The Reaction of Triphenylmethyl Halides with Triphenylphosphine in Cumene and *tert*-Butylbenzene[†]

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Reactions of triphenylmethyl bromide and chloride with triphenylphosphine at elevated temperatures under argon furnish mixtures of the reductive dehalogenation product triphenylmethane and the *tele* substitution products **2a** or **2b**, the ratio of the products depending on the reaction conditions. The formation of triphenylmethane indicates that the reaction is, at least partly, initiated by halophilic attack [eqn. (2)] or by single-electron-transfer (SET) from the phosphine [eqn. (5)]. The resulting triphenylmethanide anions or triphenylmethyl radicals would then be converted into triphenylmethane by proton or hydrogen abstraction [eqns. (4) and (6), respectively] or recombine with their phosphorus containing co-products to yield the *tele* substitution products [eqns. (3a) and (7), respectively]. The latter could, at least partly, also be formed *via* eqn. (1a). Exclusive operation of the SET initiated mechanisms of formation of both products has been proved by combination of trapping studies with molecular oxygen and proof of the absence of triphenylmethanide anions from the reaction mixtures.

Until recently phosphines have been thought to react with alkyl halides invariably as either carbophilic or halophilic nucleophiles [eqns. (1) and (2)]. The carbanion resulting in the latter

$$R_3P\!: + R_3'CX \xrightarrow[S_N2]{S_N1\text{ or}} R_3\overset{+}{P}CR_3'\!:\!X^- \qquad (1)$$

$$R_3P\!: + XCR_3' \longrightarrow R_3\overset{+}{P}X + :\!\overset{+}{C}R_3' \qquad (2)$$

case either reacts with its co-product, the halophosphonium ion [eqn. (3)] to afford the same phosphonium salt as is obtained directly according to eqn. (1), or it may abstract a proton, either from the solvent or a reagent present in the reaction mixture or added during work-up, to give the product of reductive dehalogenation [eqn. (4)].[2]

$$R_3\overset{+}{P}X + :\!\overset{-}{C}R_3' \xrightarrow[\text{two-step reaction}]{\text{concerted or}} R_3\overset{+}{P}CR_3'\!:\!X^- \qquad (3)$$

$$R_3'C\!:^- \xrightarrow{+H^+} R_3'CH \qquad (4)$$

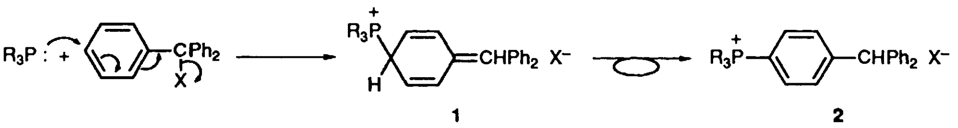
In Part 14 of the present series[3] the reactions of triphenylmethyl bromide and chloride with tributylphosphine were studied in cumene at elevated temperatures under argon. In addition to triphenylmethane, the main product, resulting from reductive dehalogenation of the starting halides, the *tele* substitution products tributyl [4-(diphenylmethyl)phenyl]phosphonium bromide and chloride (**2**, R = Bu), were isolated. The formation of the *tele* substitution products could be explained by simply replacing eqns. (1) and (3) by equations (1a) and (3a), respectively. However, the observation of the EPR spectrum of the triphenylmethyl radical when triphenylmethylbromide, tributylphosphine and cumene were mixed under argon in the cavity of an EPR spectrometer, and the high intensity of the EPR signal, even at room temperature, necessitated consideration of a non-ionic, *i.e.* of a single-electron-transfer (SET) initiated pathway [eqns. (5)–(7), R = Bu] for the formation of the observed products. Cumene, the

$$Ph_3CX + R_3P \longrightarrow Ph_3CX^{\bullet-} + R_3P^{\bullet+} \longrightarrow Ph_3C^{\bullet} + :\!X^- + R_3P^{\bullet+} \qquad (5)[‡]$$

$$Ph_3C^{\bullet} \xrightarrow{+H^{\bullet}} Ph_3CH \qquad (6)$$

$$R_3P^{\bullet+} + {}^{\bullet}CPh_3 + :\!X^- \longrightarrow \mathbf{1} \xrightarrow[\circlearrowleft]{} \mathbf{2} \qquad (7)$$

tributylphosphine radical cation and tributylphosphine were considered as the potential hydrogen atom sources in eqn. (6). When the same reactions were carried out in *tert*-butylbenzene under oxygen, various oxygenation products, including



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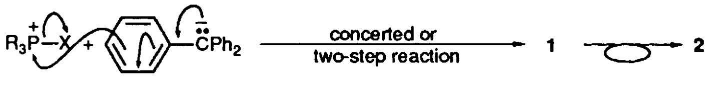

(3a)

[†] Single Electron Transfer Initiated Thermal Reactions of Arylmethyl Halides, Part 16; for Part 15, see ref. 1.

[‡] Alternatively, the same products could be formed, *via* dissociative electron transfer, in a single step.

Table 1 Reaction of triphenylmethyl bromide and chloride (Ph_3CX) with tributyl[a,b] and triphenylphosphine[c] (R_3P) under argon

						Isolated products (%)			
Entry	X	R	Solvent (amount[d])	Temperature/°C	Reaction time/h	**2**	Ph_3CH	Ph_3COH[e]	Other
1	Br	Bu	Cumene (8.5)	153	6.5	*f*	67–82	*f*	
2	Br	Bu	Cumene (8.5)	153	6.5	28	66	3	
3	Cl	Bu	Cumene (10)	153	50	*f*	26	43	
4	Cl	Bu	Cumene (10)	153	150	32	53	8	
5	Br	Ph	Cumene (8.6)	153	6.5	52	42[g]	4	*h*
6	Br	Ph	Cumene (43)	153	6.5	4	72	12	*i*
7	Br	Ph	Cumene (8.6)	105	44	41	19	9	
8	Br	*k*	Cumene (8.6)	105	44	—	91	*l*	*m*
9	Br	Ph	Bu^tPh (8.6)	153	6.5	80	6	12	*n*
10	Br	Ph	Bu^tPh (8.6)	105	44	49	10	25	*o*
11	Br	*k*	Bu^tPh (8.6)	105	44	—	3	86	
12	Cl	Ph	Cumene (10)	153	124	86	9	2	*p*
13	Cl	Ph	Cumene (10)	105	44	10	3[g]	76	*r*
14	Cl	*k*	Cumene (10)	105	44	—	*l*	92	
15	Cl	Ph	Bu^tPh (10)	153	124	93	2	4	*s*
16	Cl	Ph	Bu^tPh (10)	153	248	89	5	3	*h*

[a] From ref. 3. [b] 1.1 mol/mol halide. [c] 1.0 mol/mol halide. [d] cm^3/g halide. [e] By hydrolysis of unchanged starting halide during work-up. [f] Not isolated. [g] The same product, uncontaminated by deuteriated analogues was obtained when the reaction mixture was treated with ^2H_2O (^2H content 99%) prior to work-up. [h] *ca.* 3% of unchanged starting phosphine recovered. [i] 83% of unchanged phosphine recovered. [k] Control experiment carried out in the absence of added phosphine. [l] Traces only. [m] Significant amounts of hydrogen bromide formed as co-product. [n] *ca.* 11% of unchanged phosphine recovered. [o] *ca.* 26% of unchanged phosphine recovered. [p] *ca.* 2% of unchanged phosphine recovered. [r] *ca.* 74% of unchanged starting phosphine recovered. [s] *ca.* 4% of unchanged starting phosphine recovered.

benzophenone as the main product and minor amounts of triphenylmethanol and phenol, were obtained instead of triphenylmethane and the phosphonium salts **2** (R = Bu). The results of these trapping studies were in agreement with the operation of the SET initiated mechanism of formation of the products, under both argon and oxygen.[3] They do not, however, furnish conclusive proof for the (exclusive) operation of this mechanism since triphenylmethanide anions are known[4] to be oxidized by molecular oxygen to triphenylmethyl radicals [eqn. (8)].

$$Ph_3C{:}^- + O_2 \longrightarrow \underset{\underset{\text{products}}{\downarrow}}{Ph_3C^{\bullet}} + O_2^{\bullet -} \qquad (8)$$

The oxidation of triphenylmethanide anions by molecular oxygen had earlier[4] been studied under conditions (DMSO–Bu^tOH mixtures at room temperature) differing from those prevailing in our trapping studies.[3] A single product, triphenylmethanol, was formed in quantitative yield[4] rather than a mixture of various oxygenation products (containing only minor amounts of triphenylmethanol) as obtained by us. However, the widely different reaction conditions did not permit us to draw the conclusion that triphenylmethyl radicals rather than triphenylmethanide anions were trapped in our studies. We have now shown that triphenylmethanide anions, when treated with molecular oxygen under the conditions of our trapping experiments, afford the same products (although in a different ratio) as obtained in our trapping studies (see below). Therefore, trapping studies with molecular oxygen do not permit unambiguous differentiation of the SET mechanism [eqns. (5)–(7)], where trityl radicals are formed directly, from the carbanionic mechanism [eqns. (2), (3a) and (4)] where, in the presence of molecular oxygen, trityl radicals are formed *via* triphenylmethanide anions. It was felt, therefore, that further evidence was necessary in order to establish the SET mechanism conclusively.

Here we report our studies into the reactions of triphenylphosphine with triphenylmethyl bromide and chloride in aromatic hydrocarbons at elevated temperatures under argon and oxygen. The reason for replacing the tributylphosphine, used in our earlier studies, with triphenylphosphine was that, while the latter had been shown[5] to generate triphenylmethyl radicals from triphenylmethyl bromide (as well as from triphenylmethyl chloride, as presently found) similarly to the former, the lack of α-hydrogen atoms in triphenylphosphine could be expected (and was, indeed, found) to simplify the course of the reaction.

Results and Discussion

The products of the reaction of triphenylmethyl bromide and chloride with triphenylphosphine conducted under argon or oxygen at various conditions are listed in Tables 1 and 2,

Table 2 Reaction of triphenylmethyl bromide and chloride (Ph_3CX) with tributyl-[a,b] and triphenyl-phosphine (R_3P)[c] under oxygen

						Isolated products (%)			
Entry	X	R	Solvent (amount[d])	Temperature/°C	Reaction time/h	$Ph_2C=O$	Ph_3COH[e]	Ph_3COR'[f]	PhOH[g]
1	Br	Bu	Bu^tPh (8.6)	169	16	83–85	10–11	—	17
2[a]	Br	[h]	Bu^tPh (8.6)	169	16	90			
3	Br	Bu	Bu^tPh (8.6)	153	6.5	90	8	—	22
4[a]	Br	[h]	Bu^tPh (8.6)	153	6.5	37	52	—	
5[a]	Br	[h]	Bu^tPh (8.6)	153	6.5	40		46 (R' = Et)	
6	Cl	Bu	Bu^tPh (10)	153	14	68	12	—	<3
7	Cl	Ph	Bu^tPh (10)	153	11	42	19	11 (R' = Me)	[i]
8	Cl	[h]	Bu^tPh (10)	153	11	32	16	25 (R' = Me)	
9[a]	Cl	[h]	Bu^tPh (10)	153	6.5	6	8	77 (R' = Et)	
10	Cl	Ph	Bu^tPh (10)	105	40	32	23	34 (R' = Me)	[i,k]
11	Cl	[h]	Bu^tPh (10)	105	40	[l]	16[m]	76 (R' = Me)	

[a] From ref. 3. [b] 1.1 mol/mol halide. [c] 1.0 mol/mol halide. [d] cm^3/g halide. [e] Formed partly by trapping of trityl radicals by molecular oxygen and partly by hydrolysis of unchanged starting halide during aqueous work-up. If, prior to work-up, the reaction mixture is treated with alcoholic sodium alkoxides,[f] the unchanged halide is converted into the corresponding alkyl triphenylmethyl ether. In the latter case any triphenylmethanol isolated is, except for small amounts resulting from hydrolysis of the starting halide by traces of water present, the product of trapping of triphenylmethyl radicals by oxygen. [f] Formed, as a result of treatment of the reaction mixture with alcoholic sodium alkoxides prior to work-up, by alcoholysis of unchanged starting halide. [g] Isolated as its benzoate. [h] Control experiment carried out in the absence of added phosphines. [i] Not even traces of compound **2** (R = Ph, X = Cl) were detected by TLC. [k] In addition, 92% of triphenylphosphine oxide was isolated. Not even traces of unchanged triphenylphosphine were detected by TLC. [l] Traces only detected by TLC. [m] Since benzophenone was not detected, this is probably the product of hydrolysis of part of the starting halide by traces of water present, rather than an oxidation product.

respectively. For comparison, the products of the reaction of the same halides with tributylphosphine, studied previously,[3] are also included. Triphenylmethane and the *tele* substitution products **2** (R = Ph, Bu; X = Br, Cl, respectively) as well as some triphenylmethanol, resulting from hydrolysis of unchanged starting halide during work-up, were obtained when the reactions were conducted under argon. Triphenylmethyl chloride reacted considerably slower than the bromide (compare entries 2 and 4, 5 and 12, 7 and 13 or 9 and 15–16, Table 1) as would be expected if the SET mechanism [eqns. (5)–(7)] was operating. In no case were even traces of 4-(diphenylmethyl)(triphenylmethyl)benzene (**4**), the fully aromatic dimer of the triphenylmethyl radical, formed.

Formation of triphenylmethane indicates that at least part of the phosphines act towards triphenylmethyl halides as halophiles [eqn. (2)] and/or as single-electron donors [eqn. (5)]; the resulting triphenylmethanide anions and triphenylmethyl radicals* would be converted into triphenylmethane by protonation [eqn. (4)] and hydrogen abstraction [eqn. (6)], respectively, at some later stage. This, however, does not mean that formation of the *tele* substitution products **2** necessarily takes place *via* either or both of the sequences (2) + (3a) and (5) + (7). On the contrary, formation of part or all of the *tele* substitution products **2** according to eqn. (1a) would also be consistent with concomitant formation of triphenylmethane starting with reactions (2) and/or (5).

When, however, the reactions of the triphenylmethyl halides and phosphines were conducted under oxygen, neither triphenylmethane nor the substitution products **2** were formed in any of the experiments. Instead, various oxygenation products were obtained (Table 2). Since neither triphenylmethane (as shown earlier[3]), nor compound **2** (R = Ph, X = Cl) is converted (at least not to a significant extent) into these oxygenation products when heated in *tert*-butylbenzene in the presence of oxygen, the observations listed in Table 2 demonstrate that the total amount of both the *tele* substitution products **2** and of triphenylmethane obtained in the reactions conducted under argon are formed *via* either triphenylmethanide anions or triphenylmethyl radicals which are rapidly trapped by oxygen (if present) to give, *via* a rather complex reaction sequence,[3] the oxygenation products ultimately isolated. Formation of the *tele* substitution products **2** according to eqn. (1a) is, therefore conclusively ruled out.

Strikingly, when a freshly prepared THF solution of lithium triphenylmethanide was added to *tert*-butylbenzene heated to 153 °C in a flask through which a continuous stream of oxygen was conducted and the mixture kept for 17 h under these conditions, a mixture of triphenylmethanol (49%), benzophenone (23%), phenol (23%; isolated as its benzoate) and triphenylmethane† (9%) was obtained. In contrast, in the reactions of phosphines and triphenylmethylhalides conducted under oxygen benzophenone was invariably the main component of the mixtures of oxygenation products obtained (Table 2). Two explanations offer themselves for this change in the product composition: (i) while, in the reaction starting with lithium triphenylmethanide, the species trapped by oxygen are necessarily triphenylmethanide anions, in the reactions of phosphines with triphenylmethyl halides the species involved may possibly be triphenylmethyl

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* For an additional source of triphenylmethyl radicals in our experiments, see below.

† This product probably results from incomplete deprotonation during preparation of lithium triphenylmethanide.

radicals; (ii) while phosphines as well as phosphine radical cations* are present in the mixtures resulting in the latter reactions, these species are not present in the mixtures formed in the reaction of triphenylmethanide anions with oxygen. A choice between these two explanations does not appear to be possible at present.

The Effect of Variation of the Solvents, Reagents and the Substrates on Product Composition in the Reactions conducted under Argon (*Table 1*).—Examination of the data collected in Table 1 reveals that the ratio of *tele* substitution (**2**) and reductive dehalogenation products (Ph_3CH) increases more or less significantly (i) when the solvent cumene is replaced by *tert*-butylbenzene (compare entries 5 and 9, 7 and 10† or 12 and 15), (ii) when the reagent tributylphosphine is replaced by triphenylphosphine (compare entries 2 and 5 or 4 and 12) and (iii) when the substrate triphenylmethyl bromide is replaced by the chloride (compare entries 5 and 12, 7 and 13‡ or 9 and 15 or 16§).

The obvious conclusion is that some intermediate is formed in the course of the reactions of triphenylmethyl halides and phosphines which is trapped by cumene, tributylphosphine or its radical cation as triphenylmethane but, for obvious reasons, is not trapped by *tert*-butylbenzene, triphenylphosphine, or by its radical cation. Cumene and tributylphosphine are known[3] to be able to trap triphenylmethyl radicals by hydrogen atom transfer [eqns. (9) and (10)]. The same is true for the tributylphosphine radical cation [eqn. (11)]; the latter, however, should also be able to trap triphenylmethanide anions (by proton transfer) [eqn. (12)]. Thus, the effects of variation of the conditions on product composition appear to indicate that triphenylmethyl radicals are the intermediates of the reaction of phosphines and triphenylmethyl halides [eqns. (5)–(7)] but do not rule out the possibility that part of the reaction takes place *via* intermediate triphenylmethanide anions [eqns. (2) + (3a) or (2) + (4), R′ = Ph].

$$\mathrm{Ph_3C^{\bullet} + PhCHMe_2 \longrightarrow} \begin{array}{c}\mathrm{Ph\dot{C}Me_2}\\ \downarrow \\ \text{products}\end{array} \qquad (9)$$

$$\mathrm{Ph_3C^{\bullet} + PrCH_2PBu_2 \longrightarrow Ph_3CH +} \begin{array}{c}\mathrm{Pr\dot{C}HPBu_2}\\ \downarrow \\ \text{products}\end{array} \qquad (10)$$

$$\mathrm{Ph_3C^{\bullet} + PrCH_2\overset{+\bullet}{P}Bu_2 \longrightarrow Ph_3CH +} \begin{array}{c}\mathrm{PrCH{=}\overset{+}{P}Bu_2}\\ \downarrow \\ \text{products}\end{array} \qquad (11)$$

$$\mathrm{Ph_3C{:}^{-} + PrCH_2\overset{+\bullet}{P}Bu_2 \longrightarrow}$$
$$\begin{array}{c}\mathrm{Pr\overset{-}{\ddot{C}}H\overset{+\bullet}{P}Bu_2}\\ \downarrow \\ \text{products}\end{array} \longleftrightarrow \mathrm{Pr\dot{C}H\ddot{P}Bu_2} \qquad (12)[¶]$$

When the reaction of triphenylmethyl bromide and triphenylphosphine at 153 °C under argon was carried out in more dilute cumene solution (Table 1, entry 6), triphenylmethane was obtained as the main product in over 70% yield, although more than 80% of the phosphine introduced was recovered unchanged. This suggested that the phosphine was not involved in the formation of most of the triphenylmethyl radicals. In agreement with this, triphenylmethyl bromide, when heated for 44 h at 105 °C, is smoothly reduced to triphenylmethane (91%), ample amounts of hydrogen bromide being formed as the co-product (entry 8). This reaction is obviously initiated by homolysis of the C–Br bond of the substrate [eqn. (13)] and the resulting radicals are then trapped by cumene [eqns. (9) and (14)].

$$\mathrm{Ph_3C{-}Br \xrightarrow{heat} Ph_3C^{\bullet} + Br^{\bullet}} \qquad (13)$$

$$\mathrm{Br^{\bullet} + PhCHMe_2 \longrightarrow HBr +} \begin{array}{c}\mathrm{Ph\dot{C}Me_2}\\ \downarrow \\ \text{products}\end{array} \qquad (14)$$

Thus, SET from phosphines to triphenylmethyl halides is not the only means for the generation of triphenylmethyl radicals in our experiments. Consequently, detection of these radicals in our reaction mixtures does not prove that they were formed *via* the SET mechanism [eqn. (5)].

Triphenylmethyl chloride is practically stable at 105 °C (entry 14);|| unfortunately, its reaction with triphenylphosphine at 105 °C is also slow (entry 13). Strikingly, triphenylmethyl bromide is apparently stable when heated with *tert*-butylbenzene (entry 11). As shown, however, by our oxidation studies (entries 2, 4 and 5, Table 2) homolysis of its C–Br bond also takes place, as would be expected, in *tert*-butylbenzene, and at least some of the resulting triphenylmethyl radicals are trapped by oxygen. In the absence of both oxygen and cumene homolysis of the C–Br bond becomes reversible. As shown by these oxidation studies, homolysis of the C–Cl bond of triphenylmethyl chloride also takes place at 153 °C but not at 105 °C (compare entries 8 or 9 and 11, Table 2).

The Mechanism of the Reaction of Triphenylmethyl Halides and Phosphines.—The purpose of trapping experiments is to attempt to establish the *presence* in the reaction mixture of some reasonable reactive intermediate (triphenylmethyl radicals in our case) by forcing them to react with an added, and highly reactive, reagent, the trapping agent. After the failure of our trapping studies using either molecular oxygen or cumene as the trapping agents we decided to change our strategy and to try to establish the *absence* of an otherwise reasonable intermediate, *viz.* of triphenylmethanide anions, from our reaction mixtures.

A convenient starting point for this purpose was our observation that in none of the reactions of triphenylmethyl halides with tributyl-[3] or triphenyl-phosphines were even traces of dimer **4** formed. Dimer formation, in general, may take place according to the recombination [eqn. (15)] or the carbanionic mechanism[8] [eqn. (16)], both involving the semibenzene **3**[9] as the intermediate. (Dimethylcarbamoyl)diphenylmethyl radicals **5** (close congeners of the triphenylmethyl radicals) have been found previously[10] to be unable, under certain conditions, to recombine pairwise, to lead ultimately to the corresponding dimer (related to dimer **4**). Therefore, the non-formation of dimer **4** from triphenyl methyl halides and phosphines does not

$$\mathrm{Ph_2\dot{C}CONMe_2}$$

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[*] These radical cations may exert a decisive role in the conversion of triphenylmethylperoxy radicals, the primary trapping products of triphenylmethyl radicals by oxygen, into the final oxygenation products.[6]

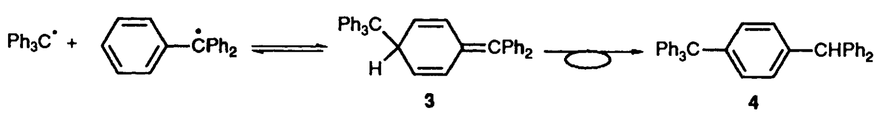
[†] The difference is less significant at lower temperature and with the chloride.

[‡] Although the chloride reacts rather slowly at 105 °C (74–76% of the substrate and the phosphine remained unchanged after 44 h), the trend mentioned is visible even here.

[§] Since the error in product yield determination is of the order of 1–2%, the difference in product composition is less significant in this case.

[¶] For related deprotonations of trialkylamine radical cations, see ref. 7.

[||] See also entry 11, Table 2.



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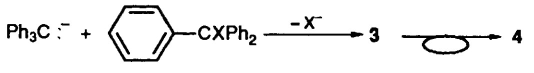

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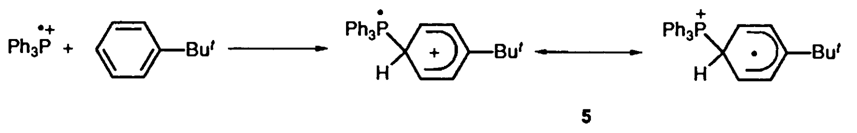

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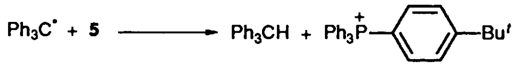

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appear to be incompatible with the intermediacy of triphenylmethyl radicals in these reactions and suggests that the non-formation of dimer **4** could, perhaps, be due to the non-formation of triphenylmethanide anions in these reaction mixtures.

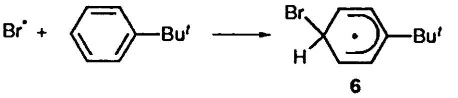
In order to prove (or disprove) this assumption, the reaction of triphenylmethyl chloride and triphenylphosphine in *tert*-butylbenzene at 153 °C under argon was repeated with dropwise addition of a freshly prepared THF solution of lithium triphenylmethanide to the hot reaction mixture. By isolation of significant amounts of dimer **4** the operation of the carbanionic mechanism of dimer formation [eqn. (16)] under these conditions was unequivocally proved. The fact that, without addition of separately prepared lithium triphenylmethanide, no dimer **4** is formed in the reactions of triphenylmethyl halides and phosphines, unequivocally proves that triphenylmethanide anions are not formed as intermediates. This, together with the results of the oxygen trapping experiments [which have ruled out eqn. (1a) as the reaction mechanism] proves that the reaction of triphenylmethyl halides with the tertiary phosphines studied takes place according to the mechanism described by eqns. (5) + (6)/(5) + (7).

An alternative explanation of the non-formation of dimer **4** [*viz.* that although triphenylmethanide anions are formed, they are unable to react with unchanged starting halide because they are instantaneously trapped by their co-products, the halophosphonium ions; eqn. (3a)] appears to be ruled out by our oxygen trapping studies, according to which the reaction of triphenylmethanide anions, if formed at all, with halophosphonium ions is not instantaneous.

Further evidence against the intermediacy of triphenylmethanide anions on the pathway leading to triphenylmethane in the reactions studied is the observation (entries 5 and 13, Table 1) that triphenylmethane, rather than its monodeuteriated derivatives, are formed when the reaction mixture is treated with 99% ^2H_2O prior to chromatographic work up. In these experiments no proton source was present in the reaction mixtures; therefore, any triphenylmethanide anions formed should either react with halophosphonium ions or survive until the mixture is treated with water or ^2H_2O during or prior to work-up, respectively, *i.e.* deuteriated material should have been formed in these cases.

Comparison of the results of experiments 10 and 11, 13 and 14, Table 1, 3 and 5, 7 and 8 or 10 and 11, Table 2, reveals that the amount of unchanged triphenylmethyl halide (detected, after work-up, as triphenylmethanol or an alkyl triphenylmethyl ether) is reduced if the reactions are carried out in the presence of added phosphines, *i.e.* that consumption of the halides is accelerated by phosphines. In other words, the phosphines do take part in the generation of the triphenylmethyl radicals, and formation of the latter does not only take place by thermally induced homolysis of the carbon-halogen bond of the starting halides.

Interestingly, small amounts of triphenylmethane were obtained even when triphenylphosphine was applied as the reagent and the reactions were run in *tert*-butylbenzene, as well as when the bromide was simply heated with *tert*-butylbenzene (entries 9–11 and 15–16, Table 1). What is the origin of the atomic hydrogen, necessary for the conversion of triphenylmethyl radicals into triphenylmethane, under these conditions? We believe that the triphenylphosphine radical cation formed according to eqn. (5) (R = Ph) is able to attack the solvent slowly [eqn. (17)] to furnish the radical cation **5** (*cf.* ref. 11) from which a hydrogen atom may be readily abstracted by a triphenylmethyl radical [eqn. (18)]. In the absence of triphenylphosphine the solvent is probably attacked by atomic bromine resulting from eqn. (13) to furnish radical **6** [eqn. (19)] which subsequently transfers a hydrogen atom to the triphenylmethyl radical [eqn. (20)]. (No attempt was made to detect the brominated solvent in the reaction mixture.) By summing up eqns. (13), (19) and (20), eqn. (21) is obtained.



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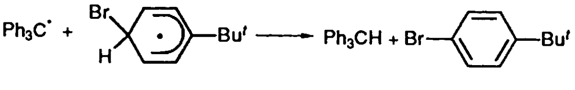

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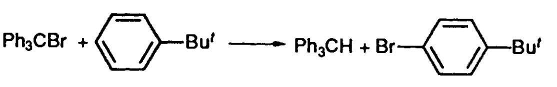

(21)

Experimental

M.p.s were determined in glass capillaries and are uncorrected. The progress of the reactions was followed by TLC (Kieselgel $60PF_{254}$, DC-Alufolien, Merck, Art. 5554). For the separations and purifications by preparative TLC 20 × 20 cm plates, coated with Kieselgel $PF_{254+366}$ were used. Known products were identified by comparison of their m.p.s, mixed m.p.s, R_f values, IR and, occasionally, ^1H NMR and mass spectra with those of authentic samples. ^1H and ^{13}C NMR spectra were recorded with a Varian XL-400 instrument, using tetramethylsilane as the internal reference. Coupling constants are in Hz. IR spectra were obtained with a Specord 75 spectrometer (Zeiss, Jena). EI mass spectra were recorded using an AEI MS 902 type instrument equipped with a direct sample introduction system; the ion accelerating voltage was 8 kV, the ionization current 100 μA; the temperature of the ion source was kept at 150 °C.

Isotope contents were determined from the 11 eV spectra of the ^{2}H-labelled samples; the accuracy was ±1%. Positive ion FAB mass spectra were obtained with a VG ZAB-2SEQ mass spectrometer with reversed geometry and equipped with a caesium ion gun; *m*-nitrobenzyl alcohol was used as the matrix solvent. EPR spectra were obtained with a JEOL JES-FE/3X instrument (100 kHz, field 3233 ± 50 G, mod. 0.26). Determination of the degree of deuteriation of various samples of triphenylmethane, by ^{1}H NMR spectroscopy, was carried out by comparing the intensity of the methine proton signal with that of the aromatic protons.

Starting Materials and Solvents.—Triphenylmethyl bromide (Merck), contaminated by small amounts of benzophenone was recrystallized from an acetic acid–acetic anhydride–phosphorus tribromide mixture (9:1:0.2, v/v). Triphenylmethyl chloride (EGA) was recrystallized from a heptane–thionyl chloride mixture (98:2, v/v). Both halides were dried and stored over KOH pellets and paraffin wax turnings at reduced pressure.

Cumene (BDH) and *tert*-butylbenzene[12] were distilled at normal pressure and stored over sodium wire under argon. Tetrahydrofuran was dried by first keeping it over KOH pellets and then refluxing it with excess $LiAlH_4$ for 6 h under argon; it was distilled and stored under argon.

Hexane solutions of butyllithium (*ca.* 1 mol dm^{-3}) (Aldrich) were used. Triphenylphosphine (*ca.* 99% Aldrich) [which did not contain detectable amounts (TLC; development EtOAc–hexane, 1:1) of triphenylphosphine oxide (R_f, phosphine *ca.* 1.0, phosphine oxide *ca.* 0.2)] was used without purification.

Synthesis of Authentic Samples of (4-*Diphenylmethylphenyl*)-*triphenylphosphonium Chloride and Bromide* (**2**, R = Ph, X = Cl *and* Br, *respectively*).—(*a*) The chloride [m.p. 254 °C (from MeCN), lit. m.p.[13] 240–242 °C] was obtained as described in the literature.[13] In spite of prolonged drying at 77 °C under reduced pressure over P_2O_5, our product still contained 1 mole of water of crystallization (^{1}H NMR). R_f (MeOH–acetone, 1:8) *ca.* 0.25. (Found: *m/z* 505.212. Calc. for $C_{37}H_{30}P^+$, *m/z* 505.209), *m/z* 505 (100%), 428 (4). δ_H($CDCl_3$, *ca.* 20 °C) 5.70 (s, ArC*H*Ph_2), 7.13, 7.26, 7.33 (3 × m, C*Ph*$_2$), 7.51, 7.53 (2 × m, C_6H_4), 7.62, 7.81, 7.92 (3 × m, $\overset{+}{P}Ph_3$). δ_C($CDCl_3$, *ca.* 20 °C) 56.79 (CH), 115.02 ($^1J_{C,P}$ 90; C_6H_4, C-1), 117.42 ($^1J_{C,P}$ 89; $\overset{+}{P}Ph_3$, 3 × C-1), 127.09 (CPh_2, 2 × C-4), 129.33 (CPh_2, 2 × C-2 + 2 × C-6), 128.79 (CPh_2, 2 × C-3 + 2 × C-5), 130.88 ($^3J_{C,P}$ 13; $\overset{+}{P}Ph_3$, 3 × C-3 + 3 × C-5), 131.64 ($^3J_{C,P}$ 13; C_6H_4, C-3 + C-5), 134.29 ($^2J_{C,P}$ 10; $\overset{+}{P}Ph_3$, 3 × C-2 + 3 × C-6); 134.34 ($^2J_{C,P}$ 11; C_6H_4, C-2 + C-6), 135.90 ($^4J_{C,P}$ 3; $\overset{+}{P}Ph_3$, 3 × C-4), 141.73 (CPh_2, 2 × C-1), 153.02 ($^4J_{C,P}$ 3; C_6H_4, C-4).

(*b*) The bromide [m.p. 235 °C (from CH_2Cl_2–Et_2O and then from MeOH–H_2O)] was similarly obtained, using 48% aqueous HBr instead of HCl. The bromide, too, contained 1 mole of water of crystallization. R_f (MeOH–acetone, 1:8) *ca.* 0.7 (Found: *m/z*, 505.212. Calc. for $C_{37}H_{30}P^+$: *m/z*, 505.209) *m/z* 505 (100%), 428 (5). δ_H($CDCl_3$, *ca.* 20 °C) 5.71 (s, ArC*H*Ph_2), 7.13, 7.26, 7.33 (3 × m, C*Ph*$_2$), 7.52, 7.54 (2 × m, C_6H_4), 7.64, 7.81, 7.91 (3 × m, $\overset{+}{P}Ph_3$). δ_C($CDCl_3$, *ca.* 20 °C): practically identical with those of the chloride.

Reactions of Triphenylmethyl Bromide and Chloride with Triphenylphosphine under Argon.—Mixtures of triphenylmethyl bromide or chloride and triphenylphosphine (3.1 mmol, each) in cumene or *tert*-butylbenzene (8.6 cm^3) were placed into thick-wall tubes, flushed with, and sealed under, argon as described in ref. 14 for the reaction of (4-chlorophenyl)di(*tert*-butylphenyl)methyl chloride with tributylamine, allowed to react under the conditions specified in Table 1 and allowed to cool. Except in experiments 5 and 13, the resulting reaction mixtures were evaporated to dryness at reduced pressure. The reaction mixtures obtained in experiments 5 and 13 were first vigorously stirred for 1 h with excess 99% ^2H_2O under argon and subsequently evaporated to dryness at reduced pressure. The dry residues were taken up in CH_2Cl_2 (60 cm^3) and water (30 cm^3) and the resulting mixtures were thoroughly shaken. The organic phases were dried ($MgSO_4$) and concentrated to *ca.* 3–4 cm^3 at reduced pressure. Addition of 40 cm^3 of diethyl ether caused the phosphonium salts **2** (R = Ph, X = Br and Cl, respectively) to precipitate. The crystalline products were triturated with the supernatants, kept for 1 day at room temperature and for 1 day in a refrigerator and filtered off. The bromide was recrystallized from methanol–water and the chloride from acetonitrile. Both phosphonium salts proved identical with the respective authentic samples (see above).

The filtrates of the crude phosphonium salts were worked up by TLC in two steps. By using toluene–hexane (1:10) as the solvent, triphenylmethane (of natural ^{2}H abundance even in experiments 5 and 13) (R_f 0.4) and, if present, unchanged Ph_3P (R_f 0.25) were obtained. Crude triphenylmethanol remained at the start and, after elution, was purified by using toluene–hexane (1:1) as the solvent (R_f 0.2). All products were eluted with methanol–CH_2Cl_2 (1:9, v/v).

For products and yields, see Table 1 entries 5–7, 9, 10, 12, 13, 15 and 16.

Control Experiments, carried out in the Absence of Triphenylphosphine.—The reactions were carried out under argon under the conditions specified in Table 1, and the reaction mixtures worked up as described above, except that the procedure for isolation of phosphonium salts was, of course, omitted. For products and yields, see Table 1 entries 8, 11 and 14.

Reaction of Triphenylmethyl Chloride with Triphenylphosphine under Oxygen.—(*a*) A vigorously stirred mixture of triphenylmethyl chloride and triphenylphosphine (3.1 mmol, each) in *tert*-butylbenzene (8.6 cm^3) was heated for 11 h at 153 °C in a stream of oxygen introduced through a glass capillary immediately above the surface of the mixture, and allowed to cool. Not even traces of the phosphonium salt **2** (R = Ph, X = Cl) were detected (TLC). A freshly prepared methanolic solution of a slight excess of sodium methoxide was added, the mixture stirred for 1 h at room temperature and evaporated to dryness at reduced pressure. The residue was taken up in CH_2Cl_2 (60 cm^3) and water (30 cm^3). The organic phase was washed with water (30 cm^3), dried ($MgSO_4$) and evaporated to dryness at reduced pressure. The residue was worked up by preparative TLC (toluene–hexane, 1:1). For products and yields, see Table 2, entry 7. (In the TLC system used triphenylphosphine oxide remained at the start and was discarded. No attempt was made to isolate any phenol formed.)

(*b*) A mixture, of identical composition to that in (*a*), of triphenylmethyl chloride, triphenylphosphine and *tert*-butylbenzene was heated for 40 h at 105 °C in a stream of oxygen and worked up as described in (*a*), except that the dry residue of the CH_2Cl_2 solution was triturated with diethyl ether, in order to induce the triphenylphosphine oxide formed to crystallize. The mixture was kept for 1 day in a refrigerator. The crystals were filtered off and washed with a small amount of diethyl ether. The combined filtrate and washings were evaporated to dryness and the residue was worked up by preparative TLC as described in (*a*). For products and yields, see Table 2, entry 10. (Again, no attempt was made to isolate any phenol formed.)

Control Experiments, carried out in the Absence of Triphenylphosphine.—The reactions were carried out under oxygen under the conditions specified in Table 2, and the reaction mixtures worked up as described above under (*a*). For products and yields, see Table 2, entries 8 and 11.

Thermolysis of Phosphonium Salt **2** (R = Ph, X = Cl) *in* tert-*Butylbenzene under Oxygen*.—A mixture of the title compound (0.4 g, 0.7 mmol) and dry *tert*-butylbenzene (8.6 cm^3) was heated for 36 h at 153 °C. The solvent was distilled off at reduced pressure, and the residue triturated with diethyl ether. The mixture was kept for 1 day in a refrigerator. The crystals of unchanged starting phosphonium salt (0.37 g, 92%) were filtered off, washed with a small amount of diethyl ether and identified by comparison with an authentic sample.

The combined filtrate and washing were found by TLC (toluene–hexane, 1:1) to contain only traces of benzophenone, somewhat larger amounts of two unidentified oxo compounds (which gave positive colour reactions with 2,4-dinitrophenylhydrazine on the TLC plate and were more polar than benzophenone), and not to contain triphenylmethanol.

Reaction of Lithium Triphenylmethanide with Oxygen.—Dry *tert*-butylbenzene (7.3 cm^3) was placed into a double-necked flask equipped with a glass capillary and a condenser with air-cooling, closed by a rubber septum through which a syringe, connected through a hose to a bubble-counter, had been passed. A continuous stream of oxygen was introduced through the capillary immediately above the surface of the liquid with continuous stirring at 153 °C. A lithium triphenylmethanide solution [freshly prepared under argon from triphenylmethane (0.64 g, 2.6 mmol) and butyllithium (3 cm^3 of a 1.0 mol dm^{-3} hexane solution, 3 mmol) in dry THF (10 cm^3)] was slowly injected through the septum within 2 h. Rapid decolourization of the organometallic took place. The mixture was stirred for a further 17 h at 153 °C with the introduction of oxygen continued, and then allowed to cool. Diethyl ether (50 cm^3) and 10% aqueous NaOH (25 cm^3) were added. The ethereal (A) and aqueous phases (B) were separated. The aqueous phase (B) was extracted with diethyl ether (30 cm^3) and treated with an ethereal (30 cm^3) solution of benzoyl chloride (0.6 g, 4.3 mmol), in order to benzoylate the sodium phenolate present. The mixture was vigorously shaken for 10 min. The ethereal phase (C) was separated, washed with water (20 cm^3) and saturated aqueous NaCl solution (20 cm^3), dried ($MgSO_4$) and evaporated to dryness. The residue was purified by TLC (ethyl acetate–hexane, 1:10) to yield phenyl benzoate (0.12 g, 23%) which proved identical with an authentic sample.

The combined ethereal phase A and ethereal extract of the aqueous phase B were washed with saturated aqueous NaCl solution (50 cm^3), dried ($MgSO_4$) and evaporated to dryness at reduced pressure. The residue was worked-up by preparative TLC (toluene–hexane, 1:1) to give triphenylmethane (55 mg, 9%; probably as a result of incomplete deprotonation of the triphenylmethane introduced), benzophenone (112 mg, 23%) and triphenylmethanol (336 mg, 49%), identified by comparison with authentic samples.

Reaction of Triphenylmethyl Chloride and Triphenylphosphine with Addition of Lithium Triphenylmethanide.—A solution of triphenylmethane (0.76 g, 3.1 mmol) in dry THF (11 cm^3) was stirred at room temperature in a similar apparatus to that used in the previous experiment in a continuous stream of argon introduced through the capillary immediately above the surface of the solution. Butyllithium (3.0 cm^3 of a 1.0 mol dm^{-3} hexane solution, 3.0 mmol) was slowly injected through the septum. The mixture was stirred for a further 2 h with introduction of argon continued, and divided into two equal parts.

A solution of triphenylmethyl chloride (0.86 g, 3.1 mmol) and triphenylphosphine (0.81 g, 3.1 mmol) in dry *tert*-butylbenzene (8.6 cm^3) was flushed with argon and stirred at 153 °C in a continuous stream of argon in a similar apparatus. After 30 min half of the above lithium triphenylmethanide solution was added dropwise at 153 °C with stirring and introduction of argon continued. Stirring and heating under argon was continued for 11 h. The mixture was then evaporated to dryness at reduced pressure. The residue was taken up in CH_2Cl_2 (100 cm^3) and water (50 cm^3). Conventional work-up of the CH_2Cl_2 phase and preparative TLC (toluene–hexane, 1:4) of its dry residue afforded 125 mg (17%) of dimer **4** identified by comparison with an authentic sample. Further products detected by TLC but not isolated, were the phosphonium salt **2** (R = Ph, X = Cl), triphenylmethane and triphenylmethanol.

In order to check the extent of lithiation of the starting triphenylmethane, the second half of the lithium triphenylmethanide solution was treated with 99% ^2H_2O (1.1 cm^3) whereupon immediate decolourization took place. The mixture was stirred for 1 h and evaporated to dryness at reduced pressure. The residue was taken up in CH_2Cl_2 (60 cm^3) and water (30 cm^3). The CH_2Cl_2 phase was dried ($MgSO_4$) and evaporated to dryness. The residue was recrystallized from ethanol to afford a product which, as shown both by mass and ^1H NMR spectroscopy, proved to be a *ca.* 1:1 mixture of Ph_3CH and Ph_3C^2H.

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