Single-electron-transfer-initiated Thermal Reactions of Arylmethyl Halides. Part 11.[1] The Reaction of Trityl Halides with Sodium Methoxide in 2,2-Dimethoxypropane

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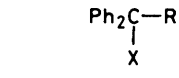
Trityl chloride (**1a**) and bromide (**1b**) furnish with sodium methoxide in 2,2-dimethoxypropane, in addition to several minor products, mixtures of the substitution products methyl trityl ether (**1c**) and *p*-methoxytriphenylmethane (**2a**), and of the reduction products triphenylmethane (**1f**) and *p*-diphenylmethyltritylbenzene (**3a**) which are the products of competing S_N and single-electron-transfer-initiated processes. Compound (**1c**) is suggested to be formed *via* two successive S_N' processes rather than by either the S_N1 or S_N2 mechanisms which are both disfavoured under the experimental conditions applied.

In a preliminary study into the reactions of trityl chloride (**1a**) with a suspension of sodium methoxide in 2,2-dimethoxypropane (DMP) we have obtained a complex mixture of products including the *ipso* substitution products (**1c**) and (**1d**),† the *tele* substitution product (**2a**), the reduction product (**1f**), the dimeric compound (**3a**) and, when the reaction was carried out in air, the peroxide (**1g**).[2,3]

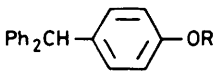
The reactions of trityl halides with nucleophiles has attracted the attention of many chemists. Of particular interest in connection with our work are the studies into the mechanisms of these reactions in apolar solvents.[4] One of the results of these studies was the development of the fiercely disputed concept of the push–pull mechanisms of nucleophilic reactions.[4c,d] Strikingly, both the proponents[4c,d] and the opponents[4a,b,5] of this theory have based their conclusions solely on kinetic data and have, apparently, tacitly assumed (i) that only heterolytic reactions take place between trityl halides and nucleophiles, and (ii) that these reactions invariably lead to the formation of *ipso* substitution products. The rejection of the possibility of parallel substitution reactions (as a consequence of which thorough product analyses were never carried out in these early studies, not even in those cases when the reactions were run in the presence of tertiary bases) is all the more amazing because the ambident reactivity both of unsubstituted trityl halides[6a–d] and their derivatives containing nucleofugal substituents in one *para* position[7a,b] had been known earlier. The ambident reactivity of unsubstituted trityl halides does lead to the formation of *e.g.* *para* (in addition to *ipso*) substitution products in general only if either the nucleophile is sufficiently basic[2,6g–i] or the medium is sufficiently acidic[6f] or the reaction temperature is high enough[6f] to bring about the rearrangement (**5**) ⟶ (**6**) (Scheme 1). However, one has to reckon with the reversible formation of intermediates (**4**) even with non-basic nucleophiles.[7c] Although this will not lead to the formation of additional products, it may considerably alter the reaction kinetics.

Russian scientists[8] were the first to observe the appearance of the e.s.r. signal of trityl radicals when trityl perchlorate or trityl chloride (**1a**) were allowed to react with excess of potassium t-butoxide in tetrahydrofuran (THF) under argon, or with sodium phenoxide in dioxane–THF, the signal intensity reaching a maximum and then gradually diminishing to zero in



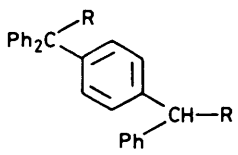
(**1**)

a; R = Ph, X = Cl
b; R = Ph, X = Br
c; R = Ph, X = OMe
d; R = Ph, X = OH
e; R = Ph, X = OBu^t
f; R = Ph, X = H
g; R = Ph, X = $OO-CPh_3$
h; R = $CONMe_2$, X = Br
i; R = $CONMe_2$, X = Cl
k; R = $CONMe_2$, X = H
l; R = Ph, X = N⩵NPh
m; R = Ph, X = CH_2OH



(**2**)

a; R = Me
b; R = Bu^t



(**3**)

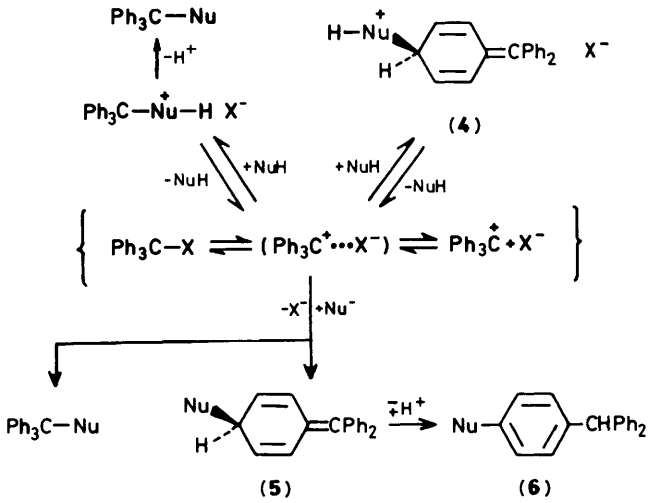
a; R = Ph
b; R = $CONMe_2$

both cases. These observations were rationalized (apparently without any product analyses being carried out) by assuming that a two-step substitution reaction, initiated by single-electron transfer (SET) from the nucleophile to the substrate, had taken place as shown in equation (1) for the reaction of the

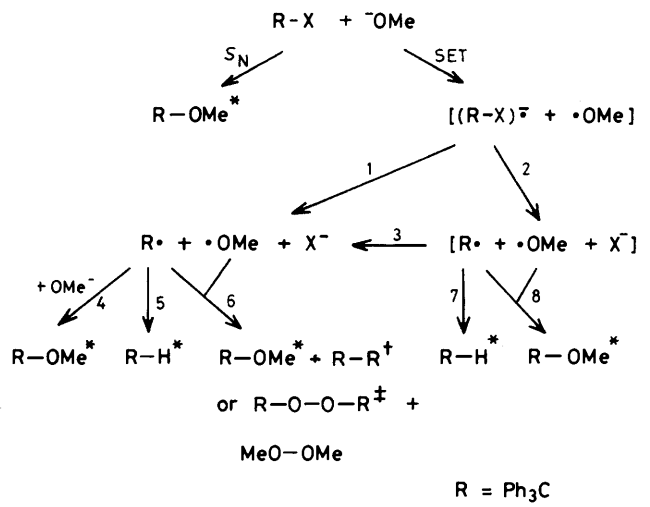
$$Ph_3C^+ + ClO_4^- + Bu^tOK \longrightarrow$$
$$Ph_3C^{\bullet} + {}^{\bullet}OBu^t + KClO_4 \longrightarrow Ph_3C\text{-}OBu^t + KClO_4 \quad (1)$$

perchlorate, the overall result being identical with that of a nucleophilic *ipso* substitution reaction. The reactions of trityl chloride (**1a**) and bromide (**1b**) with lithium and potassium t-butoxides in THF were later studied by American authors who confirmed the intermediate formation of trityl radicals in these reactions, and observed, in addition to the *ipso* substitution product t-butyl trityl ether (**1e**), the formation of an isomer of the latter, compound (**2b**) (or its semibenzene-type isomer), *i.e.* of a *tele* substitution product.[9] Since no other products were isolated, the American authors came necessarily, and similarly to their Russian colleagues,[8] to the conclusion that trityl radicals are involved in the replacement reactions leading to the substitution products (**1e**) and (**2b**).[9] In view of the omission of thorough product analyses, this conclusion does not appear to be well founded, all the less so because the formation of trityl radicals and non-substitution products [*e.g.* ditrityl peroxide (**1g**) and the so-called hexaphenylethane which is actually the dimer (**3a**)[10]] derived from these had been observed in the

† The origin of this product is not clear: it may, *e.g.*, be present as an impurity of the starting chloride (**1a**), be formed as a result of traces of water in the reaction mixture, or be formed during work-up from unchanged starting chloride (**1a**).



Scheme 1. Only one limiting structure is shown for mesomeric species throughout this paper



1 Decomposition during escape from the solvent cage
2 Decomposition within the solvent cage
3 Escape from the solvent cage
4 $S_{RN}1$ process[12]
5 Hydrogen abstraction, eventually by a chain mechanism[15d] } Outer sphere processes[14]
6 Random events[13]
7 Hydrogen abstraction either from a solvent molecule incorporated into the wall of the solvent cage, or from the geminate methoxyl radical
8 Recombination of geminate radicals which is equivalent to substitution *via* electron transfer (S_{ET}),[12] inner sphere process[14]

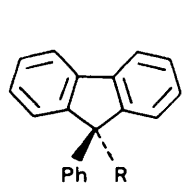
Scheme 2. • Because of the ambident reactivity of trityl halides and trityl radicals, both the *ipso* and *tele* substitution products are designated by R-OMe, and both triphenylmethane and the isomeric semibenzene (**19**) are designated by R-H. † For R = trityl, R-R = (**3a**). ‡ In the presence of oxygen

reactions of trityl halides, perchlorates *etc.* with nucleophiles.[11a–d] This obviously means that the geminate trityl and alkoxyl radicals, formed, as correctly interpreted by Bilevitch *et al.*[8] and Ashby *et al.*,[9] by SET from the alkoxide anion to trityl chloride and decomposition of the resulting radical anion within the solvent cage (Scheme 2, step 2), do not necessarily recombine to give the *ipso* and *tele* substitution products by what may be termed substitution *via* electron transfer (S_{ET} process;[12] step 8, Scheme 2). Further possible transformations of these radicals which have to be taken into consideration are summarized in Scheme 2. The radicals may escape from the solvent cage (step 3) to become detectable by e.s.r. and to form various products by random events[13] (step 6) or by hydrogen abstraction (step 5). Alternatively, *free* trityl and methoxyl radicals could be formed by an outer sphere process[14] (step 1).

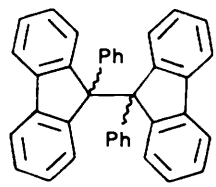
Recombination of trityl radicals with methoxide anions (step 4) (which would be one of the propagation steps of the $S_{RN}1$ chain reaction[15] leading to the *ipso* and/or *tele* substitution products) is not significant, see below. When, however, the *O*-nucleophile is replaced by an *S*-nucleophile, as in the reaction of 9-bromo-9-phenylfluorene (**7**) with benzenethiolate, the substitution product (**8**), obtained in addition to the dimeric product (**9**) and diphenyl disulphide, is claimed to be formed by the $S_{RN}1$ mechanism.[16]

In the present paper we report the results of detailed inhibition studies which unambiguously prove that when the trityl halides (**1a** and **b**) are allowed to react with sodium methoxide in 2,2-dimethoxypropane (DMP), SET-initiated and S_N reactions, leading to different products, take place simultaneously. The mechanisms of formation of the substitution products (**1c**) and (**2a**) as well as of the SET products (**1f**) and (**3a**) are discussed.

Inhibition Studies.—The reactions of trityl halides (**1a** and **b**) with sodium methoxide in DMP were carried out in the presence of nitrobenzenes and di-t-butyl nitroxide (DBNO). As noted earlier,[2] oxygen had no significant inhibitory effect (compare also entries 2 and 3 of the Table). The nitroarenes are known to act as radical-anion traps by reoxidizing them to the neutral molecules[17] [equation (2)]. As a result, they are able to inhibit reactions initiated by conversion of the substrate into its radical anion *via* SET, *e.g.* $S_{RN}1$ reactions. DBNO has been originally assumed to act as a radical trap[18] [equation (3)], but its effect may also be the result of its oxidizing ability[19]



(**7**) R = Br
(**8**) R = SPh



(**9**)

$$M^{-\cdot} + ArNO_2 \longrightarrow M + ArNO_2^{-\cdot} \quad (2)$$

$$R\cdot + (Bu^t)_2NO\cdot \longrightarrow (Bu^t)_2N\text{-}OR \quad (3)$$

$$M^{-\cdot} + (Bu^t)_2NO\cdot \longrightarrow M + (Bu^t)_2N\text{-}O^- \quad (4)$$

[equation (4)] which then would be analogous to that of the nitroarenes. In any case, DBNO is an effective inhibitor of reactions involving radical anions and radicals, *e.g.* of SET reactions.[20]

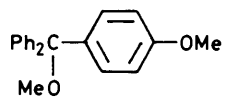
The results of the inhibition and control experiments are shown in the Table. In all except three cases (entries 2, 3, and 13), the already known products (**1c**), (**1d**), (**1f**), (**1g**), (**2a**), and (**3a**) were obtained. In experiments 2, 3, and 13 small amounts (< 5%) of a novel product, compound (**10**), were also isolated.

p-Dinitrobenzene, being rapidly converted into *p*-nitroanisole under the conditions of the reaction, and nitrobenzene (Table, entry 2) had no clear effects in our case, but the experiments conducted in the presence of *m*-dinitrobenzene (DNB) and DBNO supported the results of our preliminary inhibition

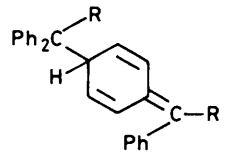
Table. Reaction of the trityl halides (**1a** and **b**) with sodium methoxide in 2,2-dimethoxypropane (DMP)[a]

No.	Starting halide	Added substances;[b] amount[c]	Conditions,[d] reaction time (h)	Products and yields[e] (%) (1f)	(3a)	(1g)	(1c)	(1d)	(2a)	Total
1[f]	(1a)		B, N 10	32—41	3.8—5.0		23—30	10—12	8—9	78—95
2[f]	(1a)	NB 1	B, N 8	21—25	7—10		20—26	17—20	2	74—86[g]
3	(1a)	NB 1	B, A 8	27	5		28	7	4	71[h]
4[i]	(1a)	DNB 0.16	B, A 6 and 12	5—6	50—52		12—21	3—4	6—7	80—85
5	(1a)	DNB 1	B, A 5.5	*k*	*k*	5	40	22		67
6	(1a)	DBNO 0.06	B, N 5	18	1.5		21	10	10	61
7	(1a)		R, N 48	15		2[l]	42	18	6	83
8	(1a)	DNB 0.16	R, A 72	5	45		24	5	3	82
9	(1a)	DBNO 0.1	R, N 48	10		3[l]	55	18	6	92
10[f]	(1b)		B, N 5	28—37	4—7		30—34	4—11	4—7	76—85
11	(1b)	DBNO 0.06	B, N 5	8	1.5		39	10	2	61
12	(1b)		R, N 48	32	1		29	8	8	78
13	(1b)	DBNO 0.1	R, N 48	17		2[l]	41	11	7	80[m]

[a] Chloride (**1a**) (2.00 g, 7.18 mmol) and bromide (**1b**) (2.32 g, 7.18 mmol), respectively, were allowed to react with sodium methoxide (4.0 mmol per mmol starting halide) in DMP (10 ml per g starting chloride and 8.6 ml per g starting bromide, respectively, *i.e.* 2.8 ml per mmol for both halides). In Experiment 2 chloride (**1a**) (1.00 g, 3.59 mmol) was used. [b] NB = nitrobenzene, DNB = *m*-dinitrobenzene, DBNO = di-t-butyl nitroxide. [c] mmol per mmol starting halide. [d] R = at room temperature, B = at the b.p. of the reaction mixture; A = in air, N = under nitrogen. [e] Yields of non-recrystallized products, isolated by t.l.c. and identified (t.l.c., i.r.) with authentic samples. [f] Three identical runs. [g] Further products: (**10**), 3.5—5.0%, included in the total yield; azoxybenzene, 68—95%, not included in the total yield. [h] Further product: (**10**) (t.l.c.). [i] Two runs, differing only in the reaction time. [k] Traces, detected by t.l.c. [l] From traces of O_2 present in the solvent and/or the flushing gas. [m] Further isolated product: (**10**), 2%, included in the total yield.



(**10**)



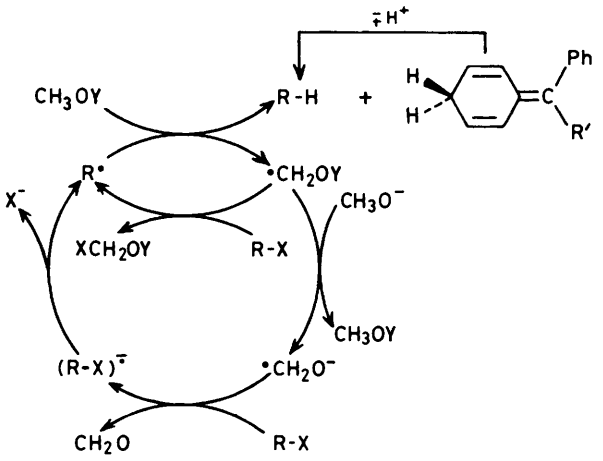
(**11**)
a; R = Ph
b; R = $CONMe_2$

studies.[2,3] When the reaction of chloride (**1a**) with sodium methoxide in refluxing DMP was carried out in the presence of one molar equivalent of DNB (Table, entry 5), a significant decrease of the total yield of products (**1f**), (**1g**), and (**3a**) was observed (*cf.* entry 1) with concomitant increase of the yield of the substitution product (**1c**). In the presence of 0.06 molar equivalents of DBNO in refluxing DMP a sharp decrease of the yields of compounds (**1f**) and (**3a**) was observed without any significant changes in the yields of the substitution products (**1c**) and (**2a**) (compare entries 1 and 6, and 10 and 11, respectively). At room temperature the reduction of the total yield of products (**1f**), (**3a**), and (**1g**) and the augmentation of the total yield of the substitution products (**1c**) and (**2a**) by added DBNO is more pronounced with the bromide (**1b**) as the substrate than with the chloride (**1a**) (compare entries 7 and 9, and 12 and 13, respectively; Table) because, at room temperature, the formation of products (**1f**), (**3a**), and (**1g**) from bromide (**1b**) competes more effectively with that of the substitution products as from chloride (**1a**). The surprising effect of the addition of 0.16 molar equivalents of DNB (entries 4 and 8, Table) will be discussed below.

The inhibition of the formation of compounds (**1f**), (**1g**), and (**3a**) both by DNB and DBNO, while these compounds do not inhibit the formation of the substitution products, demonstrates the intermediacy of radical anions and/or radicals in the formation of the former, *i.e.* that compounds (**1f**), (**1g**), and (**3a**) are the products of SET-initiated reactions of halides (**1a**) and (**1b**), and that radical anions and radicals are *not* involved in the reactions leading to the substitution products. Thus, the $S_{RN}1$ pathway does not (at least does not significantly) contribute to the formation of the substitution products.

The Mechanism of Formation of the SET Products (**1f**), (**1g**), *and* (**3a**) *from Trityl Halides and Sodium Methoxide in DMP.*—2-Halogeno-*NN*-dimethyl-2,2-diphenylacetamides (**1h**, **i**) have been shown to furnish, when treated with sodium methoxide in DMP, compounds (**1k**) and (**3b**) (in addition to substitution products).[21] The formation of compound (**1k**) has been shown to take place by two competing pathways, *viz.* a radical anion—radical chain, and a radical chain mechanism (Scheme 3α, large and small circles, respectively).

Recombination of two radicals R·, followed by prototropic rearrangement of the resulting semibenzene (**11b**), on the other hand, may lead to the formation of dimer (**3b**).



Y = $C(CH_3)_2OCH_3$, *i.e.* CH_3OY = DMP

α R = $Ph_2CCONMe_2$, R′ = $CONMe_2$

β R = Ph_3C−, R′ = Ph

Scheme 3.

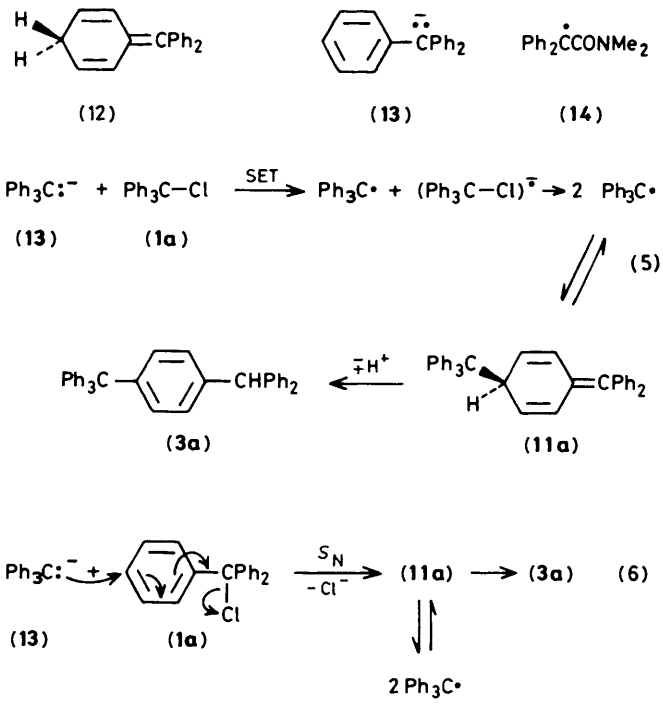
The involvement of analogous chain processes (Scheme 3β) has now been proved for the formation of compound (**1f**) from the trityl halides (**1a** and **b**) and sodium methoxide in DMP. Instead of repeating the entire argumentation described in ref. 21, the main points will only be presented for the latter case.

Thermolysis of the azo derivative (**1l**) in DMP which, too, involves the intermediacy of trityl radicals furnishes, both in the presence and absence of sodium methoxide, ample amounts of compound (**1m**) *mainly via* recombination of trityl and $^{\bullet}CH_2OY$ radicals (derived by hydrogen abstraction by trityl radicals from the solvent CH_3OY = DMP), followed by hydrolysis during work-up.[22] The non-formation of compound (**1m**) from the halides (**1a** and **b**) indicates rapid consumption of the $^{\bullet}CH_2OY$ radicals by some special mechanism operating only in the presence of these halides. It was assumed that the halides exert this effect, similarly to the related halides (**1h** and i), by the way of chain processes shown in Scheme 3β, both in the presence (large circle) and absence of methoxide anions (small circle). This assumption was proved by carrying out the thermolysis of the phenylazo derivative (**1l**) in the presence of added chloride (**1a**). When a mixture of compounds (**1l** and **1a**) (molar ratio 1:1.5) was thermolysed in the presence of excess of sodium methoxide in DMP, no hydroxymethyl derivative (**1m**) could be detected in the product mixture. When the thermolysis was repeated in the absence of sodium methoxide, the resulting mixture contained only 6% of compound (**1m**), while a 15% yield of the latter was obtained when the thermolysis of the phenylazo derivative (**1l**) in DMP was conducted in the absence of any added substances.

Recombination of two trityl radicals will lead *via* the semibenzene-type intermediate (**11a**) to the formation of the dimer (**3a**)* while their trapping by oxygen will furnish ditrityl peroxide (**1g**) irrespective of whether these radicals were generated by the reaction of trityl halides with alkoxide anions or by thermolysis of the phenylazo derivative (**1l**) either in the presence or absence of methoxide anions.

However, a surprising observation, made in the course of our inhibition studies (see above), called our attention to a further possibility of dimer formation in the reaction of trityl halides with methoxide anions.

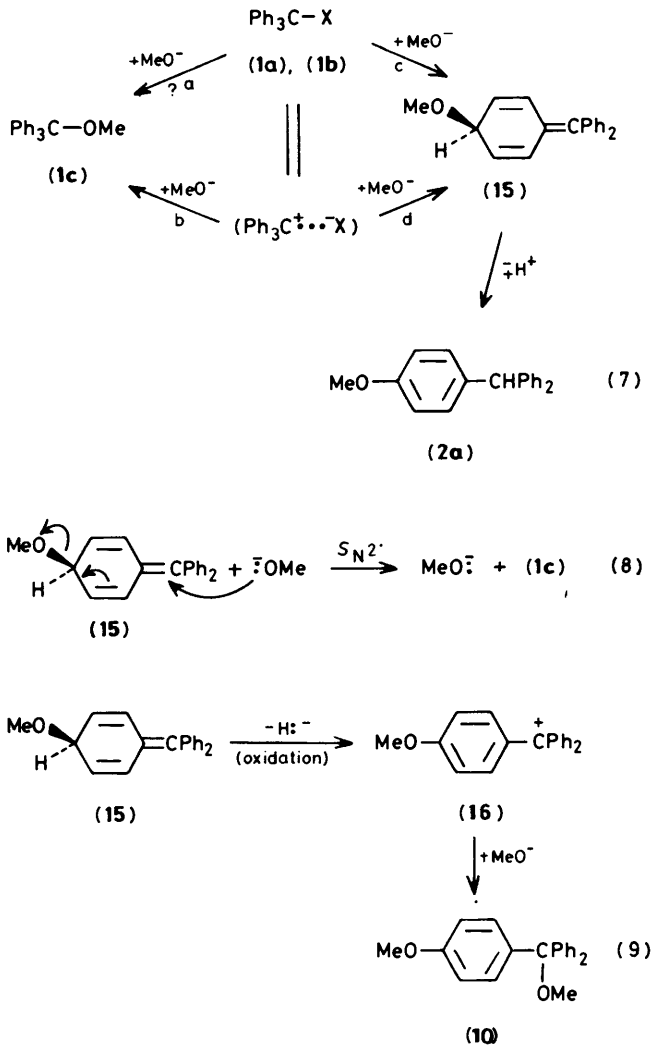
When the reaction of chloride (**1a**) with sodium methoxide



was carried out in the presence of only 0.16 mol. equiv. of DNB, a significant decrease of the yields of the SET product (**1f**) and the substitution products (**1c**) and (**2a**) with considerable concomitant *increase* of the yield of the SET product (**3a**) was observed both at elevated (compare entries 1 and 4, Table) and ambient temperatures (compare entries 7 and 8). The following explanation is offered for this observation. The formation of trityl radicals (Scheme 2) is either retarded or completely inhibited by DNB, depending on the amount added, because part of the trityl chloride radical anions is rapidly reoxidized to the starting chloride. In the presence of 0.16 mol. equiv. of DNB the formation of trityl radicals is only retarded rather than completely inhibited. Because of the low concentration of the trityl radicals their recombination to form the semibenzene (**11a**) and thence the dimer (**3a**) is less likely than their alternative reactions, *e.g.* hydrogen abstraction to furnish the semibenzene (**12**) and, by deprotonation of the latter, triphenylmethanide anions (**13**).† [An alternative pathway of formation of these anions, *viz.* reduction of trityl radicals by methoxide anions *via* SET, is probably less significant because, if it were, it should also be significant in the thermolysis of compound (**1l**) in the presence of sodium methoxide and lead there, analogously to the formation of compound (**1m**), *via* recombination of methoxyl with trityl radicals, to the formation of compounds (**1c**) and (**2a**) which, however, is not the case.[22]] In any case, ample amounts of triphenylmethanide anions (**13**) are formed under these conditions in the reaction mixture; these anions may, therefore, compete effectively with methoxide anions for the starting chloride (**1a**). This will lead either by SET [equation (5)] or in an S_N reaction [equation (6)] to a considerable increase of the yield of the dimer (**3a**) from chloride (**1a**) in the presence of a comparatively small amount of added DNB as a result of triggering, in addition to radical recombination, the efficient operation of a further mechanism

* For the base-catalysed rearrangement of the semibenzene (**11a**) into dimer (**3a**), see ref. 10*b*.

† Formation of compound (**12**) is the result of the ambident reactivity of trityl radicals in hydrogen abstraction.[22] [*Cf.* with the case of the related radicals (**14**).[23]]



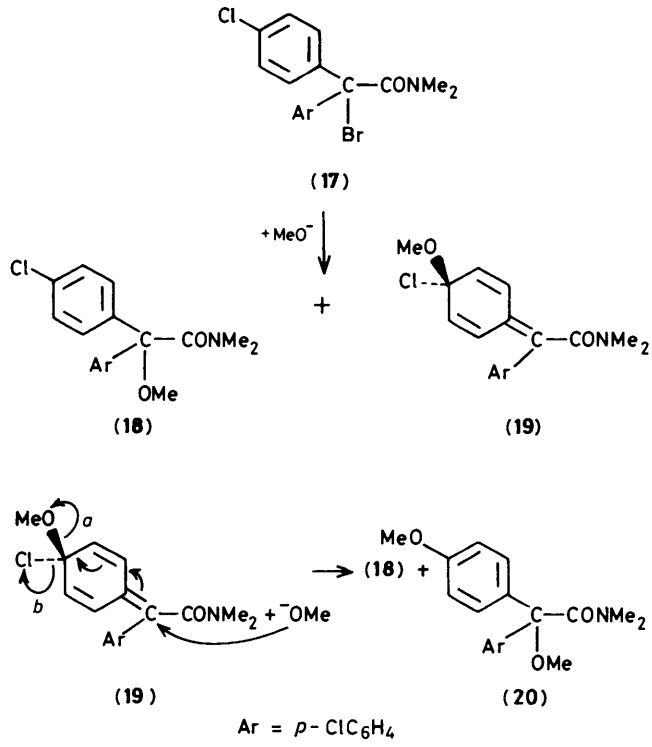
Scheme 4. a, S_N2 reaction; probably prohibited by steric factors; b, S_N2 reaction, ion-pair version; c, S_N2' reaction; d, S_N2' reaction, ion-pair version

of dimer formation which we call, for obvious reasons, the *carbanionic mechanism of dimer formation.**

Our experimental observations themselves do not permit us to differentiate between the two versions of the carbanionic mechanism of dimer formation or to estimate their relative importance. However, in a study of the reactions of triphenylmethanide anions with trityl halides in tetrahydrofuran Zieger *et al.* have found evidence that dimer (**3a**) formation from these anions and trityl chloride (and, presumably, trityl bromide as well) takes place by the SET mechanism [equation (5)].[24]

The Mechanism of Formation of the Substitution Products (**1c**), (**2a**), *and* (**10**).—Since dissociation of the halides (**1a**) and (**1b**) into free ions appears to be rather unlikely in DMP, it is reasonable to assume that methoxide anions will attack the intact halides or the corresponding ion-pairs either in the α or in one of the *para* positions to furnish the *ipso* substitution product (**1c**) or the semibenzene-type intermediate (**15**) of the

* For a different approach to the establishment of the carbanionic mechanism of dimer (**3b**) formation from the bromocarboxamide (**1h**), see ref. 21.



Scheme 5.

tele substitution product (**2a**) according to the S_N2 and S_N2' mechanisms, respectively, or their ion-pair versions[25a] (the latter may, indeed, be the actual mechanisms in the present special case, *cf.* ref. 25*b*) [see Scheme 4, equation (7)]. The non-ion-pair version of the S_N2 mechanism is, however, probably sterically hindered. The simplest means of stabilization of semibenzene (**15**) is its base-catalysed re-aromatization to compound (**2a**) by deprotonation–protonation.

A further possibility for the stabilization of compound (**15**) could be attack of a second methoxide anion at its central carbon atom with simultaneous expulsion of the first methoxide anion to furnish, by an indirect pathway, *viz.* the sequence of two successive S_N2' processes, the *ipso* substitution product (**1c**) [Scheme 4, equation (8)]. That the latter pathway of formation of compound (**1c**) is not merely speculative is shown by the formation of the dimethoxy derivative (**20**), in addition to compound (**18**) and other products, in the reaction of the 4,4-dichloro compound (**14**) with sodium methoxide in methanol.[26] The dual pathway of formation of the normal product (**18**) (see Scheme 5) must be analogous to that of compound (**1c**), except that, because of the change of the solvent, the S_N1 mechanism may not be ruled out *a priori.* However, since the intermediate (**19**) in this case contains two leaving groups (methoxide and chloride) in geminal positions, the intermediate may furnish either compound (**18**) (path a) or compound (**20**) (path b, Scheme 5).[26]

It should be pointed out that, by demonstrating that nucleophilic *ipso* substitution reactions in apolar solvents may take place by a sequence of two successive S_N2' steps rather than by either the simple S_N1 or the S_N2 mechanisms, the mechanistic difficulties which have prompted so many scientists to put great efforts into the elucidation of the mechanism of the reactions of trityl halides with nucleophiles, are solved.

Among the three pathways leading to compound (**1c**) [Scheme 4, equation (7), paths a and b, and equation (8)] the first is disfavoured by steric, and the last by electronic factors

since the aromaticity of the starting halides (**1a** and **b**) is partly lost in intermediate (**15**). Furthermore, the ionization of trityl halides to yield ion-pairs is obviously controlled both by electronic and steric effects (exerted by substituents attached to the aromatic rings), as well as by the nature of the solvent. Therefore, the relative importance of the three pathways will, in general, be controlled by the delicate balance of a series of partly antagonistic effects.

The intermediate (**15**) may be considered also to be the precursor of the dimethoxy derivative (**10**) [Scheme 4, equation (9)]. Oxidation of compound (**15**) should lead to cation (**16**) which, with a methoxide anion, furnishes compound (**10**). It is significant in this connection that compound (**10**) has been isolated only if an oxidant (nitrobenzene or DBNO) was present in the reaction mixture (Table, entries 2, 3, and 13).

Our opinion concerning the formation of substitution products predominantly by ionic mechanisms (which is in agreement with the results of our inhibition studies) is in sharp contrast to the conclusions of earlier studies,[8,9] according to which these substitutions involve the intermediacy of trityl radicals, *i.e.* they are initiated by SET (*cf.* Scheme 2). It has, however, to be pointed out that, as a result of the initiation step leading to the SET products (see above), geminate trityl and methoxyl radical pairs and, possibly, free trityl and methoxyl radicals are present in the reaction mixture. As a consequence, the existence of an additional minor pathway leading to the substitution products (**1c**) and (**2a**) by radical recombination cannot be ruled out. On the other hand, any significant contribution of the $S_{RN}1$ pathway to the formation of the substitution products (**1c**) and (**2a**) is definitely ruled out (see above).

It appears rather unlikely that either replacement of the solvent DMP by THF, or the replacement of sodium methoxide by alkali t-butoxides (the solvent and reagents used by Ashby *et al.*[9]) should result in profound changes of the mechanism of the reaction, all the more because, when attempting to react compound (**1a**) with potassium t-butoxide in refluxing DMP, we have obtained mixtures of compound (**1d**),* (**2b**), and (**3a**).[3] Since formation of compound (**3a**) requires the intermediacy of trityl radicals (*i.e.* the involvement of competing pathways initiated by SET), detection of the latter in the reaction mixture does *not* prove them to be necessarily the precursor of the substitution products.

In summary, SET and S_N processes are thought to compete when trityl halides (**1a** and **b**) are allowed to react with alkoxide anions. The balance of these two types of reactions appears to be, in general, highly sensitive to the nature of the substrate and the reaction conditions. For example in the cases studied by Kornblum [15b] (where SET processes are favoured because of the presence of nitro groups in the substrates) and by Bunnett [15a,c] (where nucleophilic attack at the non-activated aromatic substrates is extremely difficult) SET reactions take place exclusively. The observations of Arbusow and Arbusow,[11c] *viz.* that while diethyl sodium phosphite furnishes the substitution product diethyl triphenylmethylphosphonate (**21**) with trityl chloride, with trityl bromide ditrityl peroxide (**1g**) (73%) is obtained in air, and 'triphenylmethyl' [*i.e.* (**11a**); 78%] under nitrogen, are also noteworthy in this connection. Since organic bromides are more prone to enter SET reactions than the corresponding chlorides (see *e.g.* ref. 15*c*), the obvious explanation of these observations is a change from an S_N to an SET mechanism when the starting chloride is replaced by the corresponding bromide. The alternative explanation, *viz.* that

$Ph_3CP(O)(OEt)_2$
(**21**)

both reactions are initiated by SET followed by recombination within the solvent cage of the resulting geminate radicals to give the substitution product (**21**) by the S_{ET} mechanism (*cf.* Scheme 2, step 8) when starting with trityl chloride while the *same* two radicals, when formed by SET from trityl bromide, should, rather than recombine, be able to escape from the solvent cage to form *free* trityl radicals and their transformation products, appears to be untenable.

A further factor which may determine the balance of S_N and SET processes is the nature of the solvent: *e.g.* while, in methanolic solution, compound (**1h**) and sodium methoxide give exclusively (*ipso* and *tele*) substitution products,[26] in DMP SET products are also formed.[21]

Experimental

M.p.s are not corrected. I.r. spectra were recorded with a Spectromom 2000 spectrometer (Hungarian Optical Works, Budapest). ^{1}H N.m.r. spectra were obtained at 60 or 100 MHz (the frequency being stated only in the latter case) with Perkin-Elmer R12 and JNM FX-100 spectrometers, respectively.

Materials.—2,2-Dimethoxypropane (DMP; EGA Chemie; 98% purity) was refluxed with excess of $LiAlH_4$ for 6 h, in order to remove the contaminants acetone and methanol, and distilled from $LiAlH_4$ immediately before use. Sodium methoxide was obtained by dissolving metallic sodium in anhydrous methanol under nitrogen and removing the excess of solvent by distillation at reduced pressure; the last traces of solvent were removed over P_2O_5 at 150 °C and 12 mmHg.

Reaction of Trityl Halides (**1a** *and* **b**) *with Sodium Methoxide in DMP.*—The trityl halides (**1a** and **b**) were stirred with the suspension of sodium methoxide in DMP either at the boiling point of the reaction mixture or at ambient temperatures; some experiments were carried out in the presence of added di-t-butyl nitroxide (DBNO), nitro- (NB) or *m*-dinitro-benzene (DNB). For details, see Table. The solvent was removed by distillation at reduced pressures, and the residues were taken up in mixtures of CH_2Cl_2, water, and acetic acid (6.0,† 6.0, and 0.3 ml, respectively, for 1 mmol of the starting trityl halide). The aqueous phases were extracted with CH_2Cl_2, and the combined CH_2Cl_2 solutions were dried ($MgSO_4$) and evaporated to dryness at reduced pressures. The residues were worked up by preparative t.l.c. (Kieselgel 60 $PF_{254+366}$; benzene–hexane, 1:1; elution: MeOH–CH_2Cl_2, 1:1). The individual products were identified by comparison (t.l.c., i.r.) with authentic samples.

Authentic samples of methyl trityl ether (**1c**),[27] triphenylmethanol (**1d**),[27] triphenylmethane (**1f**),[28] ditrityl peroxide (**1g**),[29] 2,2,2-triphenylethanol (**1m**),[21] *p*-methoxytriphenylmethane (**2a**),[30] *p*-diphenylmethyltritylbenzene (**3a**),[31] and azoxybenzene[32] were obtained as described in the literature.

Methoxy-(p-*methoxytriphenyl*)*methane* (**10**).—(*p*-Methoxytrityl) chloride[33] (1.67 g, 5.4 mmol) was added in small portions mmol Na, and 10 ml anhydrous MeOH) at room temperature with continuous stirring. The mixture was refluxed for 4 h and evaporated to dryness at reduced pressure. The residue was taken up in CH_2Cl_2 (30 ml) and water (10 ml), and subjected to

* This compound was possibly formed by hydrolysis[6g] of initially formed compound (**1e**) during work-up of the reaction mixture (which was different from that used by Ashby *et al.*[9]).

† When large amounts of the dimer (**3a**) were formed (entries 3 and 7, Table) the amount of the CH_2Cl_2 used had to be doubled.

conventional work-up to obtain the title compound (1.4 g, 85%), m.p. 73—75 °C (from methanol) (lit.,[34] 74 °C).

Thermolysis of Triphenyl(phenylazo)methane (**1l**) *in the Presence of Trityl Chloride* (**1a**).—(a) Triphenyl(phenylazo)methane (**1l**) (0.52 g, 1.5 mmol) and trityl chloride (**1a**) (0.63 g, 2.25 mmol) were thoroughly mixed and ground. The mixture was divided into ten equal parts which were dissolved at intervals of 30 min in DMP (2.5 ml each) under argon and immediately injected through a rubber septum into a refluxing suspension of sodium methoxide (0.37 g, 6.9 mmol) in DMP (5 ml) with continuous stirring under nitrogen. After addition of the last portion, the mixture was refluxed for a further 5 h and worked up as described for the reaction mixtures obtained by allowing the trityl halides (**1a** and **b**) to react with sodium methoxide. No 2,2,2-triphenylethanol (**1m**) could be isolated, and the ^{1}H n.m.r. spectrum ($CDCl_3$) of the crude mixture did not exhibit the characteristic signal of compound (**1m**) at δ 4.55. Taking into account the sensitivity of the n.m.r. measurement, this proves that <2% (if any) of compound (**1m**) was formed.

Under comparable conditions, except for the absence of the chloride (**1a**), the thermolysis of compound (**1l**) furnished 19—20% of compound (**1m**).[22]

(b) The above experiment was repeated in the absence of sodium methoxide but otherwise under identical conditions. The dry residue of the reaction mixture was taken up in CH_2Cl_2 and 5% aqueous sodium hydroxide (50 ml each). The organic phase was dried ($MgSO_4$), evaporated to dryness, and subjected to two successive separations by t.l.c. (Kieselgel 60 $PF_{254+366}$; benzene–hexane, 1:1; acetone–hexane, 1:4) to obtain compound (**1m**) (6%), identified by comparison [m.p., R_F, δ_H (100 MHz; $CHCl_3$)] with an authentic sample.

Thermolysis of Triphenyl(phenylazo)methane (**1l**) *in DMP.*—The above experiment (b) was repeated starting with compound (**1l**) (1.04 g, 3.0 mmol) and DMP (9 ml) in the absence of added chloride (**1a**). After refluxing for 14 h under nitrogen with continuous stirring, the mixture was evaporated to dryness, and the residue was taken up in CH_2Cl_2 (50 ml) and 5% aqueous HCl (30 ml). The dry residue of the CH_2Cl_2 phase was worked up by three successive separations by t.l.c. (adsorbent as above; acetone–hexane, 1:9; benzene; dioxane–hexane, 1:9) to obtain compound (**1m**) (0.12 g, 15%), m.p. 105—107 °C (hexane).

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