

The Reduction of Triarylcarbenium Ions by Alcohols: Simple Hydride Transfer or Concerted Breakdown of *ortho*-Adducts?

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Reduction of tris-(4-methoxyphenyl)methyl chloride (2) by refluxing methanol to tris-(4-methoxyphenyl)methane (3) is, as shown by ^2H labelling, accompanied by exchange of methoxy-groups between solvent and substrate. This exchange reaction appears to be the first recognized example of an $\text{S}_{\text{N}}2\text{-Ar}$ reaction of a triarylcarbenium ion and involves the intermediacy of the *para*-adduct (9a) which implies that in the course of the reduction of triarylcarbenium ions by *n*-nucleophiles, formation of the related type (1) *ortho*-adducts is possible as required by the Olah–Svoboda mechanism.

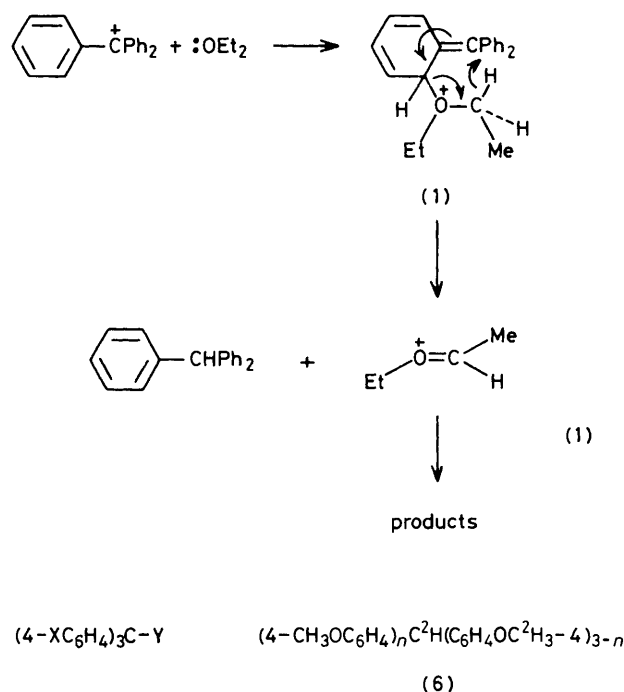
Triarylmethanols are known^{1–3} to be reduced by ethanol and mineral acid or by formic acid into the corresponding triarylmethanes. As indicated by the characteristic colour changes during the reaction and by the rate-enhancing effect of *p*- and especially *o*-methoxy-groups,³ the substrates in the reductions are the triarylcarbenium ions corresponding to the starting triarylmethanols. In agreement with this stable salts (*e.g.* the perchlorate⁴ and the hexafluorophosphate⁵) of the triphenylcarbenium ion are easily reduced while reduction of triphenylmethanol both by ethanol and hydrogen chloride and by formic acid is extremely slow.³

While it is generally agreed that these reductions take place by hydride transfer,^{4,6} there is some disagreement as to whether they are to be regarded as simple hydride transfers⁷ or as the concerted breakdown of type (1) adducts (formulated for the case of the reduction by diethyl ether) formed by *ortho*-attack of appropriate *n*-nucleophiles, including ethers, aldehydes, amines, and formic acid, as suggested by Olah and Svoboda [equation (1)].⁵

It occurred to us that some support in favour of the Olah–Svoboda mechanism could be obtained if the formation of *ortho*-adducts (1) under reduction conditions could be independently proved. In continuation of our studies into the reactions of nucleophiles with triarylmethyl halides⁸ we therefore undertook a study of the reaction of tris-(4-methoxyphenyl)methyl chloride⁹ (2) by [$^2\text{H}_4$]methanol.

Prolonged refluxing, or heating at 105 °C of compound (2) with methanol furnished tris-(4-methoxyphenyl)methane (3) as the only product in 81–94% yield. In contrast, trityl chloride, when heated with methanol at 105 °C, furnished methyl trityl ether (4) as the only product in 95% yield. While compound (4), when heated with methanolic hydrogen chloride, remained essentially unchanged and furnished at most only traces of triphenylmethane, its trimethoxy derivative (5)† is reduced under identical conditions into (3) (93% yield). The difference in the behaviour of compounds (4) and (5) again demonstrates the enhancement of the reduction rate (*via* stabilization of the triarylcarbenium ions) as a result of the introduction of one or more *p*-methoxy-groups.

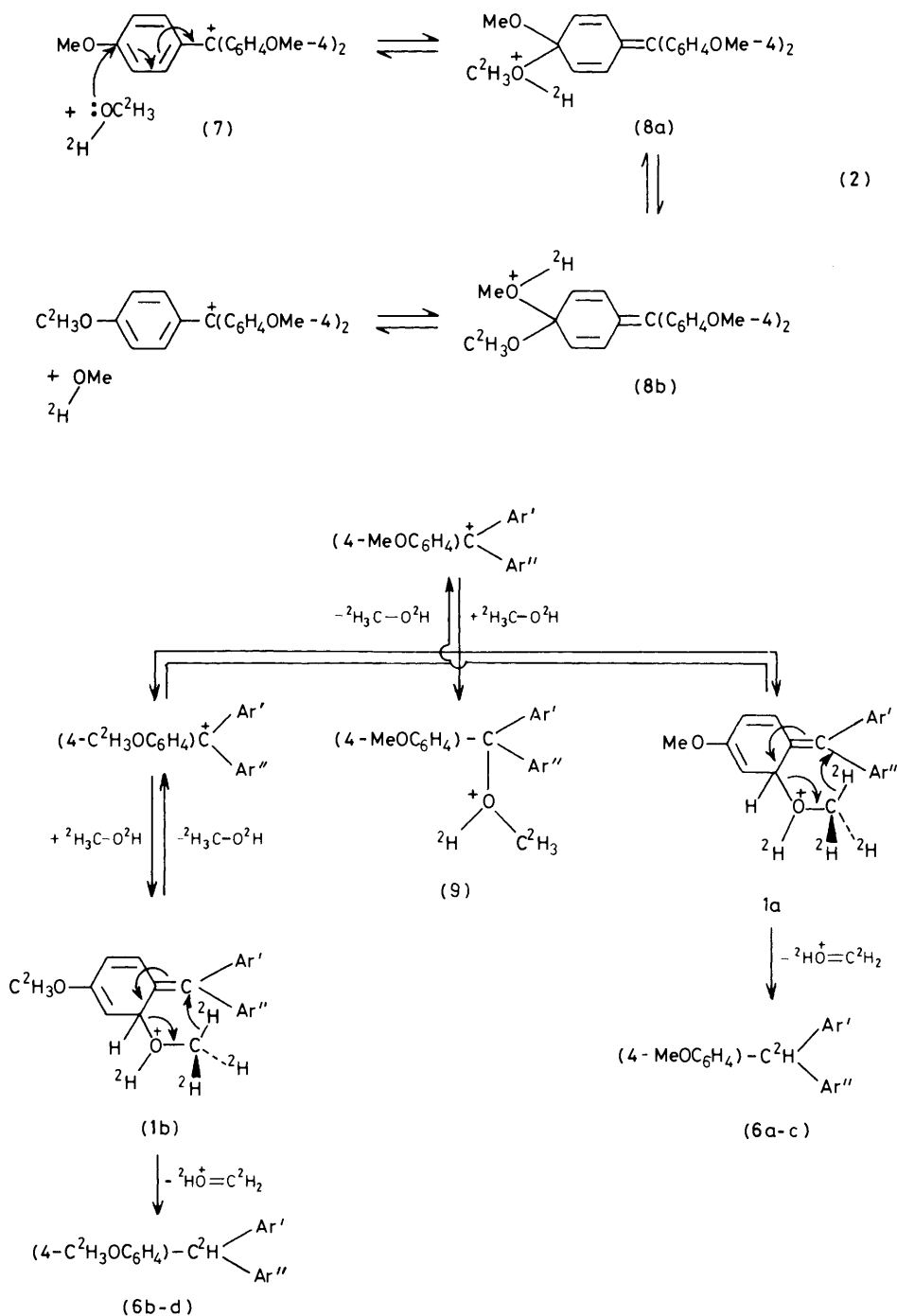
When the reduction of compound (2) was carried out by heating with [$^2\text{H}_4$]methanol (99.5 atom % [$^2\text{H}_3$]), a mixture of deuteriated analogues of compound (3) was obtained which were shown by mass spectrometry, in addition to being com-



- | | |
|---------------------|----------|
| (2) X = MeO, Y = Cl | a; n = 3 |
| (3) X = MeO, Y = H | b; n = 2 |
| (4) X = H, Y = MeO | c; n = 1 |
| (5) X = Y = MeO | d; n = 0 |

pletely deuteriated at the central carbon atom, to contain no, one, two, or three 4- $[\text{H}_3]$ methoxy-groups, respectively [(6a–d)]. From the relative intensities of the peaks of the molecular ions m/z 335, 338, 341, and 344 in the mass spectrum the abundance ratios of the compounds of the isotopic mixture were found to be (6a) : (6b) : (6c) : (6d) = 16 : 22 : 31 : 31. From this the ratio of aromatic and methoxy protons in the mixture was calculated as $12 \times 100 / (9 \times 16 + 6 \times 22 + 3 \times 31) = 4 : 1.23$, which compares favourably with the value 4 : 1.25 derived from the ^1H n.m.r. spectrum. The relative abundances of the remaining peaks of the molecular ion bundle in the mass spectrum (see Experimental section) clearly demonstrate that no products containing partially labelled methoxy-groups resulting from ^1H - ^2H exchange

† Obtained by refluxing compound (2) with excess of sodium methoxide in methanol.¹⁰



Scheme. Ar' and Ar'' are independently C₆H₄OCH₃-4 and C₆H₄OC²H₃-4

between the methoxy-groups of the substrate and the solvent are present.

We believe that the incorporation of [²H₃]methoxy-groups into the *para*-positions is independent of the reduction process and that it takes place as shown in equation (2) for the incorporation of the first [²H₃]methoxy-group. (The incorporation of the second and third [²H₃]methoxy-group is analogous.) Thus, the exchange of methoxy-groups between substrate and solvent is assumed to take place by what appears to be the first recognized example of an S_N2-Ar reaction on a triarylcarbenium ion and to involve the deuteriotropic *para* adducts (8a and b) as the intermediates, all elementary steps

being reversible. The possibility of formation of *para*-adducts under reduction conditions is thus considered as being proved. Since the electronic factors governing the formation of the *ortho*-adducts are, to a certain extent, similar to those governing the formation of *para*-adducts, the formation of *ortho*-adducts [(1a, b); Scheme] under these conditions may also be considered as likely.

As for the formation of the *para*-adducts, that of the *ortho*- and α -adducts (9) [the former being analogous to the Olah-Svoboda adducts (1)] should also be reversible; however, for, and only for, the *ortho*-adducts there exists in addition an irreversible although probably slow pathway of decomposi-

tion, *viz.* that leading to the reduction products (Scheme). As a consequence, if sufficient time is available, the reaction should lead to the exclusive formation of the reduction product, irrespectively of the relative rates of formation of the *ortho*-, *para*-, and α -adducts. [The exclusive formation of methyl trityl ether (4) from trityl chloride with methanol appears to indicate that α -attack is the fastest; because of the reduced tendency of formation of the unsubstituted trityl cation the once formed *O*-protonated ether (4) \cdot H⁺ does not revert to the cation but rather transfers the extra proton to the solvent methanol.]

With methanol and compound (2) the second reaction product should be formaldehyde. In agreement with this compound (2) and benzyl alcohol in refluxing dichloromethane furnished compound (3) (78%) and benzaldehyde (isolated as the 2,4-dinitrophenylhydrazone) (83%). Experiments to discover whether compound (2) could be used as a general reagent for the dehydrogenation of alcohols are in progress.

Experimental

The abundance ratio of compounds (6a—d) in the reaction product of compound (2) and [²H₄]methanol was determined by measuring the relative intensities of the peaks of the molecular ions in the mass spectrum obtained at 9 eV nominal ionizing electron energy with an AEI-MS-902 instrument using the direct insertion system. The source temperature was kept at 170 °C. The reproducibility of the measurement was *ca.* 0.5%, its accuracy *ca.* 2%. The ¹H n.m.r. spectrum of the mixture of compounds (6a—d) was obtained at 100 MHz with a JEOL FX-100 spectrometer using tetramethylsilane as the internal reference.

[²H₄]Methanol (99.5 atom % ²H) was purchased from E.G.A. Chemie. The ²H content of this material was checked by mass spectrometer, after converting it into [²H₃]methyl diphenylacetate.

[²H₃]Methyl Diphenylacetate.—Metallic sodium (0.5 g, 22 mmol) was dissolved under nitrogen in refluxing [²H₄]methanol (7 ml). The excess solvent was distilled off under nitrogen; the last traces of the solvent were removed at 140 °C over P₂O₅ *in vacuo*. A mixture of the sodium [²H₃]methoxide (1.2 mmol), diphenylacetyl chloride (1 mmol), and THF (5 ml) was refluxed for 5 h and evaporated to dryness. The residue was triturated with dry ether and the insoluble material was filtered off. The filtrate was evaporated to dryness and the oily residue was worked up by preparative t.l.c. (Kieselgel PF₂₅₄₊₃₆₆; acetone–benzene, 1:39) to obtain 87% of the title compound, m.p. 60 °C, m.p. of the unlabelled substance ¹¹ 60 °C, δ (CDCl₃) 4.99 (1 H, s) and 7.19 (10 H, s); no methoxy signal (which in the spectrum of the non-labelled compound appears at δ 3.65) could be detected.

The observed relative intensities *I* of the peaks of the molecular ion bundle in the 70 eV mass spectrum obtained at 170 °C are as shown in the Table. From these values the ²H content of the ²H₃CO group of the title compound was calculated as 99.4% (statistical distribution) and the amount of non-labelled material as \leq 0.15%.

Reaction of Tris-(4-methoxyphenyl)methyl Chloride (2) with Methanol.—(a) Tris-(4-methoxyphenyl)methyl chloride (2)⁹ (1.22 mmol) was refluxed with dry methanol (9 ml) for 60 h and evaporated to dryness *in vacuo*. The residue was taken up in dichloromethane and worked up by preparative t.l.c. (Kieselgel PF₂₅₄₊₃₆₆; acetone–benzene, 1:39) to obtain 81% of tris-(4-methoxyphenyl)methane (3), m.p. 48–49 °C (from methanol) (lit.,¹² 47.5–49 °C).

(b) A solution of compound (2) (2.0 mmol) in dry methanol

<i>m/z</i>	<i>I</i> (%)		Number of ² H atoms per molecule
	Title compound	Unlabelled product	
231	2.3		
230	18		
229	100	0.2	3
228	2.0	2.0	
227	0.14	18	
226	0.15	100	0
225	<0.05	0.3	
224		<0.1	

(14.7 ml) was heated in a sealed tube for 60 h at 105 °C. The mixture was worked up as described under (a) to obtain compound (3) (94%), δ (CDCl₃) 3.72 (9 H, s), 5.37 (1 H, s), and 6.77 and 6.98 (each 6 H, AA'BB').

Reaction of Tris-(4-methoxyphenyl)methyl Chloride (2) with [²H₄]Methanol.—Compound (2)⁹ (0.41 mmol) was refluxed with [²H₄]methanol (99.5% atom % of ²H; 3 ml) for 60 h. The mixture was worked-up as described above for the reaction with non-labelled methanol to obtain 65% of a mixture of tris-(4-methoxyphenyl)[²H₄]methanes containing 0–3 [²H₃]methoxy-groups (6a—d) in the ratio 16:22:31:31, *m/z* (9 eV, relative intensity; number of ²H atoms) 345 (24), 344 (99; 10), 343 (12), 342 (24), 341 (100; 7), 340 (9.2), 339 (16), 338 (69; 4), 337 (4.5), 336 (12), 335 (50;1), and 334 (0.6). The relative abundances of the ions (a) *m/z* 336, 339, 342, and 345 and (b) 334, 337, 340, and 343 were identical with the values calculated from the natural isotopic ratios of the heavy elements, taking into account, for the second group of ions, the presence of *ca.* 1% of ¹H attached to the central carbon atom as well as in each [²H₃]methoxy group (originating from the slight ¹H content of the solvent). The intensity ratio of the signals corresponding to the aromatic and methoxy protons in the ¹H n.m.r. spectrum was 4:1.25.

Reaction of Trityl Chloride with Methanol.—Trityl chloride and dry methanol were allowed to react and the resulting mixture was worked up as described above for the reaction of compound (2) with methanol [method (b)] to obtain methyl trityl ether (4) in 95% yield, m.p. 82 °C (lit.,¹³ 82 °C). At most only traces of triphenylmethane could be detected by t.l.c. in the crude product.

Reaction of Tris-(4-methoxyphenyl)methyl Methyl Ether (5) with Methanolic Hydrogen Chloride.—A mixture of compound (5)¹⁰ (2 mmol) and methanol (14.7 ml) in which dry HCl gas (2 mmol) had been previously dissolved, was heated in a sealed tube for 60 h at 105 °C and worked up as described above for the mixture obtained by allowing compound (2) to react with methanol, giving tris-(4-methoxyphenyl)methane (3) (93%). No reduction took place in the absence of hydrogen chloride.

Similar treatment of methyl trityl ether (4) furnished unchanged starting material (94%) with at most only traces of triphenylmethane detectable by t.l.c. in the crude product.

Reaction of Tris-(4-methoxyphenyl)methyl Chloride (2) with Benzyl Alcohol.—A mixture of compound (2), benzyl alcohol (each 1.6 mmol), and dichloromethane (4 ml) was refluxed under nitrogen with continuous stirring for 16 h and evaporated to dryness. The residue was dissolved in warm ethanol (8 ml), the solution was chilled, and kept overnight at –18 °C to obtain crystals of compound (3) (78%). The mother liquor of this product was treated with an ethanolic solution of 2,4-

dinitrophenylhydrazine (1.6 mmol) containing sulphuric acid to obtain benzaldehyde 2,4-dinitrophenylhydrazone (83%), m.p. 235 °C.

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