Reactions of some *p*-Substituted Triphenylmethyl Chlorides with Alcohols, Alkali-metal Alcoholates, and Tributylamine†

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The *p*-methoxylated triphenylmethyl chlorides (**4a–c**), when heated with alcohols, give mixtures of the corresponding triarylmethanes (**5a–c**) (*via* the hydride transfer to the corresponding triarylmethylium cations) and the alkyl (substituted triphenylmethyl) ethers (**7a–c**) (*via* polar substitution reactions). Part or all of the ether (**7c**) may be further converted into the substituted triphenylmethanol (**6c**). In the reaction of the mono-*p*-methoxylated halides (**4a**) and (**4c**) with methanol, the substitution products (**7a**) and (**7c**) [and/or (**6c**)] are formed as the main products, while the main product of the reaction of the di-*p*-methoxylated halide (**4b**) with methanol is the substituted triphenylmethane (**5b**). When the methanol is replaced by [$^2H_4$] methanol, no reduction product is formed from the halide (**4c**). Reaction of halide (**4c**) with ethanol furnishes exclusively the substituted triphenylmethane (**5c**). The *p*-chlorophenyl(diphenyl)methyl chloride (**4d**) gives, with methanol, mainly or exclusively the ether (**7d**), and with ethanol, under mild conditions, gives the ether (**9d**). However, under vigorous conditions, the substituted triphenylmethane (**5d**) is formed. The reduction of the *p*-methoxylated triphenylmethyl chloride (**4c**) by alcohols as well as its conversion into alkyl (*p*-methoxylated triphenylmethyl) ethers are accompanied, to a certain degree, by exchange of the *p*-methoxy group of the substrate and the alkoxy group of the alcohol; no similar exchange of the *p*-chlorine atom of halide (**4d**) was observed. Explanations for all observed differences are offered.

The reactions of the substituted triphenylmethyl chlorides (**4b–d**) with alkoxides in the corresponding alcohols give the corresponding alkyl (substituted triphenylmethyl) ethers (**7b**), (**7c**), (**9c**), and (**9d**), respectively, in excellent yields.

The reaction of the triarylmethyl chloride (**4d**) with potassium t-butoxide in THF in the presence of acetone led, among other products, to the formation of oligomeric material which indicates the operation of single-electron-transfer induced processes. Reaction of the same chloride (**4d**) with tributylamine in refluxing cumene or t-butylbenzene led to the exclusive formation of a series of products [(**5d**) and (**14**)–(**17**)] all of which may be derived from the intermediacy of the substituted triphenylmethyl radical (**18**); the latter, in turn, is thought to arise as a result of dissociative electron transfer from tributylamine to chloride (**4d**).

The triphenylmethyl halides (**1a, b**), their derivatives substituted in the aromatic ring(s), and related compounds may undergo, with nucleophiles, different types of reactions, depending on the conditions, the nature of the nucleophile, and the nature of the substituent present. Such reactions include (*i*) simple *ipso* and/or *tele* substitutions by polar mechanisms in protic solvents;[2–4] (*ii*) single-electron transfer (SET) initiated reactions in the presence of alkoxides[1,5,6] and amines[7] in aprotic solvents; these reactions involve the intermediacy of triphenylmethyl and related radicals;§ (*iii*) in the case of substrates which either exist as triarylcarbenium salts or which readily furnish carbenium ions, *e.g.* compounds (**2a**) and (**2b**), hydride transfer from *n*-nucleophiles (including alcohols and ethers containing α-hydrogen atoms, as well as formic acid) to these cations to yield the corresponding triphenylmethanes (**1c**) and (**3a**), respectively.[8,¶] Those substrates which exist, under the reaction conditions studied, as triarylcarbenium salts, *e.g.* compound (**2b**), do not undergo SET induced reactions even in aprotic solvents. Thus, compound (**2b**) furnishes, with sodium methoxide, both in methanol and in a series of aprotic solvents, the *ipso* substitution product (**3b**) as the only product.[9]

Ph_3CX (**1**)
a; $X = Cl$
b; $X = Br$
c; $X = H$
d; $X = OMe$
e; $X = OBu^t$
f; $X = OH$

$(4\text{-}RC_6H_4)_3C^+X^-$ (**2**)
a; $R = H$, $X = ClO_4$
b; $R = MeO$, $X = Cl$

$(4\text{-}MeOC_6H_4)_3CR$ (**3**)
a; $R = H$
b; $R = OMe$

Reduction of tris(4-methoxyphenyl)carbenium chloride (**2b**) by methanol to the corresponding triphenylmethane (**3a**) has been shown by deuterium tracer studies, to be accompanied by considerable exchange of the methoxy groups of the substrate and the solvent methanol.[2]

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† Single electron-transfer initiated thermal reactions of arylmethyl halides, Part 13; for Part 12, see ref. 1

‡ Partly based on the Theses of Gy. Gergácz, Technical University Budapest, 1985 and 1987.

§ For additional pathways leading to these radicals, see ref. 5.

¶ For conflicting views concerning the mechanism of these hydride-transfer reactions, see ref. 8.

Table 1. Reaction of triphenylmethyl chloride (**1a**) and its methoxylated derivatives (**4a**), (**4b**), and (**2b**) with methanol.[a]

Starting triarylmethyl chloride	Products and yields (%)	
	Triarylmethane[b]	Methyl triarylmethyl ether[c]
(**1a**)	(**1c**) —[d]	(**1d**) 95[d]
(**4a**)	(**5a**) 37	(**7a**) 56
(**4b**)	(**5b**) 80	(**7b**) 15
(**2b**)	(**3a**) 94[d]	(**3b**) —[d]

[a] The starting chlorides (1 mmol) were heated with anhydrous methanol (7.3 cm^3) in sealed tubes for 60 h at 105 °C. [b] Reduction product. [c] *ipso* Substitution product. [d] From ref. 2.

Because of the pronounced effect of the three methoxy groups of compound (**2b**) on its reactivity we thought it desirable to study the effects of one and two methoxy groups as well as of one chlorine ligand on the reactions of substituted triphenylmethyl chlorides (**4a–d**) with nucleophiles.

Results and Discussion

Preparation of the Starting Compounds (**4a–d**) *and of the Triarylmethanes* (**5a–d**).—4-Methoxyphenyl(diphenyl)methyl chloride (**4a**),[10] and its reduction product (**5a**)[11] were obtained as described in the literature. Bis-(4-methoxyphenyl)phenylmethyl chloride (**4b**) was obtained by treatment of 4-methoxybenzophenone[12] with 4-methoxyphenylmagnesium bromide and of the resulting alcohol (**6b**) with thionyl chloride. The triarylmethyl chlorides (**4c**) and (**4d**) were obtained by treatment of 4-(t-butyl)phenylmagnesium bromide with methyl 4-methoxy- and 4-chloro-benzoate, respectively, and of the resulting triarylmethanols (**6c**) and (**6d**) with thionyl chloride.

$$(4\text{-RC}_6\text{H}_4)(4\text{-R}'\text{C}_6\text{H}_4)_2\text{CCl}$$
(**4**)

$$(4\text{-RC}_6\text{H}_4)(4\text{-R}'\text{C}_6\text{H}_4)_2\text{CH}$$
(**5**)

$$(4\text{-RC}_6\text{H}_4)(4\text{-R}'\text{C}_6\text{H}_4)_2\text{C(OH)}$$
(**6**)

$$(4\text{-RC}_6\text{H}_4)(4\text{-R}'\text{C}_6\text{H}_4)_2\text{C(OMe)}$$
(**7**)

$$(4\text{-RC}_6\text{H}_4)(4\text{-R}'\text{C}_6\text{H}_4)_2\text{C(OC}^2\text{H}_3)$$
(**8**)

$$(4\text{-RC}_6\text{H}_4)(4\text{-R}'\text{C}_6\text{H}_4)_2\text{C(OEt)}$$
(**9**)

$$(4\text{-RC}_6\text{H}_4)(4\text{-R}'\text{C}_6\text{H}_4)_2\text{C(OBu}^t)$$
(**10**)

(**4**)–(**10**) **a**; R = MeO, R′ = H **d**; R = Cl, R′ = Bu^t
b; R = H, R′ = MeO **e**; R = C^{2}H$_3$O, R′ = Bu^t
c; R = MeO, R′ = Bu^t **f**; R = EtO, R′ = Bu^t

Authentic samples of the triarylmethanes (**5b–d**) were obtained by reduction of the alcohols (**6b–d**), respectively, with refluxing formic acid. The reduction required much longer times in the (**d**) than in the (**b**) and (**c**) series; this is in agreement with the superior cation-stabilizing ability of the *p*-methoxy group(s). For the same reason, the reaction mixtures in the (**b**) and (**c**) series were initially deep red, their colours gradually fading with the progress of the reaction, while not even transient colouration of the reaction mixture was observed in the (**d**) series.

Reactions with Alcohols.—The results of these studies are shown in Tables 1 and 2. Depending on the structures of the substrates, the nature of the alcohol used, and the reaction conditions applied, either reduction products of type (**5**) or *ipso* substitution products of types (**7**)–(**10**) or mixtures of these products were obtained; in some cases the original substitution products (or some of them) were hydrolysed during work-up to the corresponding alcohols of type (**6**) (Table 2, entries 1–3 and 5). Some more important observations are listed and discussed below.

(*i*) The reactions of the (4-methoxyphenyl)diphenylmethyl (**4a**) and the bis-(4-methoxyphenyl)phenylmethyl chlorides (**4b**) gave mixtures of the reduction [(**5a**) and (**5b**), respectively] and *ipso* substitution products [(**7a**) and (**7b**), respectively],* the product ratios being intermediate between those observed earlier[2] for the reactions of the non-methoxylated chloride (**1a**) (where virtually no reduction product was formed) and the tris-(4-methoxy) derivative (**2b**) (where virtually exclusive formation of the reduction product was observed) (Table 1).

(*ii*) The reaction of the chloride (**4c**) with methanol (Table 2) (both in the presence and absence of the co-solvent dichloromethane) yields mainly a substitution product, the alcohol (**6c**) with minor amounts of the reduction product (**5c**) (entries 1 and 2), while the reaction with ethanol (entries 4 and 6) yields exclusively the reduction product (**5c**). When the solvent methanol was replaced by [^{2}H$_4$]methanol (99.5 atom% ^{2}H) (entries 3 and 5) no reduction (deuterio-dechlorination) at the central carbon atom took place, the only products isolated being mixtures of the substitution product [the methyl ether (**7c**) and all its possible trideuteriomethoxy analogues (**7e**), (**8c**), and (**8e**)] and the hydrolysis products (**6c**) and (**6e**) of these ethers. The ratios of the isotopomers were determined by mass spectrometry. The following values were obtained: (**7c**):(**7e**):(**8c**):(**8e**) = 1:3:19:77, (**6c**):(**6e**) = 20:80 and, for a reaction carried out under somewhat different conditions, (**6c**):(**6e**) = 10:90. Thus, exchange of methoxy groups between substrate and solvent takes place to a considerable extent and, in this respect, the behaviour of the chloride (**4c**) is similar to that of the related chloride (**2b**); the latter, however, was completely reduced to the triarylmethane (**3a**) when refluxed with methanol.[2]†

(*iii*) Formation of the reduction product (**5c**) from chloride (**4c**) when the latter was refluxed with ethanol–CH$_2$Cl$_2$ mixtures was similarly accompanied by exchange of the methoxy group of the substrate and the ethoxy group of a solvent molecule. The

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* Whether the substitutions and reductions were accompanied by methoxy-group exchange between the substrates and the solvent was not studied.

† The exchange of the methoxy groups of compound (**2b**) with the solvent methanol has previously been stated to be independent of the reductive dechlorination at the central carbon atom and to take place by an S$_N$2Ar reduction on the tris(4-methoxyphenyl)carbenium ion.[2] Regrettably, it was also claimed[2] that this was the first example of such a reaction which, as pointed out by Professor J. F. Bunnett in a personal communication, is, however, wrong. The isomerisation of tris(4-bromophenyl)methyl chloride in liquid SO$_2$ into bis-(4-bromophenyl)-(4-chlorophenyl)methyl bromide, described by Gomberg,[13] is just such a reaction.

Table 2. Reactions of the triarylmethyl chlorides (**4c**) and (**4d**) with alcohols.[a]

		Alcohol	Cosolvent		Yields (%)	
Entry	Starting chloride	cm^3/mmol chloride (mmol/mmol chloride)		Reflux time/h	Reduction product	Substitution product
1	(**4c**)	MeOH[b] 8.33	—	30	(**5c**) 7	(**6c**)[c] 64
2	(**4c**)	MeOH[b] 1.43	CH_2Cl_2[b] 2.86	30	(**5c**) 11	(**6c**)[c] 66
3	(**4c**)	$C^2H_3O_2H$[b,d] 1.43 (35.3)	CH_2Cl_2[b] 2.86	20	—	(**6c**) + (**6e**),[e,f] 1:9,[g] 45.5[h]
4	(**4c**)	EtOH[b] 2.1 (36)	CH_2Cl_2[b] 4.2	50	(**5c**)[i] 69	—
5[k]	(**4c**)	$C^2H_3O^2H$[b,d] 0.85 (20.9)	CH_2Cl_2[b] 4.2	26 38 °C[l]	—	(**7c**) + (**7e**) + (**8c**) + (**8e**) 1:3:19:77[m] 44[h] (**6c**)[e] + (**6e**),[e] 20:80[m] 29[h]
6	(**4c**)	EtOH[b] 1.24 (20.9)	CH_2Cl_2[b] 4.2	26 41 °C[l]	(**5c**)[n] 82	—
7	(**4d**)	MeOH[b] 4.25	—	0.5	—	(**7d**) 96[o]
8[p,q]	(**4d**)	MeOH[b] 7.3	—	60[r]	(**5d**)[s] 6	(**7d**)[s] 86
9	(**4d**)	MeOH[b] 1.67	CH_2Cl_2[b] 8.33	0.5	—	(**7d**)[t] 98
10	(**4d**)	EtOH[b] 8.33	—	20	(**5d**) 12	(**9d**) 76
11	(**4d**)	EtOH[b] 7.3	—	60[r]	(**5d**)[u] 93	—
12	(**4d**)	EtOH[b] 1.67	CH_2Cl_2[b] 8.33	10	—	(**9d**)[t] 98

[a] For the general procedure used, see the Experimental section; for modified procedures, see footnotes *k* and *o*–*t*. [b] Anhydrous. [c] Mainly formed by hydrolysis during work-up of the originally formed methyl ether (**7c**). As shown from separate experiments, the hydrolysis of (**7c**) starts during elution on the t.l.c. plate with CH_2Cl_2–MeOH (1:1) (as a result of the presence of traces of water) and becomes virtually complete when the eluate is allowed to stand for several hours at room temperature. [d] 99.5 Atom% ^2H. [e] Mainly formed by hydrolysis during work-up of the originally formed dueteriated ethers (**8c**), (**8e**), and (**7e**), and of the non-deuteriated ether (**7c**). [f] Traces of the non-hydrolysed ether (**8e**), $M^{+\bullet} = 422$, were detected by mass spectrometry in the product. [g] The ratio of the alcohol (**6c**) and its deuteriated analogue (**6e**) was determined by comparing the intensities of the *m*/*z* 405 and 402 peaks [$M^{+\bullet}$ of (**6e**) and (**6c**), respectively] in the mass spectrum, and by comparing the intensity of the 4-methoxy signal with those of the t-butyl and ArH signals in the ^1H n.m.r. spectrum. [h] Total yield. The ratio of the isotopomers was taken into account for calculation of the yield. [i] Contaminated, according to its ^1H n.m.r. spectrum, by *ca.* 5% of the ethoxy homologue (**5f**) [extra weak signals in addition to those of an authentic sample of (**5c**): *ca.* δ 1.3 (blurred by the t-butyl signal) and 3.97 (q)]. The presence of the contaminant is revealed also by the mass spectrum exhibiting the $M^{+\bullet}$ peak (*m*/*z* 400) of (**5f**). [k] Dry THF was used as the eluant after t.l.c. separation of the products. [l] Boiling point of the reaction mixture. [m] For the determination of the isotopomer ratios, see the text and Tables 3 and 4. [n] Contaminated, according to its ^1H n.m.r. spectrum, by *ca.* 20% of the ethoxy homologue (**5f**). The intensity ratio of the ethoxy quartet (δ_H 3.97) and the 4-methoxy singlet (δ_H 3.74) was *ca.* 17:100. [o] The crystalline product, m.p. 153–154 °C (from MeOH–DMF), separated from the reaction mixture on cooling (Found: C, 79.75; H, 7.95; Cl, 8.55. $C_{28}H_{33}ClO$ requires C, 79.9; H, 7.9; Cl, 8.4%); δ_H(60 MHz): 1.25 (18 H, s, 2 × Bu^t), 2.98 (3 H, s, MeO), and 7.25–7.5 (12 H, m, ArH). [p] The dry residue of the reaction mixture was extracted with CH_2Cl_2 without previous treatment with aqueous $NaHCO_3$ solution. [q] Hexane was used as the solvent for the t.l.c. separation. [r] The reaction mixture was heated for 60 h at 105 °C in a sealed tube. [s] No 4-methoxy analogues (**5c**) and (**7c**) of the resulting products (**5d**) and (**7d**) were detected when these products were subjected to t.l.c. (hexane) although, as shown by separate experiments, compounds (**5c**) [and its 4-ethoxy analogue (**5f**)] and (**7c**) are readily separated from compounds (**5d**) and (**7d**), respectively, under these conditions. [t] The product was isolated by treatment of the dry residue of the reaction mixture with aqueous $NaHCO_3$ and subsequent crystallization. [u] The product was isolated by crystallization of the dry residue of the reaction mixture without pretreatment with aqueous $NaHCO_3$. No contamination by the 4-ethoxy derivative (**5f**) of the reduction product (**5d**) was detected by t.l.c. (hexane; *cf.* footnote *s*).

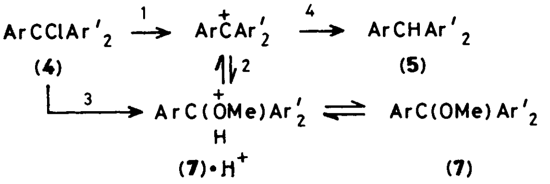
extent of this exchange (5–20%) was markedly lower than that of the exchange of methoxy and [$^2H_3$]methoxy groups.

(*iv*) Reaction of the chloride (**4d**) with methanol (both in the absence and presence of CH_2Cl_2 as the co-solvent) similarly furnished the methoxy substituted product (**7d**) which, in contrast with the analogous product of the **c** series, did not undergo hydrolysis to the corresponding alcohol (**6d**) during work-up. Only under forcing conditions (entry 8, Table 2) were small amounts of the reduction product (**5d**) obtained. With ethanol, depending on the reaction conditions, the analogous ethyl ether (**9d**) was obtained either exclusively or in the form of a mixture with minor amounts of the reduction product (**5d**), the latter becoming the main product under forcing conditions (compare entries 10–12 of Table 2).

(*v*) Comparison of the reactions of the chlorides of the 4-methoxy (**4c**) and the 4-chloro series (**4d**) with ethanol reveals that the former is much more susceptible to reduction to the corresponding triarylmethane.

A further difference between the chlorides (**4c**) and (**4d**) is that, while ethanolysis (and methanolysis), and reduction of the former are accompanied by partial exchange of the 4-methoxy group of the substrate and the alkoxy groups of the solvents, no similar replacement of the 4-chloro substituent of (**4d**) takes place.

The effects of substrate structure, nature of the alcohol used, and reaction conditions on the reactions of triarylmethyl chlorides with alcohols, in particular, on the product ratios, may be rationalised in terms of Scheme 1. Two distinct pathways are



Scheme 1. For explanations, see the text.

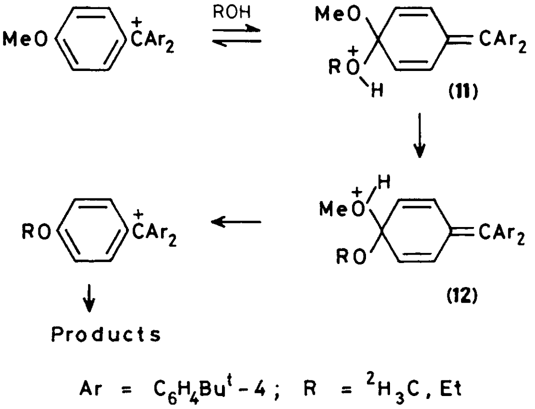
assumed for the conversion of the halides (**4**) into the protonated methyl ethers (**7**)·H$^+$, *viz.* one involving triarylcarbenium ions as intermediates* (S_N1 pathway, reactions 1 and 2) and one not involving such intermediates (non-S_N1 pathways,† reaction 3). Because of the presence of a hydride donor (an alcohol) in the reaction mixture, conversion of the triarylcarbenium ions into the corresponding triarylmethanes (**5**) (reaction 4) competes with their conversion into the protonated ethers (**7**)·H$^+$. For a given triaryl carbenium ion the relative rates of reactions 2 and 4 should depend on the hydride-donating ability of the alcohol used. That is, since ethanol is known to be a better hydride donor than methanol, the ratio v_4/v_2 of the reaction rates should, under identical conditions, be larger with ethanol than with methanol. It is, furthermore, assumed that while formation of the hydride-transfer products (**5**) (reaction 4) is irreversible, reaction 2 is reversible, at least for sufficiently stable triarylcarbenium ions.

The latter assumption is supported by (*a*) the observation that the ethyl ether (**9d**) or the reduction product (**5d**) were obtained as the main or exclusive products, depending on whether the reaction of chloride (**4d**) with ethanol was carried out under mild or forcing conditions (Table 2, entries 10–12), and (*b*) that the ethyl ether, when heated with ethanolic hydrogen chloride, was converted into the triarylmethane (**5d**). Similarly, methyl tris(4-methoxyphenyl) ether (**3b**) was smoothly converted into the corresponding triarylmethane when refluxed with methanolic hydrogen chloride, while methyl triphenylmethyl ether (**1d**) did not change on similar treatment.[8a]

According to Scheme 1, the amount of the hydride-transfer products (**5**) should increase when (*a*) the stability of the cations corresponding to the starting chlorides (**4**) increases [since ionisation of both the starting chlorides (**4**) and of the protonated ethers (**7**)·H$^+$ is thereby favoured], (*b*) the hydride-donating ability of the alcohol used increases, and (*c*) more vigorous conditions (higher temperatures, longer reaction times) promoting heterolysis of the protonated ethers (**7**)·H$^+$ are applied. All these expectations are borne out by findings (*i*)–(*v*) mentioned above, *e.g.* by the observation that the relative amount of the hydride-transfer products increases with the number of *para*-methoxy groups present and when the 4-chloro is replaced by the 4-methoxy substituent.

The non-formation of the deuteride-transfer product from the chloride (**4c**) when refluxed in [$^2H_4$]methanol–CH_2Cl_2 (Table 2, entries 3 and 5), and formation of the analogous hydride-transfer product (**5c**), which takes place to a certain extent with methanol under similar conditions, are thought to result from different kinetic isotope effects (k.i.e.) on the two competing reactions (reactions 2 and 4, Scheme 1) of the triarylcarbenium ions. In the former, a primary k.i.e. (estimated value k_H/k_D *ca.* 3–4[14]) operates while in the latter it is a secondary k.i.e. Thus, the rate of reduction of the chloride (**4c**) is considerably reduced when the solvent is changed from methanol to [$^2H_4$]methanol while the rate of nucleophilic substitution at the central carbon atom will be slightly reduced. As a result, the relative rate of substitution and reduction may be expected to increase considerably when the solvent methanol is replaced by its [$^2H_4$]analogue.

The non-formation of the deuteride-transfer product from (**4c**) under our experimental conditions does not mean that deuteride transfer from [$^2H_4$]methanol to triarylcarbenium ions is impossible in principle. On the contrary, we believe that under more vigorous conditions, in which heterolysis of the central C–O bond of the alkyl triarylmethyl ethers formed is favoured, *i.e.* regeneration of the corresponding triarylcarbenium ions, the deuteride transfer products would become the main or even exclusive products, *cf.* ref. 8(*a*).



Scheme 2.

The exchange of alkoxy groups between the substrates and the solvent (Table 2, entries 3–6) is thought to take place as shown in Scheme 2. The initial step clearly competes with hydride (or deuteride) transfer to the carbenium cation (reaction 4, Scheme 1); the extent of alkoxy exchange should, therefore, decrease with the hydride-(deuteride)-donating ability of the alcohol used, *i.e.*, in agreement with our findings, be greater for [$^2H_4$]methanol than for ethanol. The co-product of alkoxy exchange between the chloride (**4c**) and [$^2H_4$]methanol is 'light' methanol, which explains the observation that the 'light' methyl ether (**7c**) is formed in addition to all the trideuteriomethoxy analogues in the reaction of chloride (**4c**) with [$^2H_4$]methanol (Table 2, entry 5).

The failure of the chloride (**4d**) to undergo similar exchange of the 4-chlorine substituent for an alkoxy group of the solvent alcohol does not necessarily mean that the nucleophilic solvent is unable to attack the chlorine-bearing aromatic carbon atom of (**4d**). A more probable explanation appears to be the inability of the resulting semibenzene-type intermediate (**13**) to undergo the necessary subsequent prototropic rearrangement, whereas the analogous rearrangement (**11**) ⟶ (**12**) takes place readily in the 4-methoxy series.

Reaction of the Triarylmethyl Chlorides (**4b–d**) *with Sodium Methoxide and Ethoxide in the Corresponding Alcohols.*—The exclusive products, obtained in 90–95% yield were the methyl ethers (**7b**) and (**7c**), and the ethyl ethers (**9c**) and (**9d**), respectively.

Attempts to Induce SET Reactions of the Chloride (**4d**).—While triphenylmethyl chloride and bromide (**1a, b**) undergo exclusively polar substitution reactions with alkoxides in protic solvents,[4] in aprotic solvents competition between polar and

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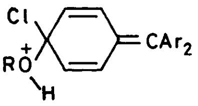
* The assumption of carbenium ions as distinct intermediates is supported by the colour changes accompanying the reactions of chloride (**4c**) with methanol and ethanol.

† The exact nature of the non-S_N1 pathways is irrelevant in the present connection. For a non-S_N1 pathway involving semibenzene-type intermediates, see ref. 5.



(13)

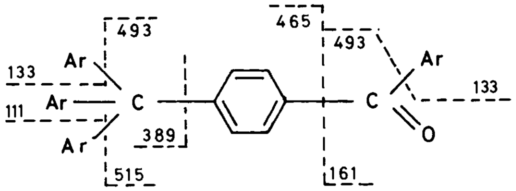
SET induced reactions has been observed.[1,5] The reaction of the chloride (**4d**) with alkoxides (sodium methoxide, potassium t-butoxide) in aprotic solvents (benzene, THF) was, therefore, studied. Chloride (**4d**), rather than (**4a–c**), was chosen for this study since the 4-methoxy groups of compound (**2b**) have been found to reduce, as a result of their cation-stabilising effect, the ability of this compound to act as a single-electron acceptor.[9]

Reaction of the chloride (**4d**) with sodium methoxide both in refluxing THF and benzene led to mixtures of the methyl ether (**7d**) and the alcohol (**6d**), the latter probably resulting from hydrolysis of unchanged starting material during work-up. With potassium t-butoxide in refluxing THF, the only product obtained from (**4d**) was the alcohol (**6d**); since t-butyl triphenylmethyl ether (**1e**) is known to be hydrolysed under mild conditions to the alcohol (**1f**),[1] the precursor of the alcohol (**6d**) may be the ether (**10d**).

The enolate anion of acetone is known to be a better electron donor than the methoxide anion.[15] The reaction of (**4d**) with potassium t-butoxide was therefore repeated in the presence of 1 mol equiv. of acetone. As shown by its mass spectrum, a mixture of oligomeric products was obtained in this case, in addition to the alcohol (**6d**). The formation of oligomers (*cf.* refs. 1 and 16) suggests the operation of SET processes in the presence of acetone; however, all our attempts to isolate pure individual oligomers failed. Similar results were obtained when the amount of acetone added was increased, the reaction was carried out with u.v. irradiation, or the solvent THF was replaced by the less volatile t-butylbenzene.

Triethylamine in refluxing benzene is known to act as single-electron donor towards halides related to compounds (**1a**, **b**).[7] Chloride (**4d**) was therefore allowed to react with tributylamine in refluxing cumene and t-butylbenzene. (Higher temperatures are known to promote SET reactions of halides relative to competing S_N reactions.[16,17]). When the reaction was carried out in cumene, four products, namely, the triarylmethane (**5d**) (23%), the 'dimeric' ketone (**14**) (1.6%), and the two benzophenones (**15**) (2.7%) and (**16**) (60%), were obtained. When the solvent cumene was replaced by t-butylbenzene, the three ketonic products (**14**) (5–26%), (**15**) (23–29%), and (**16**) (17–30%) were obtained, but not the triarylmethane (**5d**). In one case the triarylmethanol (**17**) was obtained instead of the dimeric ketone (**14**); these two compounds had, in the t.l.c. system used, very similar R_F values. When the reaction in t-butylbenzene was carried out with continuous bubbling of dry oxygen through the refluxing mixture, only the two benzophenones (**15**) (27%) and (**16**) (18%) were obtained. When the reaction was carried out under argon, the triarylmethane (**5d**) was the main product both in cumene (52%) and t-butylbenzene (46%), compound (**17**) being the minor product (*ca.* 7%) in both solvents. The benzophenones (**15**)[18] and (**16**)[19] are known compounds.

The structures of compounds (**14**) and (**17**) were deduced from their mass spectra, combined with mechanistic considerations (see below). Thus, peak matching of the molecular ion of compound (**14**) led to the molecular formula $C_{44}H_{47}ClO$; furthermore, elimination of a chlorophenyl group (corroborated by the observation of the corresponding metastable peak at *m/z* 423.7) furnished a fragment the formula of which was shown, by peak matching, to be $C_{38}H_{43}O$; finally, the base peak of the mass spectrum was shown, by peak matching, to correspond to the triarylcarbenium cation $(4\text{-}ClC_6H_4)(4\text{-}Bu^tC_6H_4)_2C^+$. The main fragmentation modes of compound (**14**) are shown below.

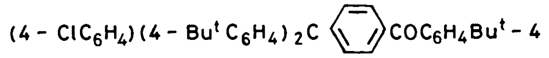


$Ar = 4\text{-}Bu^tC_6H_4$

$Ar' = 4\text{-}ClC_6H_4$

Elimination of a t-butylphenyl group from the molecular ion of compound (**17**) (corroborated by the corresponding metastable peak at *m/z* 517.2), on the other hand, furnished a fragment of formula, shown by peak matching, to be $C_{44}H_{48}ClO$.

The formation of compounds (**5d**) and (**14**)–(**17**) suggests that, in our experiments, tributylamine acts as a single-electron donor towards the triarylmethyl chloride (**4d**) and induces, probably by dissociative ET, the formation of the corresponding triarylmethyl radical (**18**) [equation (1)]. The latter subsequently furnishes, by hydrogen abstraction from the solvent cumene (but not from the solvent t-butylbenzene), the triarylmethane (**5d**) either directly [equation (2a)] or indirectly *via* a semibenzene-type intermediate [(**19**) or its isomers with the hydrogen atom attached to an *ortho* position or to one of the $4\text{-}Bu^tC_6H_4$ groups; equation (2b); *cf.* refs. 4, 5, 7, and 16]. Alternatively, radical (**18**) may either react (in both solvents) with oxygen to give the triarylmethylperoxyl radical (**21**) [equation (3)], or be reduced by a second molecule of the amine to the triarylmethanide anion (**20**) [equation (4); *cf.* ref. 7]. [For an alternative mode of formation of the triarylmethanide anion (**20**), see equation (2).] Triarylmethyl hydroperoxides are known to fragment on being heated to give benzophenones and phenols, a further product of this thermolysis being the corresponding triarylmethanol.[20] This suggests that the peroxy radical (**21**) could be the precursor of the ketones (**15**) and (**16**) [equations (5)]; isolation of the corresponding phenols, *viz.* 4-(t-butyl)- and 4-chloro-phenol has not been attempted. Experiments to uncover the details of these transformations are in progress.



$(4\text{-}ClC_6H_4)(4\text{-}Bu^tC_6H_4)_2C\text{-}C_6H_4\text{-}COC_6H_4Bu^t\text{-}4$

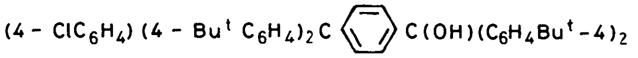
(14)

$(4\text{-}ClC_6H_4)(4\text{-}Bu^tC_6H_4)C{=}O$

(15)

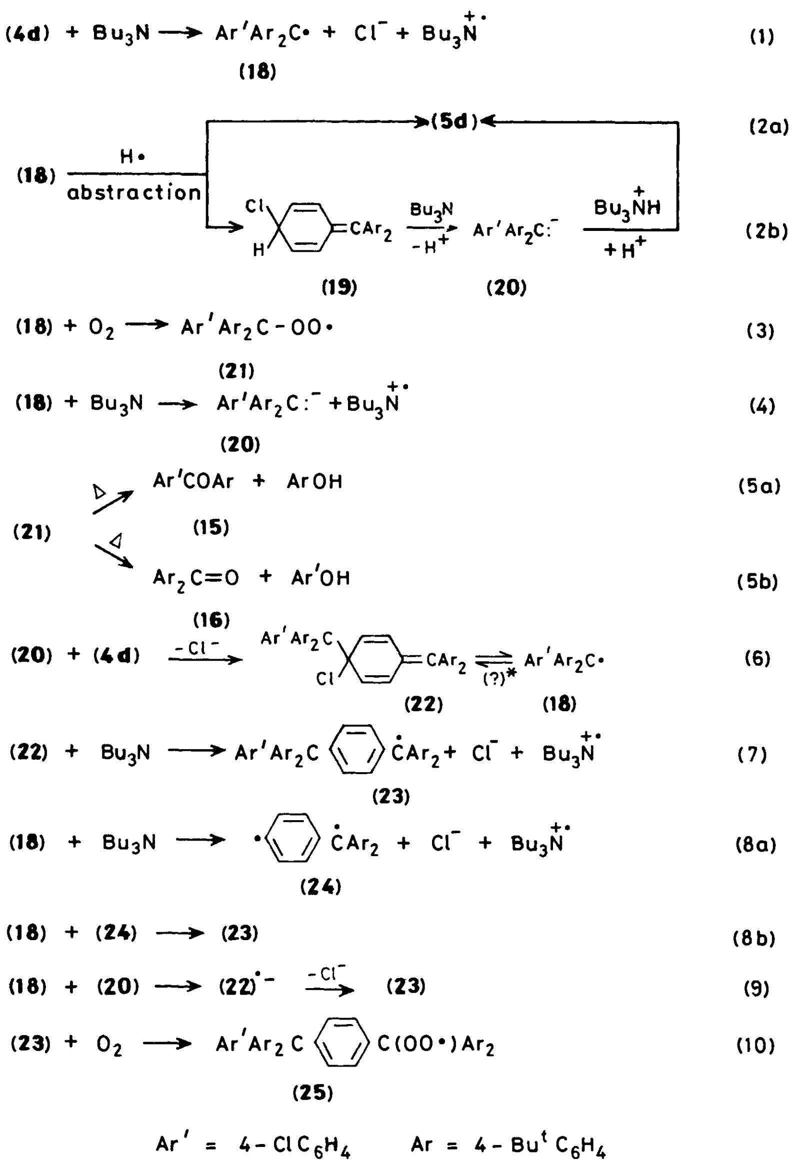
$(4\text{-}Bu^tC_6H_4)_2C{=}O$

(16)



$(4\text{-}ClC_6H_4)(4\text{-}Bu^tC_6H_4)_2C\text{-}C_6H_4\text{-}C(OH)(C_6H_4Bu^t\text{-}4)_2$

(17)



Reaction of the carbanion (**20**) with unchanged starting halide leads to the dimer (**22**) [first step of equation (6); *cf.* refs. 7 and 16]; formation of dimer (**22**) by recombination of two radicals (**18**), *i.e.* a reversal of the second step of equation (6) is, by analogy with a related case,[7] unlikely. Dimers of type (**22**), *e.g.* the dimer of the triphenylmethyl radical, are known to dissociate easily into two triarylmethyl radicals,[21] in the present case into two radicals (**18**) [second step of equation (6)]. Alternatively, dimer (**22**) should be able to react with a molecule of tributylamine to give, again, probably by dissociative ET, the 'dimeric' radical (**23**) [equation (7)]. Dehalogenations of dimers of type (**22**) have been observed by Gomberg[22] (dehalogenations by 'molecular' silver) and by Aruzov[23] (dehalogenations by sodium diethylphosphite); dehalogenation by these reagents probably also takes place by a dissociative ET mechanism. Two further modes of formation of the 'dimeric' radical (**23**) are shown in equations (8a) + (8b), and (9). Mechanisms analogous to equations (8a) and (8b) have been formulated before for related cases;[23,24] since they involve the intermediacy of diradicals, in the present case that of diradical (**24**), we consider them to be less likely. A mechanism analogous to equation (9) has also been formulated.[25]

Reaction of the 'dimeric' radical (**23**) with oxygen leads to the 'dimeric' peroxyl radical (**25**) [equation (10)] wich may be the precursor of both the 'dimeric' ketone (**14**) and the triarylmethanol (**17**) (*cf.* above).

In the course of the formation of the dimer (**22**) according to equations (1), (2b), and (6) or equations (1), (4), and (6) 1 mol equiv. of tributylamine is consumed. Since, in our experiments, equimolar amounts of tributylamine and halide (**4d**) were used, reaction (7) leading to the 'dimeric' radical (**23**) may be expected to be rather inefficient. The same applies to the two further modes of formation of the 'dimeric' radical (**23**) mentioned above. Furthermore, all modes of formation of (**23**) from the 'monomeric' radical (**18**) clearly compete with the reaction of the latter with oxygen [equation (3)] which ultimately leads to the formation of benzophenones (**15**) and (**16**) [equations (5a) and (5b)]. The non-formation of the 'dimeric' ketone (**14**) and of the triarylmethanol (**17**) [both being conversion products of (**23**), see above] under conditions where the halide (**4d**) and tributylamine are allowed to react in the presence of oxygen can therefore easily be accounted for.

Formation of the triarylmethane (**5d**) as the main product when equimolar amounts of the chloride (**4d**) and tributylamine

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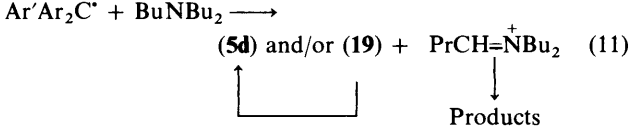
* See the text.

were allowed to react in t-butylbenzene under argon suggests that, in the absence of oxygen, the tributylaminium radical cation is able to transfer an α-hydrogen atom to the triarylmethyl radical (**18**) [equation (11)].



$$\mathrm{Ar'Ar_2C^{\bullet} + Bu\overset{+\bullet}{N}Bu_2 \longrightarrow (\mathbf{5d})\ and/or\ (\mathbf{19}) + PrCH{=}\overset{+}{N}Bu_2 \qquad (11)}$$

$$\mathrm{PrCH{=}\overset{+}{N}Bu_2 \longrightarrow Products}$$

In the absence of oxygen this reaction does not take place, presumably because the triarylmethyl radical (**18**) is rapidly trapped by oxygen [equation (3)]. Although no references to reactions in which an α-hydrogen atom is directly transferred from an aminium radical cation to a suitable acceptor was found in the literature, aminium radical cations are known to undergo, in the presence of base, successive loss of a proton and an electron [equations (12) and 13)] the overall result of which is equivalent to the loss of an α-hydrogen atom; *cf.* refs. 26(*a*)–(*d*). Furthermore, direct removal of groups from the α-position of aminium radical cations by homolysis of α:βC–C bonds are also known [equation (14)].[26d]

$$\mathrm{RCH_2\overset{+\bullet}{N}(CH_2R)_2 + B{:} \longrightarrow R\dot{C}H\ddot{N}(CH_2R)_2 + BH^+} \qquad (12)$$

$$\mathrm{R\dot{C}H\ddot{N}(CH_2R)_2 + A \longrightarrow RCH{=}\overset{+}{N}(CH_2R)_2 + A^{-\bullet}} \qquad (13)$$

$$\mathrm{R'R''CH\overset{+\bullet}{N}R_2 \xrightarrow{-R''\bullet} R'CH{=}\overset{+}{N}R_2} \qquad (14)$$

Experimental

Melting points are uncorrected and were determined in glass capillaries. Purification was effected by t.l.c., unless otherwise stated, using Kieselgel 60 $PF_{254+366}$ as the adsorbent. I.r. spectra were recorded with Spektromom 2000 (Hungarian Optical Works, Budapest) and Specord 75 (Carl Zeiss, Jena, GDR) instruments. ^1H N.m.r. spectra were run at 60 and 100 MHz on Perkin-Elmer R12 and JEOL FX-100 instruments, respectively, for $CDCl_3$ solutions (unless otherwise stated), with tetramethylsilane as the internal reference. Mass spectra were obtained with an AEI-MS-902 instrument, operating at 70 eV, using direct insertion.

Comparisons of i.r. spectra, m.p.s and mixed m.p.s, and t.l.c. were made with those of authentic samples.

Bis(4-*methoxyphenyl*)*phenylmethanol* (**6b**).—M.p. 75 °C (from CCl_4–hexane); δ_H(60 MHz) 2.85 (1 H, br s, exchangeable, OH), 3.70 (6 H, s, 2 × MeO), 6.72 and 7.10 (2 + 2 H, AA′BB′ system, *J* 9 Hz, 2 × 4-$MeOC_6H_4$), and 7.2 (5 H, s, Ph). This was obtained in 72% yield from 4-methoxybenzophenone[27] essentially as described in literature,[28] except that the Grignard reagent prepared from 4-bromo- rather than 4-iodo-anisole was used (lit.,[29] m.p. 76–77 °C).

4-*Methoxyphenylbis*(4-*t-butylphenyl*)*methanol* (**6c**) *and* 4-*Chlorophenylbis*(4-*t-butylphenyl*)*methanol* (**6d**).—These were prepared similarly by treating the Grignard derivative of 4-bromo(t-butyl)benzene (42.6 g, 0.2 mol) with methyl 4-methoxybenzoate and methyl 4-chlorobenzoate (15 g, 0.09 mol), respectively.

Compound (**6c**): 83% yield, m.p. 146–148 °C (from CCl_4–hexane) (Found: C, 83.5; H, 8.4. $C_{28}H_{34}O_2$ requires C, 83.5; H, 8.5%); δ_H(100 MHz) 1.30 (18 H, s, 2 × Bu^t), 2.70 (1 H, br s, exchangeable, OH), 3.77 (3 H, s, MeO), 6.80 and 7.17 (2 × 2 H, AA′BB′ system, *J* 9 Hz, $MeOC_6H_4$), and 7.12 and 7.29 (4 × 2 H, AA′BB′, 2 × $Bu^tC_6H_4$).

Compound (**6d**): 87% yield, m.p. 169–170 °C (from Pr^iOH) (Found: C, 79.55; H, 7.6; Cl, 8.6. $C_{27}H_{31}ClO$ requires C, 79.7; H, 7.7; Cl, 8.7%); δ_H(60 MHz) 1.27 (18 H, s, 2 × Bu^t), 2.65 (1 H, br s, exchangeable, OH), 7.04 and 7.27 (2 × 2 H, AA′BB′ system, *J* 9 Hz, ClC_6H_4), and 7.19 (8 H, s, 2 × $Bu^tC_6H_4$); *m*/*z* (180 °C) 408 (10%), 407 (8), 406 (27, $M^{+\bullet}$), 391 (6.0, $M^{+\bullet}$ − Me), 389 (4.3, $M^{+\bullet}$ − OH), 375 (2.6), 371 (1.5, $M^{+\bullet}$ − Cl), 359 (1.0), 349 (2.5, $M^{+\bullet}$ − Bu^t), 333 (2.3), 296 (17), 295* (70, $M^{+\bullet}$ − ClC_6H_4), 279 (5.8), 275 (18), 273 (53, $M^{+\bullet}$ − $Bu^tC_6H_4$), 266 (3.3), 257 (12), 244* (10, $M^{+\bullet}$ − 162), 229 (3.0), 189* (10, $M^{+\bullet}$ − 217), 188.5 (7.5), 188 (30), 162 (14), 161 (100, $Bu^tC_6H_4CO^+$), 139 (39, $ClC_6H_4CO^+$), 119 (13), and 57 (70).

4-*Methoxyphenyl*(*diphenyl*)*methyl Chloride*[10] (**4a**).—δ_H(60 MHz) 3.74 (3 H, s, MeO), 6.75 and 7.11 (2 × 2 H, AA′BB′ system, *J* 9 Hz, 4-$MeOC_6H_4$), and 7.23 (10 H, s, 2 × Ph).

Bis(*methoxytriphenyl*)(*phenyl*)*methyl Chloride* (**4b**), 4-*Methoxyphenylbis*(4-*t-butylphenyl*)*methyl Chloride* (**4c**), *and* 4-*Chlorophenylbis*(4-*t-butylphenyl*)*methyl Chloride* (**4d**).—These were obtained by refluxing the alcohols (**6b**), (**6c**), and (**6d**), respectively, with excess $SOCl_2$ in ether or CH_2Cl_2 in the conventional manner.

Compound (**4b**): 82% yield, m.p. 126 °C (from CH_2Cl_2–hexane) (lit.,[29] m.p. 114–115 °C); δ_H(60 MHz) 3.75 (6 H, s, 2 × MeO), 6.75 and 7.11 (2 × 2 H, AA′BB′ system, *J* 9 Hz, 2 × 4-$MeOC_6H_4$), and 7.2 (5 H, s, Ph).

Compound (**4c**): 88% yield, m.p. 213–215 °C (from ether), 223—224 °C (from heptane-benzene) (Found: C, 79.7; H, 7.95; Cl, 8.55. $C_{28}H_{33}ClO$ requires C, 79.9; H, 7.9; Cl, 8.4%); δ_H(100 MHz) 1.30 (18 H, s, 2 × Bu^t), 3.77 (3 H, s, MeO), 6.78 and 7.13 (2 × 2 H, AA′BB′, 4-$MeOC_6H_4$), and 7.11 and 7.29 (4 × 2 H, AA′BB′, 2 × $Bu^tC_6H_4$).

Compound (**4d**): 94% yield, m.p. 209–210 °C (from heptane) (Found: C, 76.1; H, 7.55; Cl, 17.1. $C_{27}H_{30}Cl_2$ requires C, 76.22; H, 7.1; Cl, 16.65%); δ_H(100 MHz) 1.30 (18 H, s, 2 × Bu^t), 7.09 and 7.29 (4 × 2 H, AA′BB′, 2 × $Bu^tC_6H_4$), and 7.21 (4 H, s, ClC_6H_4).

Bis(4-*methoxyphenyl*)*phenylmethane* (**5b**), (4-*Methoxyphenyl*)*bis*(4-*t-butylphenyl*)*methane* (**5c**), *and* 4-*Chlorophenylbis*(4-*t-butylphenyl*)*methane* (**5d**).—These were obtained from the reduction of the chlorides (**4b**), (**4c**), and (**4d**), respectively, in refluxing 85% formic acid, essentially by the method described in ref. 28.

Compound (**5b**): 95% yield, m.p. 101–102 °C (from ethanol) (lit.,[30] m.p. 101.5 °C); δ_H(60 MHz) 3.65 (6 H, s, 2 × MeO), 5.30 (1 H, CH), 6.65 and 6.85 (4 × 2 H, AA′BB′ system, *J* 9 Hz, 2 × $MeOC_6H_4$), and 7.1 (5 H, m, Ph).

Compound (**5c**): 76% yield, m.p. 113–114 °C (from ethanol) (Found: C, 86.7; H, 8.8. $C_{28}H_{34}O$ requires C, 87.0; H, 8.85%); δ_H(100 MHz) 1.28 (18 H, s, 2 × Bu^t), 3.74 (3 H, s, MeO), 5.38 (1 H, s, CH), 6.77 and 7.01 (2 × 2 H, AA′BB′ system, $MeOC_6H_4$), and 7.03 and 7.24 (4 × 2 H, AA′BB′ system, 2 × $Bu^tC_6H_4$).

Compound (**5d**): 93% yield, m.p. 150 °C (from ethanol) (Found: C, 83.1; H, 7.9; Cl, 9.2. $C_{27}H_{31}Cl$ requires C, 82.95; H, 8.0; Cl, 9.05%); δ_H(60 MHz) 1.26 (18 H, s, 2 × Bu^t), 5.38 (1 H, s, C–H), 6.8—7.6 (12 H, m, ArH).

Reaction of the Triarylmethyl Chlorides (**4a**) *and* (**4b**) *with Methanol*.—The title chlorides (1 mmol) were heated with anhydrous methanol (7.3 cm^3) in sealed tubes for 60 h at 105 °C. The methanol was distilled off to give mixtures of the corresponding triarylmethanes and methyl ethers (**5a**)[11] and (**7a**), and (**5b**) and (**7b**), respectively, which were separated by t.l.c. [benzene–hexane (1:1) then methanol–CH_2Cl_2 (1:9)]. The

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* Metastable peaks.

Table 3. Partial mass spectrum (70 eV; 160 °C) of the mixture of compound (**7c**) and its deuteriated analogues (**7e**), (**8c**), and (**8e**).

Ion	m/z	Relative abundance[a] (%)	Number of ^2H atoms	Origin of ion
$M^{+\bullet}$	422	77	6	(**8e**)
	419	22	3	(**7e**) + (**8c**)
	416	1	0	(**7c**)
$M^{+\bullet}$ − α-MeO	388	79	3	(**7e**) + (**8e**)
$M^{+\bullet}$ − α-C^2H^3O	385	21	0	(**7c**) + (**8c**)

[a] Expressed as $100i/\Sigma i$ for each ion type.

Table 4. Partial mass spectrum (70 eV; 160 °C) of the mixture of compound (**6c**) and its deuteriated analogue (**6e**).

Ion	m/z	Relative abundance[a] (%)	Number of ^2H atoms	Origin of ion
$M^{+\bullet}$	405	80	3	(**6e**)
	402	20	0	(**6c**)
$M^{+\bullet}$ − Bu^tPh	272	78.5	3	(**6e**)
	269	21.5	0	(**6c**)

[a] Expressed as $100i/\Sigma i$ for each ion type.

individual components were identical with authentic samples. For the yields, see Table 1.

For the preparation of authentic samples of the triarylmethanes (**5a**) and (**5b**), see ref. 11 and above, respectively; for the preparation of authentic samples of the methyl ethers (**7a**) and (**7b**), see ref. 5 and below, respectively.

Compound (**5a**): δ_H(60 MHz) 3.68 (3 H, s, MeO), 5.40 (1 H, s, CH), 6.71 and 6.95 (2 × 2 H, AA′BB′ system, *J* 9 Hz, $MeOC_6H_4$), and 7.1 (10 H, m, 2 × Ph).

Compound (**7a**): δ_H(60 MHz) 2.96 (3 H, s, COMe), 3.66 (3 H, s, Ar*OMe*), 6.70 and 7.09 (2 × 2 H, AA′BB system, *J* 9 Hz, $MeOC_6H_4$), and 7.05–7.5 (10 H, m, 2 × Ph).

Reactions of the Triarylmethyl Chlorides (**4c**) *and* (**4d**) *with Alcohols.—General procedure.** Mixtures of the chlorides (**4c**) (0.3–1.0 g, 0.7–2.4 mmol) and (**4d**) (0.5–1.0 g, 1.2–2.35 mmol), respectively, with alcohols and, eventually, the co-solvent CH_2Cl_2 were refluxed or heated in sealed tubes for 0.5–60 h as stated in Table 2, and evaporated to dryness. The residues were triturated with 5% aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The CH_2Cl_2 solutions were dried ($MgSO_4$) and evaporated to dryness. The residues were worked-up by preparative t.l.c. [toluene–hexane (7:3) then CH_2Cl_2–MeOH (1:1)]. All products were identified by comparison with authentic samples. For the yields, see Table 2.

The ratio of the ether (**7c**) and its isotopomers obtained in experiment 5 was determined by mass spectrometry (Tables 3 and 4). Thus, making the reasonable assumptions that (*i*) the non-deuteriated alcohol is formed during work-up by hydrolysis of the non-deuteriated ether (**7c**) and of its α-trideuteriomethoxy analogue (**8c**) while the precursors of the deuteriated alcohol (**6e**) are the *p*-mono- (**7e**) and the bis-(trideuteriomethoxy) ethers (**8e**) and that (*ii*) the specific rates of these processes are practically identical (any differences being caused by second- and higher-order k.i.e.s). The relative abundances of m/z 405 and 402 in the mass spectrum (Table 4) of the mixture of compounds (**6c**) and (**6e**), respectively, should be equal to the sum of the relative abundances of the precursors (**7c**) and (**8c**), and (**7e**) and (**8e**), respectively. By combining the values (**6c**) = (**7c**) + (**8c**) and (**6e**) = (**7e**) + (**8e**) from Table 4 with the relative abundances of m/z 422 and 416 from Table 3, the ratio (**7c**):(**7e**):(**8c**):(**8e**) = 1:3:19:77 is obtained for the composition of the mixture of ether (**7c**) and its isotopomers.

However, equally reasonable are the assumptions that (*i*) the fragment ions m/z 388 and 385 in the mass spectrum of the mixture of the ether (**7c**) and its isotopomers (Table 3) are formed solely by elimination of the α-methoxy and α-trideuteriomethoxy groups, respectively, from the various molecular ions, and (*ii*) the specific rates of both the formation and further fragmentations of these fragment ions are, for the reason discussed above, practically identical. The relative abundance of m/z 388 and 385 in the 70 eV mass spectrum shown in Table 3 should then be equal to the sum of the relative abundances of their precursors (**7e**) and (**8e**), and (**7c**) and (**8c**), respectively. By combining the values of the relative abundances of m/z 388 and 385 with the relative abundances of m/z 422 and 416 in the same spectrum, the ratio (**7c**):(**7e**):(**8c**):(**8e**) = 1:2:20:77 is obtained for the composition of the mixture of ether (**7c**) and its isotopomers: practically the same composition as above. The identity of the results obtained on the basis of two different sets of assumptions mutually supports the validity of these assumptions.

The ratio of compounds (**6c**) and (**6e**) in the mixture was found to be 20:80 both on the basis of the relative abundances of their molecular ions (m/z 402 and 405) (Table 4) and on the basis of the relative intensities of the methoxy and t-butyl signals in the ^1H n.m.r. spectrum which amounted to only 20% of the value calculated for the pure 'light' compound (**6c**).

Conversion of the Ethyl Ether (**9d**) *into the Triarylmethane* (**5d**).—A mixture of the ethyl ether (**9d**) (435 mg, 1 mmol), dry ethanol (7.5 cm^3), and dry HCl gas (73 mg, 2 mmol) was heated for 60 h at 105 °C in a sealed tube to give, after conventional work-up, the triarylmethane (**5d**) (371 mg, 95%) which proved to be identical with an authentic sample.

Reactions of the Triarylmethyl Chlorides (**4b**)–(**4d**) *with Sodium Alkoxides in Alcohols.*—(*a*) Chloride (**4b**) was allowed to react with refluxing methanolic NaOMe (4 mol equiv.) as described for the corresponding reaction of the trimethoxy analogue (**2b**) in ref. 9 to give *bis(4-methoxyphenyl)phenylmethyl methyl ether* (**7b**) in 93% yield as an oily product (Found: C, 78.8; H, 6.75. $C_{22}H_{22}O_3$ requires C, 79.0; H, 6.65%); δ_H(60 MHz) 3.00 (3 H, s, COMe), 3.73 (6 H, s, 2 × Ar*OMe*), 6.77 and 7.28 (2 × 4 H, AA′BB′ system, *J* 9 Hz, 2 × OC_6H_4), 7.10–7.55 (5 H, m, Ph).

(*b*) Metallic sodium (0.38 g, 9.5 mmol) and the chloride (**4c**) (1.0 g, 2.4 mmol) were dissolved in anhydrous methanol (10 cm^3), and in ethanol (10 cm^3). The two mixtures were refluxed for 30 min during which period crystalline products began to separate. The cooled mixtures were diluted with water (30 cm^3) to give *4-methoxyphenylbis(4-t-butylphenyl)methyl methyl* (**7c**) (0.91 g, 92%) and *ethyl ethyl ether* (**9c**) (0.92 g, 90%), respectively.

Compound (**7c**): m.p. 147–148 °C (from aqueous methanol) (Found: C, 83.8; H, 8.9. $C_{29}H_{36}O_2$ requires C, 83.6; H, 8.7%); δ_H(100 MHz) 1.29 (18 H, s, 2 × Bu^t), 3.02 (3 H, s, COMe), 3.76 (3 H, s, Ar*OMe*), 6.79 and 7.30 (2 × 2 H, AA′BB′, $MeOC_6H_4$), and 7.29 (8 H, s, 2 × $Bu^tC_6H_4$).

Compound (**9c**): m.p. 154–155 °C (from aqueous ethanol) (Found: C, 83.2; H, 9.1. $C_{30}H_{38}O_2$ requires C, 83.65; H, 8.9%); δ_H(100 MHz) 1.28 (18 H, s, 2 × Bu^t), 1.20 and 3.07 (3 H, t and 2 H, q, EtO), 3.74 (3 H, s, MeO), 6.79 and 7.31 (2 × 2 H, AA′BB′, $MeOC_6H_4$), and 7.29 (8 H, s, 2 × $Bu^tC_6H_4$).

(*c*) Metallic sodium (92 mg, 4 mmol) and the chloride (**4d**) (425 mg, 1 mmol) were dissolved in anhydrous ethanol (5 cm^3). The mixture was refluxed for 5 min and allowed to cool to give *4-chlorophenylbis(t-butylphenyl)methyl ethyl ether* (**9d**) (0.40 g,

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* For modifications of the general procedure see the footnotes to Table 2.

92%), m.p. 174–175 °C (from ethanol–DMF or propan-2-ol) (Found: C, 80.15; H, 8.3; Cl, 8.05. $C_{29}H_{35}ClO$ requires C, 80.1; H, 8.1; Cl, 8.15%); δ_H(100 MHz) 1.21 and 3.07 (3 H, t and 2 H, q, OEt), 1.29 (18 H, s, 2 × Bu^t), 7.22 and 7.39 (2 × 2 H, AA′BB′, $MeOC_6H_4$), and 7.28 (8 H, s, 2 × $Bu^tC_6H_4$).

Reactions of the Triarylmethyl Chloride (**4d**) *with Alkali-metal Alkoxides in Aprotic Solvents.*—(*a*) A mixture of the chloride (**4d**) (4.0 g, 9.4 mmol), NaOMe (2.04 g, 37.6 mmol) and anhydrous THF (40 cm^3) was refluxed for 15 h with continuous stirring under nitrogen and then evaporated to dryness. The residue was triturated with 5% aqueous $NaHCO_3$ (50 cm^3) and taken up in CH_2Cl_2 (70 cm^3). The organic solution was dried ($MgSO_4$) and evaporated to dryness. The residue was worked up by column chromatography [Kieselgel 60, Korngrösse 0.063–0.200 mm; hexane $\longrightarrow$ hexane–toluene (1:1)] to give the ether (**7d**) (1.0 g, 25%) and the alcohol (**6d**) (2.3 g, 48%), both of which were identical with authentic samples.

When the solvent was replaced with dry benzene and the refluxing continued for 30 h, (**7d**) and (**6d**) were obtained in 50 and 29% yields, respectively.

(*b*) A mixture of the chloride (**4d**) (1.0 g, 2.35 mmol), $KOBu^t$ (1.05 g, 9.4 mmol) and anhydrous THF (10 cm^3) was refluxed for 20 h with continuous stirring under nitrogen and worked up essentially as described in (*a*), except that t.l.c. [toluene–hexane (7:3)] was used instead of column chromatography, to give the alcohol (**6d**) (0.4 g, 42%).

(*c*) When experiment (*b*) was carried out in the presence of dry acetone (0.17 cm^3, 7.35 mmol), a mixture of oligomeric products (but no pure individual oligomer) was obtained in addition to the alcohol (**6d**) (0.46 g, 49%).

Reaction of the Chloride (**4d**) *with Tributylamine.*—(*a*) A mixture of the chloride (**4d**) (1.0 g, 2.35 mmol), tributylamine (0.56 cm^3, 2.35 mmol), and dry cumene (10 cm^3) was refluxed for 17 h and evaporated to dryness. The residue was taken up in water and CH_2Cl_2, and the organic layer was dried ($MgSO_4$) and evaporated to dryness. The residue was worked up by t.l.c. [benzene–hexane (1:1) then benzene for the mixture of compounds (**14**) and (**15**)] to give the triarylmethane (**5d**) (212 mg, 23%), which was identical with an authentic sample (see above), the 'dimeric' ketone (**14**) (24 mg, 1.6%), and the benzophenones (**15**) and (**16**), (17 mg, 2.7% and 414 mg, 60%, respectively).

Compound (**14**): m.p. 179–180 °C (from ethanol); $\nu_{max.}$(KBr) 1 670 cm^{-1}; δ_H(100 MHz) 1.30 (18 H, s, 2 × Bu^t), 1.36 (9 H, s, Bu^t), and 7.0–7.8 (20 H, m, ArH) (Found: $M^{+\cdot}$, 626.327. $C_{44}H_{47}ClO$ requires *M*, 626.332); *m*/*z* (200 °C), 628 (23%), 627 (25), 626 (70, $M^{+\cdot}$), 611 (8.5, $M^{+\cdot}$ − Me), 591 (8.0, $M^{+\cdot}$ − Cl), 571 (5), 569 (15, $M^{+\cdot}$ − Bu^t), 515* (68, $M^{+\cdot}$ − ClC_6H_4), 495 (24), 493 (80, $M^{+\cdot}$ − $Bu^tC_6H_4$), 465 (4), 391 (35), 389 [100, $(Bu^tC_6H_4)_2(ClC_6H_4)C^+$], 354 (13), 305.5 [3.0, $(M - Me)^{++}$], 298 [30, $(M - Me)^{++}$], 161 (60), and 57 (50). A small peak at *m*/*z* 760 (2.0) indicated contamination by the triarylmethanol (**17**), see below.

Compound (**15**): m.p. 84 °C (from ethanol) [lit.,[18] m.p. 79–81 °C (from 95% ethanol)]; *m*/*z* (170 °C) 274 (12%), 272 (36, $M^{+\cdot}$), 259 (35), 257* (100, $M^{+\cdot}$ − Me), 243 (0.35), 237 (0.32, $M^{+\cdot}$ − Cl), 229* (1.7, $M^{+\cdot}$ − 15 − 28), 201 (3.0), 161 (9.0, $M^{+\cdot}$ − ClC_6H_4), 139 (23, $M^{+\cdot}$ − $Bu^tC_6H_4$), 128.5 (1.8, 257^{++}), and 111 (11, $ClC_6H_4^+$).

Compound (**16**): m.p. 133–134 °C (from ethanol) [lit., m.p. 134.1–135.5 °C (from methanol)[19a] and 133–134 °C[19b]]; $\nu_{max.}$(KBr) 1 650 cm^{-1}; δ_H(100 MHz) 1.37 (18 H, s, 2 × Bu^t), 7.48 and 7.75 (4 × 2 H, AA′BB′, 2 × $Bu^tC_6H_4$); *m*/*z* (150–200 °C) 295 (7%), 294 (30, $M^{+\cdot}$), 280 (21), 279* (100, $M^{+\cdot}$ − Me), 263 (0.6), 251* (0.85, 279 − 28), 237 (3.0), 161 (17), 132 (12), 118 (12), and 104 (13).

(*b*) When the solvent cumene was replaced by dry t-butylbenzene, and the mixture refluxed for 10–30 h (4 experiments), compounds (**14**) (5–26%), (**15**) (13–29%), and (**16**) (17–30%) were obtained. In one case compound (**17**) (2.3%) [which, in the t.l.c. system used, had almost the same R_F value as compound (**14**)] was obtained instead of compound (**14**).

Compound (**17**): m.p. 168–169 °C (from aqueous ethanol) [Found: *m*/*z* 627.334. $C_{44}H_{48}ClO$ requires (M − $Bu^tC_6H_4$), 627.340]; *m*/*z* (200 °C) 762 (11), 761 (15), 760 (29, $M^{+\cdot}$), 745 (5.5, $M^{+\cdot}$ − Me), 649 (19, $M^{+\cdot}$ − ClC_6H_4), 629 (17), 627* (52, $M^{+\cdot}$ − $Bu^tC_6H_4$), 611 (7.0), 493 (9.5), 487 (3.5), 465 [6.5, $(Bu^tC_6H_4)_2(ClC_6H_4)C(C_6H_4)^+$], 391 (18), 389 [55, $(Bu^tC_6H_4)_2(ClC_6H_4)C^+$], 365 [4.5, $(M - 2Me)^{++}$], 317 [4.3, $(M - Me - ClC_6H_4)^{++}$], 306 [7.0, $(M - Me - Bu^tC_6H_4)$], 296 (15), 295 (65), 279 (16), 161 (100), and 57 (87).

(*c*) When experiment (*b*) was carried out in the presence of a continuous stream of dry oxygen, and the solution was refluxed for 6.5 h, only the benzophenones (**15**) (27%) and (**16**) (18%) were isolated.

(*d*) A mixture of the chloride (**4d**) (1.0 g, 2.35 mmol), tributylamine (0.56 cm^3, 2.35 mmol), and dry cumene (10 cm^3) was injected through a metal needle into a thick-walled glass tube (length *ca.* 26 cm, inner diameter *ca.* 9 mm) with a narrow bottleneck (inner diameter *ca.* 3 mm) *ca.* 8 cm below its open end. A stream of dry argon was introduced through a suitable capillary into the solution for *ca.* 5 min. The capillary was removed and the glass tube was connected through rubber tubes to a vacuum-pump and to an argon source, and alternately evacuated and filled with argon ten times. Finally the argon pressure in the tube was reduced to just below 760 mmHg and the tube was rapidly sealed at the bottleneck. The solution occupied *ca.* 80% of the available volume of the sealed tube. The tube was placed into a flask containing cumene and heated for 60 h by refluxing the solvent in the flask. The mixture was allowed to cool and worked up as described in (*a*), except that the solvent used in the second t.l.c. step in which the less polar fraction of the first t.l.c. step was rechromatographed eluting with benzene–hexane (1:9). Elution CH_2Cl_2–MeOH with (1:1) gave the triarylmethane (**5d**) (0.53 g, 53%) and compound (**17**) (0.12 g, 6.8%) both of which were identical with authentic samples.

(*e*) When the solvent cumene was replaced by dry t-butylbenzene compounds (**5d**) and (**17**) were obtained in 46 and 7% yields, respectively.

Acknowledgements

The authors are indebted to Mrs. Balogh-Batta and staff for the microanalyses, to Dr. G. Tóth and staff for the n.m.r. spectra, and to Mrs. Székely-Csirke for the i.r. spectra.

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* Metastable peaks.

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Received 14*th March* 1988; *Paper* 8/01022F