen. Work-up, as described in (*a*), furnished 60–76% benzophenone, 22–42% phenyl benzoate, and 7.5% triphenylmethanol (**1d**).

Reaction of Triphenylmethane (**1c**) *with Oxygen.*—Triphenylmethane (**1c**) (0.87 g, 3.6 mmol) or a mixture of triphenylmethane (0.87 g, 3.6 mmol) and tributylphosphine (0.81 g, 1.1 mol equiv.) were heated in t-butylbenzene (10 cm^3) for 6.5 h under oxygen. Unchanged (**1c**) (91 and 90%) was recovered, and only 4 and 3%, respectively, benzophenone was isolated.

Thermolysis of Triphenylmethyl Halides (**1a**) *and* (**1b**) *in the Presence of Oxygen.*—(*a*) A solution of compound (**1a**) (1.16 g, 3.6 mmol) in Bu^{t}Ph (10 cm^3) was refluxed for 16 h under oxygen and evaporated to dryness. In order to hydrolyse any unchanged starting material, the residue was refluxed with a 4:1 dioxane–water mixture (20 cm^3) and again evaporated to dryness. The residue was taken up in dry benzene and the solution evaporated to dryness. Finally the residue was purified by column chromatography (Kieselgel G; hexane $\longrightarrow$ dioxane–hexane, 1:25) to give benzophenone (0.58 g, 90%).

(*b*) When a similar mixture of bromide (**1a**) and Bu^{t}Ph was heated for 6.5 h at 153 °C under oxygen and the mixture worked up as described in (*a*), benzophenone (0.24 g, 37%) and triphenylmethanol (0.48 g, 52%) (**1d**) were obtained. As shown by the result of the following experiment, most of the latter was formed by hydrolysis of unchanged bromide (**1a**) during work-up.

(*c*) When bromide (**1a**) was allowed to react with oxygen as described in (*b*) but with the crude product mixture subjected to ethanolysis by refluxing for 5 min with ethanolic (15 cm^3) NaOEt (from 82 mg, 3.6 mmol of sodium), and then worked up as above, benzophenone (0.26 g, 40%) and ethyl triphenylmethyl ether (0.47 g, 46%) were obtained.

(*d*) When experiment (*c*) was repeated with chloride (**1b**) (1.0 g, 3.6 mmol), 40 mg (6%) of benzophenone, 800 mg (77%) of ethyl triphenylmethyl ether and 75 mg (8%) of triphenylmethanol (**1d**) were obtained.

Thermolysis of Triphenylmethyl Hydroperoxide (**1e**).—Mixtures of hydroperoxide (**1e**) (*ca.* 0.85 g) and t-butylbenzene (10 cm^3 per gram of hydroperoxide) were refluxed (b.p. 169 °C) for 6 h under argon, or sealed under argon as described above, and heated for 6 h to 153 °C. Work-up, as described above for the reaction of bromide (**1a**) with tributylphosphine under oxygen, gave 55 and 48% benzophenone, 26 and 49% triphenylmethanol (**1d**), and 9 and 13%, respectively, phenyl benzoate. In addition, benzophenone diphenyl ketal (**11**) (6%) was isolated in the first case, and by chromatography (the first fraction with hexane as the solvent) 4-(t-butyl)biphenyl (4%; identified by comparison of t.l.c. and m.s. with those of an authentic sample) was isolated in the second.

When a similar mixture of hydroperoxide (**1e**) and t-butylbenzene was refluxed for 4 h under oxygen, 62%

benzophenone, 14% triphenylmethanol (**1d**), and 7% phenyl benzoate were obtained.

When similar mixtures of hydroperoxide (**1e**), t-butylbenzene, and tributylphosphine or tributylamine (1 mol equiv.) were sealed under argon and heated for 6.5 and 9 h, respectively, to 153 °C, 11 and 18% benzophenone, 88 and 80%, respectively, triphenylmethanol (**1d**), and some phenyl benzoate ($<7\%$) were obtained.

Decomposition of Phenol in t-Butylbenzene at Elevated Temperatures.—Solutions of phenol (330 mg) in t-butylbenzene (10 cm^3) were sealed under argon as described above and heated for 7 h to 153 °C, or refluxed (b.p. 169 °C) for 6 h either under argon or under oxygen. The unchanged phenol was extracted with aqueous NaOH and isolated in the form of phenyl benzoate (46–57% in the argon, 43% in the oxygen experiments) as described above. ($\geqslant 90\%$ of phenol was recovered from its solutions in t-butylbenzene in control experiments in the form of its benzoate.)

When tributylphosphine or tributylamine (1.2 mol equiv.) were added to the solutions and the mixtures heated for 7 h to 153 °C under oxygen, *ca.* 57% the phenol was recovered in the form of its benzoate.

Thermolysis of Bis(triphenylmethyl) Peroxide (**1f**) *in t-Butylbenzene.*—Solutions of peroxide (**1f**) (930 mg) in t-butylbenzene (10 cm^3) were refluxed (b.p. 169 °C) for 4 h in air, or sealed under argon and heated for 8 h to 153 °C. The mixtures were worked up by t.l.c. (benzene–hexane 1:3) to give 33 and 34% tetraphenylethylene, 37 and 19% the benzophenone diphenyl ketal (**11**) benzophenone, and 18 and 25%, respectively, benzophenone [probably formed by hydrolysis of the ketal (**11**) during work-up].

When these experiments were carried out in the presence of added tributylphosphine (2.2 mol equiv.), 40 and 31% tetraphenylethylene, 31 and 22%, respectively, of the ketal (**11**), and 19% benzophenone were obtained.

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Appendix

One of the referees has stressed the importance of the reactions of triphenylmethylperoxy and triphenylmethoxy radicals with the phosphine in our experiments conducted in the presence of molecular oxygen. Such reactions may certainly occur with that part of the phosphine which has not been converted into phosphine radical-cations [equation (6)]. Based on analogy with similar cases, *e.g.* ref. 32, these reactions may be assumed to lead, *via* the intermediacy of phosphoranyl radicals (**15**) and (**16**), to the formation of tributylphosphine oxide and triphenylmethyl radicals [equations (17) and (18)]. Reaction of the latter with molecular oxygen should regenerate the peroxy radicals, the net result being autoxidation of the phosphine by a

$$Ph_3C\text{–}OO\cdot + PBu_3 \longrightarrow \underset{\mathbf{(15)}}{Ph_3C\text{–}OO\text{–}\dot{P}Bu_3} \longrightarrow Ph_3CO\cdot + O{=}PBu_3 \quad (17)$$

$$Ph_3CO\cdot + PBu_3 \longrightarrow \underset{\mathbf{(16)}}{Ph_3CO\,\dot{P}Bu_3} \longrightarrow Ph_3C\cdot + O{=}PBu_3 \quad (18)$$

radical-chain mechanism. After consumption of the phosphine the peroxy radicals should abstract hydrogen, and subsequently reactions (9)–(13) mentioned above should take place.

Alternatively, the triphenylmethylperoxy radicals could, rather than abstract hydrogen, recombine with a phosphine radical cation [equation (19)] to give phosphonium cation (**17**).

$$\mathrm{Ph_3C{-}OO\cdot} + \overset{+\bullet}{\mathrm{P}}\mathrm{Bu_3} \longrightarrow \underset{\textbf{(17)}}{\mathrm{Ph_3C{-}OO{-}}\overset{+}{\mathrm{P}}\mathrm{Bu_3}} \qquad (19)$$

$$\textbf{(17)} \longrightarrow \mathrm{Ph_3CO\cdot} + \cdot\mathrm{O}\overset{+}{\mathrm{P}}\mathrm{Bu_3} \qquad (9a)$$

$$\mathrm{Ph_3CO\cdot} \longrightarrow \mathrm{Ph_2}\dot{\mathrm{C}}\mathrm{(OPh)} \qquad (10)$$

$$\mathrm{Ph_2}\dot{\mathrm{C}}\mathrm{(OPh)} + \cdot\mathrm{O}\overset{+}{\mathrm{P}}\mathrm{Bu_3} \longrightarrow \underset{\textbf{(18)}}{\mathrm{Ph_2C(OPh)(O}\overset{+}{\mathrm{P}}\mathrm{Bu_3)}} \xrightarrow{\mathrm{H_2O}}$$

$$\mathrm{Ph_2C{=}O} + \mathrm{HOPh} + \mathrm{O{=}PBu_3} + \mathrm{H^+} \qquad (11a)$$

Homolysis of the O–O bond of the latter [equation (9a) which would be analogous to equation (9)], followed by reaction (10) and radical recombination would furnish the phosphonium cation (**18**) which, during work-up, would break down to products [equation (11a), analogous to equation (11)].