The Ambident Reactivity of Triphenylmethyl Radicals in Hydrogen-abstraction Reactions and the Mechanism of the Base-catalysed Rearrangement of (Diphenylmethylene)cyclohexadienes (a Type of Semibenzene) into Triphenylmethane

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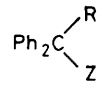
Thermolysis of tri([$^2H_5$]phenyl)(phenylazo)methane (**2**) in non-deuteriated 2,2-dimethoxypropane in the presence of non-deuteriated sodium methoxide furnishes, among other products, mixtures of the deuteriated analogues of triphenylmethane (**1c**) and of deuteriated analogues of (*p*-biphenylyl)diphenylmethane (**3a**). The former was shown to be a mixture of the hexadecadeuterio derivative (**6c**) and the isomeric monoprotiopentadecadeuterio derivatives (**6a** and **b**), while the latter proved to be a mixture of the pentaprotio derivative (**3d**) and the isomeric hexaprotio derivatives (**3b** and **c**). The formation of compound (**6b**) proves the ambident reactivity of triphenylmethyl radicals in hydrogen-abstraction reactions, while the observed ratio of compounds (**6a** and **b**) indicates the rearrangements of the intermediate semibenzenes (**7**) and (**8**) to be multistep conducted-tour rearrangements (Scheme 1).

The ambident reactivity of trityl systems (radicals,[1-6] cations or ion pairs containing the trityl cation,[7-11] anions,[3,12,13] and halides[1,6,14-18]) in various reactions is well known. However, as far as we have been able to ascertain, no example of ambident reactivity of trityl radicals in hydrogen-abstraction reactions is known yet. Since (dimethylcarbamoyl)diphenylmethyl radicals, generated by thermolysis of *NN*-dimethyl-2,2-diphenyl-2-phenylazoacetamide (**1a**) in 2,2-dimethoxypropane (DMP) in the presence of sodium methoxide, are known[19] to furnish, in hydrogen-abstraction reactions, products with the newly incorporated hydrogen atom attached to either the α or one of the aromatic carbon atoms,† it was felt important to establish whether the behaviour of trityl radicals is similar.

To this end the thermolysis of both triphenyl(phenylazo)methane (**1b**) (as a model compound) and of tri([$^2H_5$]phenyl)(phenylazo)methane (**2**) (>99 atom% ^2H in the labelled phenyl rings) in *non*-deuteriated DMP in the presence of *non*-deuteriated sodium methoxide was studied.

Triphenyl(phenylazo)methane (**1b**) is known[21] to furnish, on thermolysis, trityl and phenyl radicals which, by a variety of successive reactions, furnish the final products. Thermolysis of compound (**1b**) in DMP in the presence of sodium methoxide furnished, in addition to the known thermolysis products, *viz.* thehydrogen-abstractionproduct(**1c**)[1-3,22,23](20—24%)andthe recombination products tetraphenylmethane (**1d**)[1-3,22,24] (4—5.5%) and (*p*-biphenylyl)diphenylmethane (**3a**)[2,3] (12—13%),‡ the following new thermolysis products: 2,2,2-triphenylethanol (**1e**) (19—21%), the dimeric compound (**4**)[4b] (3.5—7%), and bis-(*p*-biphenylyl)phenylmethane (**5**)[14] (1.5%).§ Thermolysis of the



(**1**)

	R	Z
a;	$CONMe_2$	N=NPh
b;	Ph	N=NPh
c;	Ph	H
d;	Ph	Ph
e;	Ph	CH_2OH
f;	Ph	OH
g;	Ph	
h;	Ph	Cl

$(C_6{}^2H_5)_3C-N{=}N-Ph$

(**2**)

$(C_6H_5)_2CHC_6H_4Ph-p$

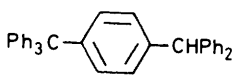
(**3a**)

$(C_6{}^2H_5)_2CRC_6{}^2H_4Ph-p$

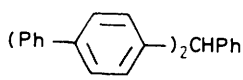
(**3b**) R = H
(**3d**) R = ^2H

$(C_6H^2H_4)(C_6{}^2H_5)C^2HC_6{}^2H_4Ph-p$

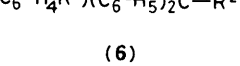
(**3c**) ¶



(**4**)



(**5**)



(**6**)

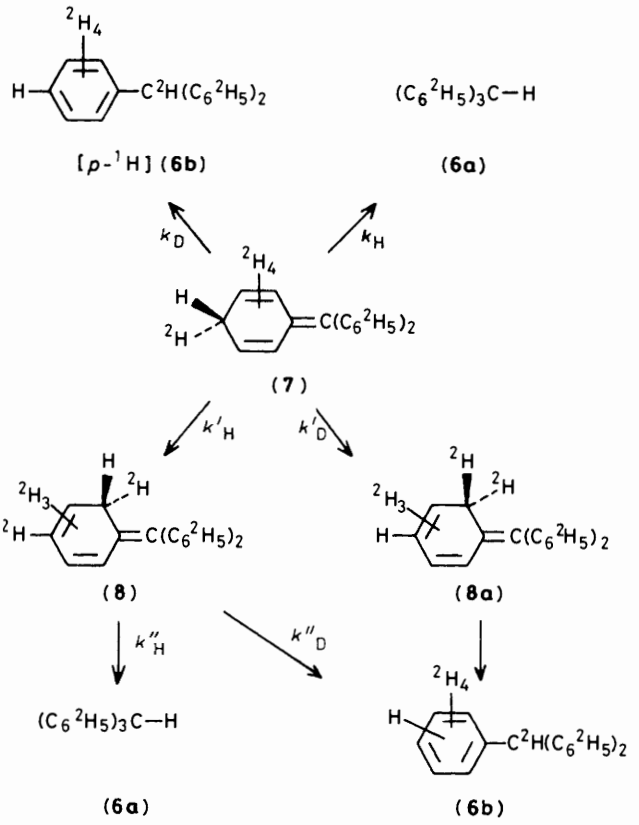
	R^1	R^2
a;	^2H	H
b;	H	^2H
c;	^2H	^2H
d;	H	H

† Ambident reactivity has been observed even for benzyl radicals.[20]
‡ In some experiments small amounts (≤2.5%) of triphenylmethanol (**1f**) (*cf.* ref. 25) and of biphenyl (≤1.3%) were also isolated. Biphenyl appears to have been obtained so far in the thermolysis of the azo compound (**1b**) only if carried out in benzene;[23] in the presence of this solvent at least part of it is not formed by recombination of two phenyl radicals but *via* participation of a molecule of the solvent.
§ The mechanisms of formation of compounds (**1e**), (**4**), and (**5**) will be discussed later.
¶ The isomeric structure with the ^1H atom attached to the phenylene, rather than the phenyl, nucleus is equally possible.

Table 1. Compositions of the mixtures of compounds (**6a**—**c**) and of compounds (**3b**—**d**) obtained by thermolysis of tri([$^2H_5$]phenyl)-(phenylazo)methane (**2**) in DMP in the presence of sodium methoxide[a]

	Experiment 1	Experiment 2	Experiment 3
[(**6a**) + (**6b**)]/(**6c**)[b]	52.5:47.5	42.5:57.5	40:60
α-^{1}H/*Ar*-^{1}H[c]	1:2.8[d]	1:3.55[d]	1:2.45[d]
		1:3.3[e]	
(**6a**):(**6b**)[f]	1:2.21	1:2.74[d]	1:1.76[g]
		1:2.52[e]	
(**6a**):(**6b**):(**6c**)[h]	16.7:35.8:47.5	12:30.5:57.5	15:25:60
[(**3b**) + (**3c**)]/(**3d**)[i]	*k*	55.7:44.3	56.2:43.8
α-^{1}H/*Ar*-^{1}H[c]	*k*	1:11.3[d]	1:15.2[d]
(**3b**):(**3c**)[l]	*k*	4.6:1	1.6:1
(**3b**):(**3c**):(**3d**)[m]	*k*	46:9.7:44.3	35:21.2:43.8

[a] Three essentially identical runs. [b] Calculated from the relative abundances of the peaks of the molecular-ion bundles (see Table 3) after correction for natural ^{13}C abundances, and assuming that the monoprotio compounds (**6a** and **b**) contain 100% ^1H in one position, while the deuterium content in all other positions as well as in all positions of the perdeuterio compound (**6c**) is uniformly 99.2 atom %. [c] Relative intensities of the α-H and the aromatic signals in the 100 MHz ^1H n.m.r. spectra of the mixtures of compounds (**6a**—**c**) and (**3b**—**d**), respectively. [d] Solvent CCl_4. [e] Solvent [$^2H_6$]acetone. [f] Calculated from the ^1H n.m.r. data on the basis of the assumption stated in note *b*. [g] Average of the three experiments 1:2.31. [h] Calculated from the m.s. and ^1H n.m.r. data on the basis of the assumption stated in note *b*. [i] Calculated from the relative abundances of the peaks of the molecular-ion bundles (see Table 4) after correction for natural ^{13}C abundances, and assuming that compounds (**3b** and **c**) contain 100 atom % ^1H in six, (**3d**) in five positions, while the deuterium content is 99.2% uniformly distributed over the remaining positions. [k] Not determined. [l] Calculated from the ^1H n.m.r. data on the basis of the assumption stated in note *i*. [m] Calculated from the m.s. and ^1H n.m.r. data on the basis of the assumption stated in note *i*.



Scheme 1.

labelled compound (**2**) furnished, as expected and shown by t.l.c., the same products (in deuteriated forms) but only the deuteriated analogues of the hydrogen-abstraction product (**1c**) as well as those of the recombination products (**1d**) and (**3a**) were isolated and examined.

Examination of the Deuteriated Hydrogen-abstraction Product and Discussion of its Mechanism of Formation.—(A) The deuteriated hydrogen-abstraction product was shown by its mass spectrum to be a mixture of the hexadecadeuterio (no ^1H present) (**6c**) and the pentadecadeuterio (= monoprotio) compounds [(**6a** + **b**), see below] in roughly equal amounts (see Table 1), the mixture containing at most traces of the diprotio compound (**6d**). As shown by a separate experiment, no incorporation of ^1H atoms into the rings of an authentic sample of compound (**6a**) takes place under the conditions of the reaction.* Therefore compounds (**6a**—**c**) are to be considered as independent reaction products which are not interconverted in the course of the reaction.

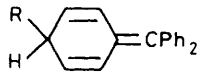
(B) The pentadecadeuterio (= monoprotio) compound was shown by the ^1H n.m.r. spectrum of the deuteriated hydrogen-abstraction product to be a mixture of isomers with their single ^1H atom attached to the α position [(**6a**)] and to one of the aromatic carbon atoms [(**6b**)], respectively, the ratio of the isomers (**6a** and **b**) being roughly equal to 1:2.3 (see Table 1). Compounds (**6a** and **b**) result from hydrogen abstraction by [$^2H_{15}$]trityl radicals from the solvent or, probably to a lesser extent (*cf.* ref. 19), from methoxide ions.

The formation of compound (**6b**) (which is possibly a mixture of isomers with the ^1H atom attached to different positions of the aromatic nuclei, see below) requires attachment of the ^1H atom to one of the [$^2H_5$]phenyl rings of the [$^2H_{15}$]trityl radicals, *i.e.* the intermediacy of *e.g.* the semibenzenes (**7**) and/or (**8**) which (see Scheme 1), by base-catalysed deprotonation–protonation and dedeuteronation–deuteronation, respectively, subsequently rearrange to furnish either compound (**6a**) [indirect pathway of formation of compound (**6a**); formation of the latter by direct hydrogen abstraction to the aliphatic carbon atom of the [$^2H_{15}$]trityl radicals should, of course, be also possible] or the isomeric mixture (**6b**). The formation of at most traces of compound (**6d**) appears to indicate that dedeuteronation–deuteronation, and therefore deprotonation–protonation of compounds (**7**) and (**8**) as well, takes place by some sort of conducted-tour mechanism.[26]†

Base-catalysed rearrangements of the *p*-semibenzenes (**9a** and **b**) into their fully aromatic isomers [(**4**), *etc.*] are known from the literature.[4b,8,26b] Moreover, the rearrangement of com-

* This is probably the result of the failure of compound (**6a**) to be deprotonated under these conditions, as shown by the fact that no deuteriation takes place when the perprotio analogue is refluxed with sodium methoxide in DMP in the presence of [$^2H_6$]acetone as the potential deuterium source.

† The term 'conducted-tour mechanism' has been coined for all types of base-catalysed *C*-deprotonation–*C*-protonation processes in the course of which the proton cleaved from the substrate by the base migrates from one hydrogen-bonding site to the next without ever becoming completely detached from the anion of the substrate,[26a] regardless of whether the overall process results in the inversion of a chiral ≥C–H group[26a] or in isomerization by a proton shift, *e.g.* a [1,5] proton shift;[26b] the consequence (and diagnosis) of such conducted-tour prototropic rearrangements will be the absence of $^1H/^2H$ exchange between substrate and any potential $^2H^+$ source present.



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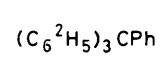


(10)

a; R = Ph_3C
b; R = $MeOOCCMe_2$
c; R = Ph

pound (**9b**) is known to take place, under conditions comparable to those under which the rearrangements of compounds (**7**) and/or (**8**) took place in our experiments,* by the conducted-tour mechanism.[26b]

A difficulty in the interpretation of the experimental results issues from the observed ratio of compound (**6a**) and the mixture (**6b**). Were (**6a**) exclusively formed *via* either of the intermediates (**7**) and (**8**), then the ratio (**6a**):(**6b**) should be identical with the average value of the kinetic isotope effect (k.i.e.) k_H/k_D of the rearrangements (**7**) or (**8**) ⟶ (**6a**) + (**6b**). For the k.i.e. of the rearrangement (**7**) ⟶ (**6a** + **b**) Olah and Svoboda have considered a value of *ca.* 3—4 as reasonable.[9] Assuming that the k.i.e. of the rearrangement (**8**) ⟶ (**6a** + **b**) has the same value, a value of 3:1—4:1 would be expected for the ratio of compounds (**6a** and **b**); this value would be even larger if part of compound (**6a**) were directly formed. The observed ratio (**6a**):(**6b**) was 1:2.3. The reversal of the observed, relative to the expected, value may be explained by assuming that the main pathway of conversion of intermediates (**7**) and (**8**) into the final products (**6a** and **b**) is not their direct deprotonation–protonation and dedeuteronation–deuteronation, respectively; instead, formation of the final products is preceded by repeated interconversions of the intermediates. The effect of *e.g.* the intervention of intermediates (**8**) and (**8a**) in the course of the rearrangement (**7**) ⟶ (**6a**) + (**6b**) may be understood with the aid of Scheme 1. [A similar scheme could be drawn starting with the semibenzene (**8**) and involving the intermediacy of type (**7**) semibenzenes. Calculations based on the latter scheme would lead to similar results to those based on Scheme 1 and discussed below.] Assuming that only direct prototropic and deuterotropic rearrangements of compound (**7**) into compounds (**6a** and **b**), respectively, take place (intervention of a single semibenzene-type intermediate), the amount of compound (**6a**) formed, expressed in a percentage of the consumed compound (**7**) (or of the $[^2H_{15}]$trityl radicals having served as its precursors) will be $100k_H/(k_H + k_D) = 100(k_H/k_D)/(1 + k_H/k_D)$. Similarly, if the rearrangement of compound (**7**) into compound (**6a**) were to take place exclusively *via* compound (**8**) (intervention of two semibenzene-type intermediates), the amount of compound (**6a**) formed, expressed as above, will be $100k'_Hk''_H/(k'_H + k'_D)(k''_H + k''_D) = 100(k'_H/k'_D)(k''_H/k''_D)/(1 + k'_H/k'_D)(1 + k''_H/k''_D) = 100(k_H/k_D)^2/(1 + k_H/k_D)^2 = 100[k_H/(k_H + k_D)]^2$ assuming $k_H/k_D = k'_H/k'_D = k''_H/k''_D$ (which does not appear to be unreasonable). Similarly, the amount of compound (**6a**) expressed as above will be $100(k_H/k_D)^n(1 + k_H/k_D)^n = 100[k_H/(k_H + k_D)]^n$ in the case of intervention of n semibenzene-type intermediates,† *i.e.* the greater n, the smaller will be the amount of compound (**6a**) formed, as well as the ratio [(**6a**)]/[(**6b**)] = {100 − [(**6a**)]}, the overall k.i.e. for the particular pathway. This is illustrated by the model calculations summarized in Table 2. The apparent k.i.e., *i.e.* the observed ratio [(**6a**)]/[(**6b**)] will be identical with some weighted average of the individual ratios [(**6a**)]/[(**6b**)] corresponding to the different values of n. The value of 1 : 2.3 observed for this ratio indicates that protium abstraction by the α-carbon atom of the $[^2H_{15}]$trityl radical [which would lead to the exclusive formation of compound (**6a**)] is considerably less efficient than the protium abstractions by its *ortho*- and *para*-carbon atoms. The same must be true for protium and deuterium abstraction by trityl and $[^2H_{15}]$trityl radicals, respectively, *i.e.* the direct pathways of formation of the protium- and deuterium-abstraction products (**1c**) and (**6c**), respectively, are considerably less efficient than the indirect pathways involving one or more semibenzene-type intermediates.

Table 2. Calculated ratios of compounds (**6a** and **b**) resulting from the hydrogen-abstraction reaction of $[^2H_{15}]$trityl radicals as a function of the number n of semibenzene-type intermediates involved, for different values of the k_H/k_D k.i.e.

	$k_H/k_D = 3$			$k_H/k_D = 4$		
	Relative amounts (%)		Ratio	Relative amounts (%)		Ratio
n	(**6a**)[a]	(**6b**)	(**6a**)/(**6b**)	(**6a**)[a]	(**6b**)	(**6a**)/(**6b**)
0[b]	100	0		100	0	
1	75	25	3:1[c]	80	20	4:1[c]
2	56.25	43.75	1.3:1	64	36	1.78:1
5	23.7	76.3	1:3.22	32.8	67.2	1:2.05
7	13.3	86.7	1:6.49	21.0	79.0	1:3.77

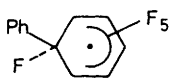
[a] Calculated by using the formula $100(k_H/k_D)^n/(1 + k_H/k_D)^n$. [b] Direct formation of the α-C–H bond. [c] Identical with the value of the k.i.e.

In order to facilitate the calculations summarized in Table 2, it was assumed as a first approximation that process (**7**) ⟶ (**8a**) is irreversible or, to put it in more general terms, that type (**8a**) intermediates which contain two geminal ^2H atoms do not revert to type (**7**) intermediates containing one ^1H and ^2H each in geminal position. Although this assumption is definitely not valid, it is easily seen that its application is permissible as a first approximation. The reversal of intermediate (**8a**) (either directly or indirectly *via* one or more further semibenzene-type intermediates) into the isomeric semibenzene (**7**) will certainly have an effect on all the figures listed in Table 2, and in particular will result in an increase of the ratios [(**6a**)]/[(**6b**)], without, however, affecting the general trends displayed by the figures of Table 2. This is, in part, the result of the facts that there are all together nine sites which may act as the migration termini for the migrating deuteron of intermediate (**8a**) (the α-carbon atom, the *para*- and the other *ortho*-carbon atom of the non-aromatic ring and the *ortho*- and *para*-carbon atoms of the two other rings‡), and that deuteron migration to only one of these will result in regeneration of intermediate (**7**); as a consequence, this process will not be very efficient.

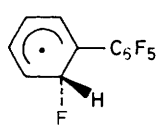
* For the formation and rearrangements of *o*-semibenzene-type compounds related to compound (**8**) into their aromatic isomers, see refs. 27 and 28.

† The amount of compound (**6a**) formed *via* direct protium abstraction by the α-carbon atoms of $[^2H_{15}]$trityl radicals (no intervention of semibenzene-type intermediates, $n = 0$) as a percentage of these radicals consumed on this pathway is also correctly described by this formula.

‡ A related interannular shift of fluorine (whose mechanism, however, should be different from that of the rearrangements discussed here) in the rearrangement of the radicaloid σ-complex (a) into isomer (b) has been postulated by Bolton *et al.*[29]



(a)



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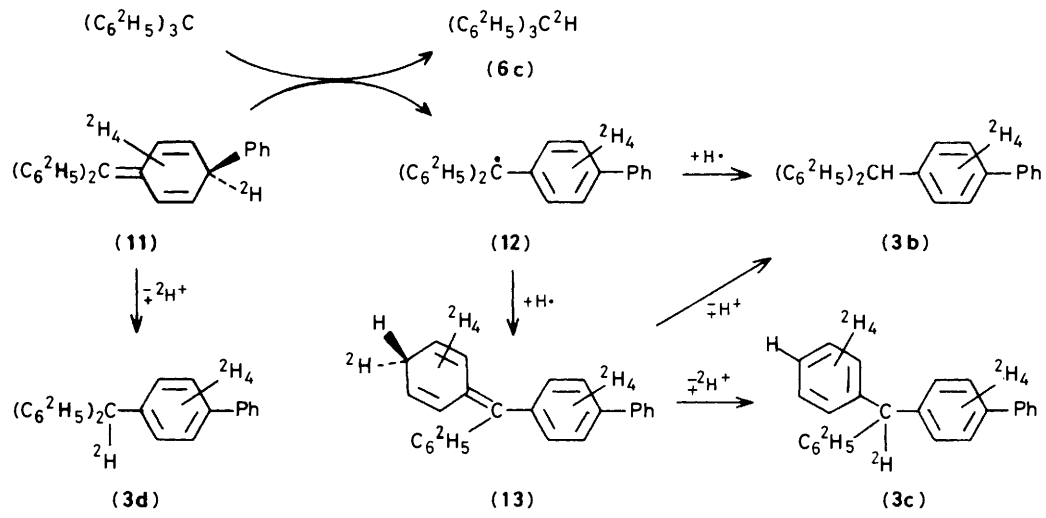


Scheme 2. Only one limiting structure is shown throughout this paper for mesomeric species

Further support for the assumption that the semibenzene ⟶ triarylmethane rearrangements are multistep reactions comes from a consideration of the ratio of the isotopically isomeric compounds (**3b** and **c**), obtained as further products of the reaction under discussion (see below).

The formation of compound (**6c**), the [$^2H_{16}$]analogue of compound (**1c**), requires deuterium abstraction by [$^2H_{15}$]trityl radicals. The ultimate source of the extra deuterium atom is necessarily the [$^2H_5$]phenyl groups of the starting compound (**1b**). One (but not necessarily the only) pathway for this deuterium transfer will be discussed below in connection with the formation of compounds (**3b** and **c**).

Examination of the Deuteriated Recombination Products and Discussion of their Mechanisms of Formation.—(A) The deuteriated analogue of compound (**1d**) contains, according to its mass spectrum, 15 deuterium atoms and may be assumed to be identical with phenyltri([$^2H_5$]phenyl)methane (**10**) which is formed by recombination of phenyl and [$^2H_{15}$]trityl radicals. This demonstrates that neither in the course of the preparation of the precursor (**2**), nor during formation of the deuteriated analogue of compound (**1d**), has any undesirable ^2H–^1H exchange taken place.

(B) The deuteriated analogue of compound (**3a**) was shown by its mass spectrum to be a mixture of the hexa- (see below) and the penta-protio [(**3d**)] derivatives, present in roughly equal amounts. Compound (**3d**) is the alternative recombination product of [$^2H_{15}$]trityl and phenyl radicals, the primary product being intermediate (**11**) which, by subsequent dedeuteronation–deuteronation, furnishes the final product (**3d**) (Scheme 2).

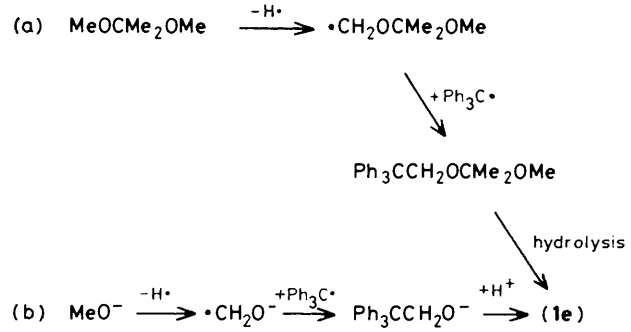
(C) The hexaprotio derivative is, according to the ^1H n.m.r. spectrum of the mixture of the deuteriated analogues, itself a mixture of isomers with the extra protium atom attached to the α-carbon atom [(**3b**)] and one of the aromatic carbon atoms [*e.g.* (**3c**)], respectively. Although the determination of the isomer ratio (**3b**)/(**3c**) was, because of the presence of the unlabelled phenyl group, less accurate as that of the ratio [(**6a**)]/[(**6b**)] (see above), compound (**3b**) definitely proved to be the major isomer.

The common intermediate of compounds (**3b** and **c**) is the same semibenzene-type isomer (**11**) which has been assumed to be the intermediate of compound (**3d**). ^2H loss from (**11**) would lead to radical (**12**) which by ^1H uptake either at the aliphatic or one of its aromatic carbon atoms would directly lead to compound (**3b**) or furnish *e.g.* the *p*-semibenzene (**13**). Subsequent deprotonation–protonation of the latter would furnish compound (**3b**) by an indirect pathway, while dedeuteronation–deuteronation would lead to compound (**3c**) (Scheme 2). As a consequence, the final outcome should be the coupling of formation of compounds (**3b** and **c**), containing one ^1H atom more, with the formation of another product, containing one ^2H atom more, *i.e.* one ^1H atom less than would have been expected. A product of the latter type is obviously compound (**6c**); therefore, a possible pathway of formation of compounds (**3b** and **c**) and (**6c**) is that shown in Scheme 2.

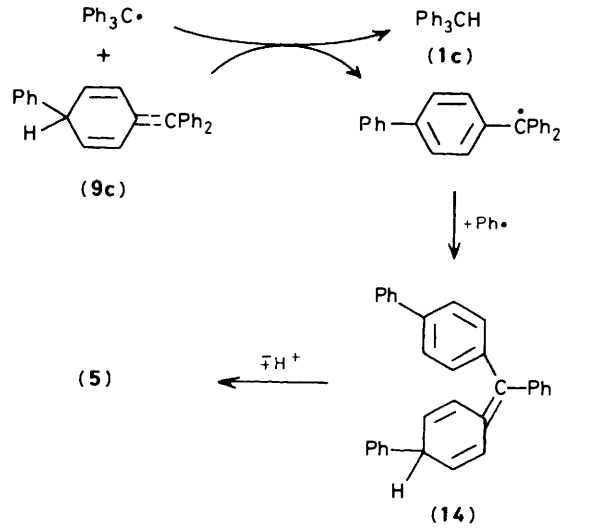
The ratio of the α- and *Ar*-protio compounds (**3b** and **c**) is > 1 which significantly differs from the observed ratio 1:2.3 of the α- and *Ar*-protio compounds (**6a** and **6b**) obtained in the same reaction. Assuming that, similarly to the case of intermediate (**7**) (Scheme 1), re-aromatization of intermediate (**13**) to furnish products (**3b** or **c**) does not take place necessarily in a single step but may involve a series of steps with the result that the ^1H and ^2H atoms become scrambled over the carbon atoms, the probability of formation of the α-protio product (**3b**) from (**13**) relative to that of the *Ar*-protio products (**3c**) should be greater than the probability of formation of the α-protio product (**6a**) from (**7**) relative to that of the *Ar*-protio products (**6b**) because the ratio of the numbers of *ortho*- and *para*-protium and deuterium atoms in intermediate (**13**) is 4:8 while in intermediate (**7**) it is 1:9.

The Mechanism of Formation of the Novel Thermolysis Products (**1e**), (**4**), and (**5**).—Compound (**1g**), an analogue of compound (**1e**), had been isolated as one of the products of the thermolysis of compound (**1b**) carried out in tetrahydrofuran.[3] The mechanisms of formation of these two compounds are obviously analogous (*cf.* ref. 3) except that formation of compound (**1e**) requires an extra hydrolysis and protonation step, respectively, during work-up (Scheme 3); the main pathway of formation of compound (**1e**) is probably pathway (a) (*cf.* ref. 19).

The formation of compound (**4**) *via* intermediate (**9a**) during thermolysis of compound (**1b**) in the presence of base could be anticipated. Since the formation of intermediate (**9a**) is reversible and its rearrangement into the product (**4**) is base-[4b] (and acid-[30]) catalysed, compound (**4**) was never obtained by thermolysis of compound (**1b**) carried out under neutral conditions. [The mechanism discussed is analogous to the



Scheme 3.



Scheme 4. A similar but today somewhat obsolete mechanism has been suggested by Schoepfle and Tepp for the formation of compound (**5**) in the reaction of trityl chloride (**1h**) with phenylmagnesium bromide.[14b]

mechanism of formation of compound (**3d**) *via* intermediate (**11**) (see above), as well as of the non-deuteriated analogue (**3a**).]

The formation of compound (**5**) may be rationalized starting with intermediate (**9c**) as shown in Scheme 4. In addition to triphenylmethyl* any other radical present should be able to abstract hydrogen from intermediate (**9c**). Alternatively, compound (**9c**) could be deprotonated to the anion which, by reaction with a phenyl radical and subsequent electron loss (*cf.* refs. 3 and 13) would then furnish intermediate (**14**).

Experimental

^{1}H N.m.r. spectra were obtained with JEOL FX-100 and Perkin-Elmer R-12 spectrometers at 100 and 60 MHz, respectively, using an external lithium lock for the FX-100 spectra taken in CCl_4 solutions. I.r. spectra were obtained in KBr pellets with a Spektromom 2000 instrument (Hungarian Optical Works). Degrees of deuteriation of individual compounds were determined by ^{1}H n.m.r. and/or mass spectral measurements, using an AEI MS 902 for the latter. Operating conditions in the determinations of degrees of deuteriation (Tables 3 and 4) were as follows: 11–12 eV [where $<1\%$ of $(M-1)^+$ is produced from the non-deuteriated analogues], direct insertion. Intensity values were determined using the meter of the ion current amplifier. In order to avoid possible errors caused by non-constant evaporation rates of the individual samples, the relative abundances of the individual peaks of the molecular bundles were measured going first from the lowest to the highest masses, and then repeating the measurements in the opposite direction. The two sets of the resulting data were found to be identical within $\pm 2\%$ in all cases. Ratios of isotopomers and of isomers differing only in the positions of the deuterium label were determined by combination of ^{1}H n.m.r. and mass spectral measurements.

Table 3. Measured relative abundances of the ions of the molecular-ion bundle in the low-voltage mass spectra of various samples of deuteriated triphenylmethanes

	I (%)			
m/z	Sample 1 [a,b]	Sample 2 [a,b]	Sample 3 [a,c]	Sample 4 [a,d]
262	0.1	1.1	1.9	2.2
261	1.5	17	19	20
260	20.1	*100*	*100*	*100*
259	*100*	97	76	70
258	12.5	9.8	8.6	10.5
257	0.6	0.6	0.5	0.6

[a] Sample 1 = compound (**6a**), obtained by reduction (H_2/Pd–C, dioxane) of [$^2H_{15}$]trityl chloride. Samples 2—4 = mixtures of compounds (**6a**—**c**), obtained by thermolysis of tri([$^2H_5$]phenyl)-(phenylazo)methane (**2**) in DMP in the presence of sodium methoxide, experiments 1, 2, and 3 (essentially identical runs) respectively. [b] 11 eV, direct insertion, 130 °C. [c] 11 eV, direct insertion, 150 °C. [d] 12 eV, direct insertion, 140 °C.

Materials.—2,2-Dimethoxypropane (98% purity; EGA Chemie) was refluxed with excess of $LiAlH_4$ in order to remove the contaminating 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 methanol by distillation at reduced pressure and subsequently keeping the product over P_2O_5 at 15 °C and 12 mmHg.

[$^2H_{15}$]Trityl chloride was obtained according to the method of Olah and Svoboda,[9] starting with [$^2H_6$]benzene (99.5 atom % ^{2}H; EGA Chemie). The deuterium content of this product was checked by reduction (H_2/Pd–C; dioxane) and ^{1}H n.m.r. and mass spectrometric examination of the resulting tri([$^2H_5$]-phenyl)methane (**6a**), δ_H (100 MHz; [$^2H_6$]acetone; Me_4Si) 5.75 (s, $\geqslant$C–H) and 7.0—7.3 (ArH), intensity ratio Ar^{1}H: $\geqslant$C–^{1}H = 1:7.7, corresponding to 0.87 atom % of ^{1}H attached to the aromatic rings.† The mass spectrum of compound (**6a**) was obtained at an ionizing voltage of 11 eV which produces less than $(M-1)^+$ from the protio compound (**1c**). The relative abundances of the ions in the molecular ion bundle are shown in Table 3, column 2. Assuming that compound (**6a**) contains ^{1}H attached exclusively to the α-carbon atom, and that the distribution of ^{1}H and ^{2}H over all other positions is uniform, the value of 99.2 atom % was calculated for the average degree of deuteriation of the aryl

* For similar hydrogen-abstraction reactions by trityl radicals, see *e.g.* refs. 1, 23, and 31.

† This is in good agreement with the observed intensity ratio 1:24.4 of the Ar^{1}H and the OMe signals in the 100 MHz ^{1}H n.m.r. spectrum of methyl [$^2H_{15}$]trityl ether, obtained from a sample of the same [$^2H_{15}$]trityl chloride by treatment with methanolic sodium methoxide, which corresponds to 0.82 atom % ^{1}H attached to the aromatic rings.

groups of compound (**6a**) and, thence, of [$^2H_{15}$]trityl chloride, its precursor, from these values after correcting for natural ^{13}C abundances; this corresponds, in reasonable agreement with the value deduced from the ^1H n.m.r. spectrum, of 0.8 atom % of ^1H attached to the aromatic rings.

Triphenyl(phenylazo)methane (**1b**).—A $CHCl_3$ (100 ml) solution of 1-phenyl-2-tritylhydrazine[32] (4.0 g, 11.5 mmol) was thoroughly shaken for 20 min with a mixture of finely pulverized iodine (3.2 g, 12.6 mmol) and 5% aqueous Na_2CO_3 solution (80 ml). The chloroform layer was washed with saturated aqueous Na_2SO_3 solution (30 ml) and water (50 ml), dried ($MgSO_4$), and evaporated at reduced pressure to about a quarter of its original volume. Three parts (v/v) of ethanol were added, and the mixture was allowed to stand for 2 h at room temperature and 24 h in a refrigerator to obtain the title compound (2.8 g, 70%), m.p. 112—113 °C (lit.,[25] 111—113 °C). This product proved homogeneous (t.l.c.) and sufficiently pure for the thermolysis experiments (see below), although the m.p. was raised to 113 °C by recrystallization from CH_2Cl_2–EtOH.

Tri([$^2H_5$]phenyl)(phenylazo)methane (**2**), m.p. 112—113 °C, was similarly obtained in 72% yield, starting with 1-phenyl-2-([$^2H_{15}$]trityl)hydrazine,[25] δ_H (100 MHz; CCl_4; Me_4Si) *ca.* 7.3 (3 H, m, NPh, *m*- and *p*-H) and *ca.* 7.65 (2 H, m, NPh, *o*-H), *i.e.* no incorporation of protium into the [$^2H_5$]phenyl rings of the [$^2H_{15}$]trityl group is detectable.

Thermolysis of Triphenyl(phenylazo)methane (**1b**) *and Tri*([$^2H_5$]*phenyl*)(*phenylazo*)*methane* (**2**).—(a) A mixture of compound (**1b**) (6.97 g, 20 mmol), sodium methoxide (4.32 g, 80 mmol), and DMP (56 ml) was refluxed for 10 h with continuous stirring under nitrogen. The solvent was removed by distillation at reduced pressure, and the residue was taken up in a mixture of CH_2Cl_2 (120 ml), H_2O (120 ml), and acetic acid (6 ml). The aqueous layer was extracted with CH_2Cl_2 (2 × 40 ml), and the combined CH_2Cl_2 solutions were dried ($MgSO_4$) and evaporated to dryness at reduced pressure. The residue (7.1 g) was worked up by column chromatography (Kieselgel 60, 0.063—0.200 mm; benzene–hexane 0:100 ⟶ 30:70) and, for those fractions where necessary, subsequent preparative t.l.c. (Kieselgel 60 $PF_{254+366}$; dioxane–benzene, 1:4). Two identical experiments were carried out, and the following product yields of non-recrystallized products, identified by comparison (t.l.c., i.r., m.p.) with authentic samples (see below), given in parentheses were obtained: (**1c**) (24.2, 20.0%), (**1d**) (3.9, 5.3%), (**1e**) (20.5, 18.7%), (**1f**)* (2.5%), (**3a**) (13.3, 11.9%), (**4**) (6.8, 3.6%), (**5**)* (1.5%), and biphenyl* (1.3%), the total yields being 68.7 and 64.8%, respectively.

(b) Compound (**2**) (727 mg, 2 mmol) was thermolysed (three identical runs) and the resulting mixtures were worked up as described in (a), except that only the mixtures (**3b** + **c** + **d**) and (**6a** + **b**) as well as phenyltri([$^2H_5$]phenyl)methane (**10**) were isolated (in two, all three, and two runs, respectively).

The mixture of compounds (**6a**—**c**) gave δ_H (100 MHz; CCl_4; Me_4Si) 5.43 (s, ≥C–H), 6.85–7.2 (m, ArH); δ_H (100 MHz; [$^2H_6$]acetone; Me_4Si) 5.58 (s, ≥C–H) and 7.0—7.3 (m, ArH). For the relative abundances of the peaks of the molecular-ion bundle in the 11—12 eV mass spectra of the mixtures obtained in experiments 1—3, see Table 3, columns 3—5. From these, after correcting for natural ^{13}C abundances and taking into account the ^1H content of the starting compound (**2**) (see footnote *b* to Table 1) originating from the [$^2H_{15}$]trityl chloride, its precursor, the ratio of the *sum* of the amounts of compounds (**6a** + **b**) and of compound (**6c**) (which is identical with the ratio of protium and deuterium abstraction by the intermediate [$^2H_{15}$]trityl radicals) was calculated. The results are shown in Table 1. Molecules containing more than one ^1H atom could not be detected although, because of the relative accuracy (10%) of the measurements, the presence of molecules containing two [compound (**6d**)], three, and four to six ^1H atoms in 1, 0.1, and 0.02% amounts, respectively, may not be ruled out with complete certainty. The ratio of the two isomeric monoprotio compounds (**6a** and **b**) was determined by measuring the relative intensities of the aliphatic and aromatic signals in the ^1H n.m.r. spectrum. The results are shown in Table 1.

Phenyltri([$^2H_5$]phenyl)methane (**10**) had *m/z* (relative intensity) (180 °C) 335 ($M^{+\cdot}$, 51%), 258 (M − Ph, 33), 253 (M − $C_6{}^2H_5$, 100), 174 (M − Ph − $C_6{}^2H_5$ − ^2H, 28), 170 (M − 2 $C_6{}^2H_5$ − H, 18), and 169 (M − 2 $C_6{}^2H_5$ − ^2H, 13).

Mixture of compounds (**3b**—**d**) gave δ_H (100 MHz; CCl_4; Me_4Si) 5.47 (s, ≥C–H) and 7.0—7.5 (m, ArH). For the relative abundances of the peaks of the molecular-ion bundle in the 11—12 eV mass spectra of the mixtures obtained in experiments 2 and 3, see Table 4. From these, similarly as in the case of the mixture of compounds (**6a** and **b**) (*cf.* footnote *i* to Table 1), the ratio of the *sum* of the hexaprotio compounds (**3b** and **c**), and of the pentaprotio compound (**3d**) (which is identical with the ratio of the products of recombination of [$^2H_{15}$]trityl radicals in the *para* position and phenyl radicals with and without concomitant protio-dedeuteriation) was calculated. The results are shown in Table 1. Molecules containing seven or more protium atoms were not detected. The ratio of the two isomeric hexaprotio compounds (**3b** and **c**) was determined by measuring the relative intensities of the aliphatic and aromatic signals in the 100 MHz ^1H n.m.r. spectrum. The results are shown in Table 1.

Table 4. Measured relative abundances of the ions of the molecular-ion bundles in the low-voltage mass spectra of two samples of mixtures of deuteriated (*p*-biphenylyl)diphenylmethanes (**3b**—**d**), obtained by thermolysis of tri([$^2H_5$]phenyl)(phenylazo)methane (**2**)[a] in DMP in the presence of sodium methoxide

	I (%)	
m/z	Sample 1[b,c]	Sample 2[d,e]
337	2.8	2.5
336	26.2	26
335	*100*	*100*
334	93	95
333	10.7	11
332	0.7	0.6
331	0.1	0.1

[a] Three essentially identical runs; product of first not studied. [b] Product of experiment 2. [c] 11 eV, direct insertion, 150 °C. [d] Product of experiment 3. [e] 12 eV, direct insertion, 140 °C.

Synthesis of Authentic Samples.—Triphenylmethane (**1c**),[33] tetraphenylmethane (**1d**),[14b] triphenylmethanol (**1f**),[34] (*p*-biphenylyl)diphenylmethane (**3a**),[14b] and bis-(*p*-biphenylyl)-phenylmethane (**5**)[14b] were obtained by published procedures.

2,2,2-Triphenylethanol (**1e**) was obtained by hydroxymethylation of triphenylmethanide anions with paraformaldehyde. Thus, a solution of triphenylmethane (**1c**) (2.44 g, 10 mmol) in anhydrous tetrahydrofuran was added within 10 min through a syringe to a 1M-butyl-lithium solution in n-hexane (10 ml, 10 mmol) with continuous stirring under nitrogen. The mixture was refluxed for 4 h and cooled. Paraformaldehyde (dried over P_2O_5; 0.9 g) was added at 15 °C whereby the red solution turned light yellow. The mixture was stirred for ½ h at room temperature and poured into ice-cold water (50 ml)–ice (10 g). The product was extracted with ether (three portions, total 100 ml). The combined organic solutions were dried ($MgSO_4$), the

* Isolated only in the second experiment.

solvent was distilled off at reduced pressure, and the residue was crystallized from methanol to obtain the title compound (1.5 g, 55%), m.p. 105—106 °C, identical (m.p., i.r., t.l.c.) with an authentic sample,[35] δ_H (60 MHz; $CDCl_3$; Me_4Si) 1.8 (1 H, t, *J* 6 Hz, exchangeable, OH), 4.65 (2 H, d, *J* 6 Hz, CH_2), and 7.28 (15 H, s, Ph).

p-(*Diphenylmethyl*)*tritylbenzene* (**4**),[36] e.i.-m.s. (70 eV; direct insertion; 170 °C) *m/z* 486 (53%, $M^{+\cdot}$), 409 (100, *M* − Ph), 319 (18, *M* − Ph_2CH), 243 (28, Ph_3C^+), 241 (16), 167 (31, Ph_2CH^+), and 165 (57).

Attempted Base-catalysed Rearrangement of Tri([$^2H_5$]-*phenyl*)*methane* (**6a**) *into Isomers containing the* ^1H *Atom attached to an Aromatic Ring*.—The title compound (**6a**) (see above) was allowed to react with sodium methoxide in DMP under the conditions of the thermolysis of compound (**1b**), and the resulting mixture was worked up as that resulting from the thermolysis experiment to furnish 89% of unchanged starting material which, according to its ^1H n.m.r. spectrum, did not contain ^1H atoms attached to aromatic carbon in excess of that of the starting (**6a**); δ_H (100 MHz; CCl_4; Me_4Si) 5.55 (s, ⩾C–H).

Attempted Deuteriation of Triphenylmethane (**1c**).—The previous experiment was repeated with compound (**1c**) in the presence of 0.2 mol equiv. [$^2H_6$]acetone to obtain 97% of unchanged starting material which, according to both its ^1H n.m.r. and mass spectra, did not contain ^2H.

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