The Reduction of Triarylcarbenium Ions by *n*-Nucleophiles. The Operation of the Intramolecular Version of the Olah–Svoboda Mechanism in the Reductive Cyclization of the Tris-(2,6-dimethoxyphenyl)carbenium Ion

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Refluxing of tris-(2,6-dimethoxyphenyl)carbenium hydrogen dichloride (**2b**)·$2H_2O$ with chloroform furnished 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthene (**11**). This cyclization process with concomitant hydride transfer to the central carbon atom is rationalized by assuming concerted breakdown of any of the intermediates (**6**), (**7**), and (**9**) (Scheme 3), *i.e.* the operation of the intramolecular version of the disputed Olah–Svoboda mechanism of hydride transfer to triarylcarbenium ions.

Triarylcarbenium ions are well documented as hydride-ion acceptors,[1] and have also found preparative use, for example, in the dehydrogenation of cycloheptatriene to tropylium ion,[2] oxidation of ketone acetals and ethers by hydride transfer,[3] and for the oxidation of alcohols to ketones and aldehydes, *via* the trimethylsilyl ethers of the alcohols, under mild conditions.[4]

Olah and Svoboda suggested the primary formation of type (**1**) adducts in the course of the hydride-transfer reactions between triphenylcarbenium ion and *n*-nucleophiles (ethers, alcohols, amines, and formic acid), and subsequent concerted breakdown of the adduct (**1**) to the products (Scheme 1).[5]

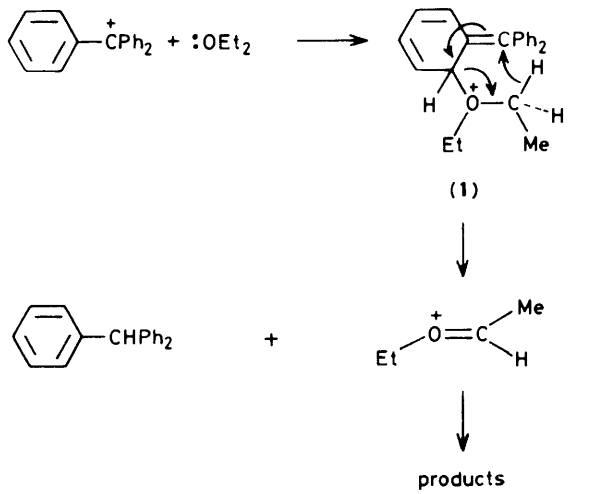
In contrast to the former mechanism, Stewart and Toone prefer to regard these reactions as simple hydride transfers.[6]

Reduction of tris-(4-methoxyphenyl)carbenium chloride (**2a**) by refluxing methanol to tris-(4-methoxyphenyl)methane (**3a**) has been shown to be accompanied by the exchange of methoxy groups between solvent and substrate. This exchange reaction involves the intermediacy of the *para*-adduct (**4**) and suggests that the formation of related *ortho*-adducts, required by the Olah–Svoboda mechanism, is also possible.[7] This result could, however, be regarded only as an indirect proof of the operation of the Olah–Svoboda mechanism in the reduction of the tris-(4-methoxyphenyl)carbenium ion by methanol.

Here we report on our studies which furnished direct evidence in favour of the Olah–Svoboda mechanism.

Compound (**2b**) was obtained, in the form of its dihydrate, by treating compound (**3b**)[8] with thionyl chloride in dichloromethane.† ‡ Compound (**2b**) was reduced to compound (**3c**) with triethylsilane.[1,2]

Reaction of compound (**3b**) with dilute aqueous hydrochloric acid furnished compound (**5**).[8] Treatment of compound (**2b**) under the same conditions also resulted, as could be expected, in the formation of compound (**5**) in 94% yield. The course of the ring closure (Scheme 2) may be rationalized by assuming the primary formation of the intermediate (**6**)·HCl_2^-, which is subsequently converted into (**5**) either *via* compound (**8**) or *via* compounds (**7**) and (**8**); the mechanistic details of this conversion are not known. A characteristic feature of the conversion (**2b**) ⟶ (**5**) is, in any case, that the ring closure is accompanied by the introduction of a hydroxy group at the central carbon atom (type I cyclization). The Olah–Svoboda type breakdown of the intermediates (**6**) and (**7**), or of the demethylation product (**9**) (Scheme 3) of compound (**6**), has not been observed in this case.



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

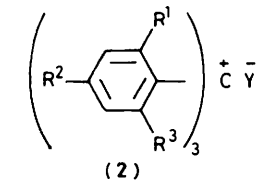
Both carbinols (**3b**) and (**5**), when heated with pyridinium chloride, were transformed into compound (**10**).[8] By heating compound (**2b**) with pyridinium chloride, small amounts (4%) of compound (**11**) (Scheme 3) could be isolated in addition to compound (**10**) (50%). An authentic sample of compound (**11**) was obtained by triethylsilane reduction of compound (**2b**).

The formation of compound (**10**) from compounds (**2b**) or (**3b**) may be explained by repeated type I cyclizations, *via* cations (**8**) and (**12**), similar to the formation of carbinol (**5**) discussed above. The formation of compound (**11**) in the reaction of compound (**2b**) with pyridinium chloride suggests the possibility of the involvement of a new type of cyclization reaction, which is accompanied by the reduction of the central carbon atom (type II cyclization).

Considering the important role of the nucleophiles present in the formation of compound (**5**) (demethylation, attack at the central carbon atom) as outlined in Scheme 2, it appeared reasonable to expect that the type II cyclizations will be facilitated when carrying out the reactions in the absence of external nucleophiles.

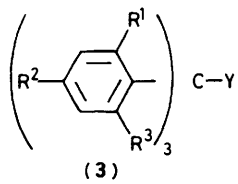
Prolonged refluxing of compound (**2b**) in chloroform furnished compound (**11**) in 90% yield. Under these conditions

† For the structure of the related compound (**2c**), see ref. 9.
‡ Compound (**2b**; Y = Cl) was mentioned by Kessler,[10,11] but the method of its preparation has, to our knowledge, not been published.



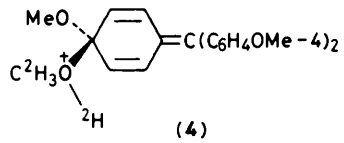
(2)

	R^1	R^2	R^3	Y
a;	H	MeO	H	Cl
b;	MeO	H	MeO	HCl_2
c;	H	MeO	H	HCl_2



(3)

	R^1	R^2	R^3	Y
a;	H	MeO	H	H
b;	MeO	H	MeO	OH
c;	MeO	H	MeO	H



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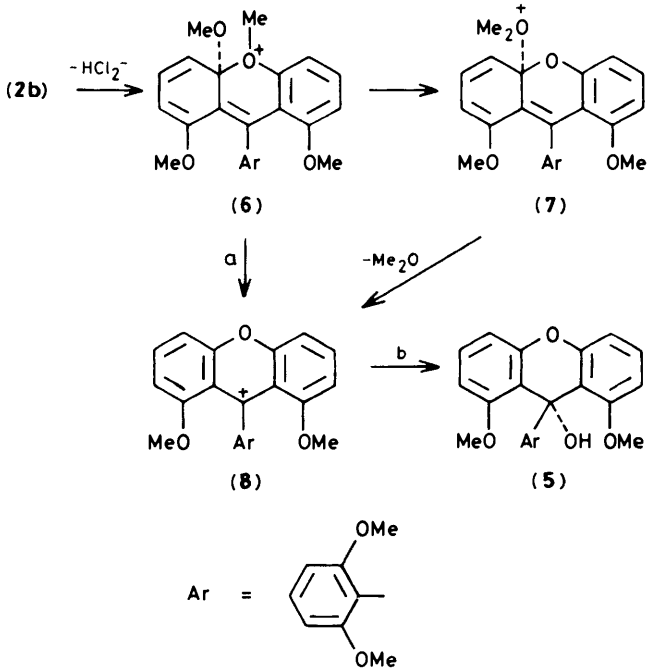
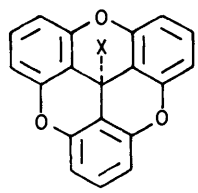
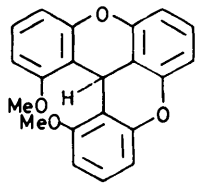


Scheme 2. a, Either concerted or stepwise. b, the addition of HO^- could take place simultaneously with the loss of MeO^- or Me_2O



(10) X = OH
(15) X = H



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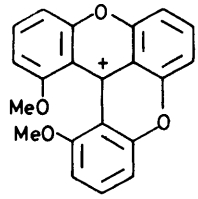
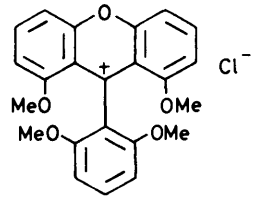
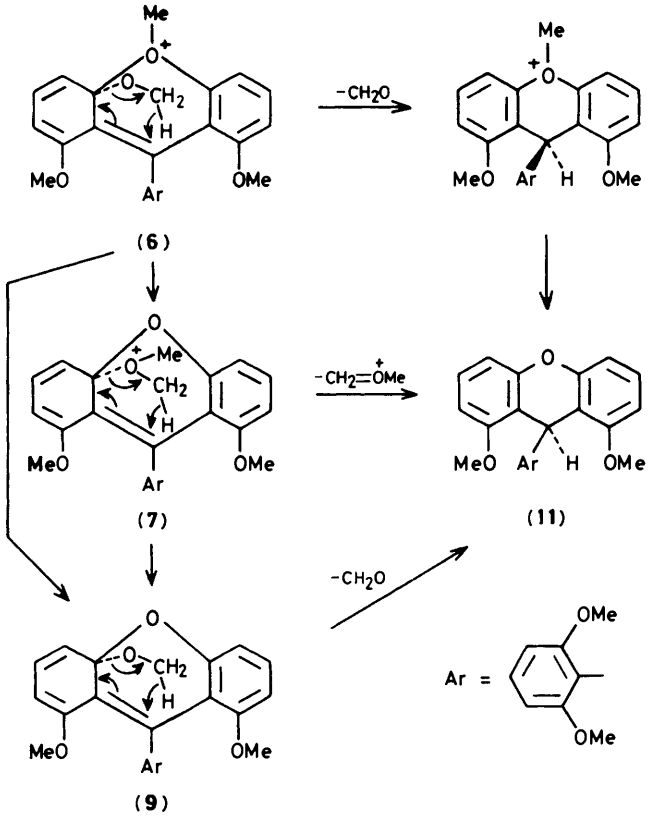


(12)



(14)



Scheme 3.

only the methoxy groups of the starting compound (**2b**) can serve as the source of the hydride anion required for the reduction of the central carbon atom. The non-formation of compound (**3c**) in this reaction as well as the high product yield indicate that the reduction of the central carbon atom is somehow coupled with and does not occur independently from the ring-closure process (*e.g.* by hydride abstraction from a methoxy group of a second starting or of a product molecule), *i.e.* that the reduction takes place *via* hydride transfer by concerted breakdown of any or several of the intermediates (**6**), (**7**), and (**9**) (Scheme 3). Since the intermediates (**6**), (**9**), and particularly (**7**) are analogues of the adduct (**1**), the conversion of compound (**2b**) in refluxing chloroform into compound (**11**) may be regarded as an indication for the operation of the intramolecular version of the Olah–Svoboda mechanism.

In the reaction of compound (**2b**) with pyridinium chloride (see above) the type I and II cyclizations proceed as competing reactions.

Since compound (**2b**) was converted into compound (**11**) under aprotic conditions, it was expected that compound (**13**) could be obtained by refluxing compound (**14**) [prepared from compound (**5**) with thionyl chloride] with chlorobenzene. This reaction, however, furnished compounds (**5**) (formed from unchanged starting material during work-up) and (**10**). Neither of compounds (**13**) and (**15**) could be isolated, which indicates the inefficiency of type II cyclizations of the cations (**8**) and (**12**).

An authentic sample of compound (**15**) was obtained, in spite of an unsuccessful attempt described in the literature,[12] by triethylsilane reduction of compound (**10**).

Experimental

^{1}H N.m.r. spectra were obtained for $CDCl_3$ solutions at 100 MHz with a JEOL FX-100 spectrometer using tetramethylsilane as the internal reference.

Tris-(2,6-dimethoxyphenyl)carbenium Hydrogen Dichloride (**2b**)·2H_2O.—Thionyl chloride (2.1 g, 17.6 mmol) was added to a solution of compound (**3b**)[8] (5.0 g, 14.7 mmol) in dichloromethane (100 ml) at −20 °C, and the reaction mixture was stirred for 30 min under nitrogen. The dark violet crystals, precipitated after addition of n-hexane (300 ml), were filtered off, washed with n-hexane, and air-dried to give compound (**2b**)·2H_2O (7.2 g, 92%), m.p. 168—170 °C (Found C, 56.55; H, 6.0; Cl, 13.2. $C_{25}H_{27}ClO_6$·HCl·2H_2O requires C, 56.5; H, 6.1; Cl, 13.3%); δ_H 3.59 (s, 6 × MeO), 6.57 (d, *J* 8 Hz, 6 × *m*-H), 7.66 (t, *J* 8 Hz, 3 × *p*-H).

Tris-(2,6-dimethoxyphenyl)methane (**3c**).—A solution of compound (**2b**)·2H_2O (1.0 g, 1.9 mmol) and triethylsilane (1.2 ml) in acetic acid (8 ml) was stirred for 1 h at ambient temperature. Water (50 ml) was added, and the precipitate was filtered off to obtain compound (**3c**) (0.76 g, 95%), m.p. 182—184 °C. Recrystallization from ethanol raised the m.p. to 186—188 °C (lit.,[12] 186—187 °C). The ^{1}H n.m.r. spectrum of our product was identical with that described for a sample obtained by triethylsilane reduction of compound (**3b**);[12] see also ref. 10.

9-(2,6-*Dimethoxyphenyl*)-1,8-*dimethoxyxanthen*-9-*ol* (**5**).—(a) A solution of compound (**2b**)·2H_2O (3.0 g, 5.7 mmol) in a mixture of concentrated hydrochloric acid (5 ml) and water (500 ml) was refluxed for 14 h and allowed to cool. The precipitate was filtered off to obtain compound (**5**) (2.13 g, 93%), m.p. 298—300 °C; recrystallization from a mixture of dichloromethane and acetone raised the m.p. to 301—303 °C (lit.,[8] 300.5—303.5 °C). Compound (**5**) had been obtained from compound (**3b**) by an identical procedure.[8]

(b) A solution of compound (**14**) (0.2 g, 0.48 mmol) in dichloromethane (10 ml) was shaken with 5% aqueous $NaHCO_3$ solution (10 ml) for some minutes. The aqueous layer was extracted with two portions (5 ml) of dichloromethane and the combined organic layers were dried ($MgSO_4$) and evaporated to dryness. The residue was triturated with acetone to yield compound (**5**) (0.15 g, 80%), identical (m.p., i.r., R_F) with the sample obtained as described in (a).

Reaction of Compound (**2b**)·2H_2O *with Pyridine Hydrochloride*.—A mixture of compound (**2b**)·2H_2O (3.0 g, 5.7 mmol), pyridine hydrochloride (8.0 g, 70 mmol), and pyridine (0.9 g, 11.4 mmol) was heated for 14 h at 205 °C under argon. The mixture was allowed to cool and triturated with 10% hydrochloric acid (100 ml). The insoluble material was filtered off and washed with 10% hydrochloric acid to give a solid (1.4 g), which was triturated with dichloromethane (50 ml). The insoluble residue (0.2 g) was worked up by preparative t.l.c. to furnish 9-(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthene (**11**) (0.08 g, 4%), which was identical (m.p., i.r., R_F) with an authentic sample obtained as described below. The acidic mother liquor was made alkaline (pH 14) by the addition of solid potassium hydroxide with cooling and continuous stirring. The yellow colour of the solution faded, and a precipitate was formed which was filtered off after cooling to yield 12c*H*-4,8,12-trioxa-4*H*,8*H*-dibenzo[*cd*,*mn*]pyren-12c-ol (**10**) (0.85 g, 50%), m.p. 200—220 °C (decomp.) [lit.,[8] 200—229 °C (decomp.)], which was recrystallized from toluene to furnish a sample of m.p. 205—220 °C (decomp.), which proved identical (i.r., ^{1}H n.m.r.) with an authentic sample.[8] δ_H 2.28 (br, OH), 6.99 (m, 6 × ArH), and 7.32 (m, 3 × ArH).

9-(2,6-*Dimethoxyphenyl*)-1,8-*dimethoxyxanthene* (**11**).—(a) A solution of compound (**5**) (0.25 g, 0.6 mmol) and triethylsilane in acetic acid (4.5 ml) was refluxed for 1 day under argon. The mixture was evaporated to dryness, and the residue was triturated with ethanol to obtain compound (**11**) (0.2 g, 83%), which was identical (m.p., i.r., R_F) with the sample obtained as described in (b).

(b) Compound (**2b**)·2H_2O (1.2 g, 2.3 mmol) was refluxed with dry chloroform (32 ml) for 16 h. The solution was diluted with dichloromethane (120 ml) and extracted with 5% aqueous sodium hydroxide solution (80 ml). The aqueous phase was extracted with dichloromethane (20 ml). The combined organic solutions were dried ($MgSO_4$) and evaporated to dryness. The residue was triturated with methanol (10 ml) to yield compound (**11**) (0.77 g, 90%), m.p. 291—293 °C. An analytically pure sample, m.p. 292—294 °C, was obtained by recrystallization from a mixture of dichloromethane and ethanol (Found: C, 72.9; H, 6.0. $C_{23}H_{22}O_5$ requires C, 73.0; H, 5.9%); δ_H 3.60 (s, 2 × MeO), 3.68 (s, 2 × MeO), 5.98 (s, →C–H), 6.38 (dd, J_o 8, J_m 1.5 Hz, 2- + 7-H), 6.41 (d, J_o 8 Hz, 3'- + 5'-H), 6.64 (dd, J_o 8, J_m 1.5 Hz, 4- + 5-H), 7.01 (*t*, J_o 8 Hz, 4'-H), 7.03 (t, J_o 8 Hz, 3- + 6-H) (primed locants refer to the 2,6-dimethoxyphenyl group).

9-(2,6-*Dimethoxyphenyl*)-1,8-*dimethoxyxanthylium Chloride* (**14**)·3H_2O.—A mixture of compound (**5**) (0.4 g, 1 mmol), dichloromethane (16 ml), and thionyl chloride (0.36 ml, 5 mmol) was stirred for 30 min at ambient temperature. n-Hexane (60 ml) was added to the solution. The precipitate was filtered off after the mixture had been allowed to stand for several hours, washed with n-hexane, and dried first in air and finally *in vacuo* over KOH to give compound (**14**)·3H_2O (0.4 g, 86%), m.p. 191—192 °C (Found C, 58.5; H, 5.95; Cl, 7.1. $C_{23}H_{21}ClO_5$·3H_2O requires C, 59.2; H, 5.8; Cl, 7.6%).

Thermolysis of 9-(2,6-*Dimethoxyphenyl*)-1,8-*dimethoxyxanthylium Chloride* (**14**)·3H_2O.—Compound (**14**)·3H_2O (0.5 g, 1.08 mmol) was refluxed with chlorobenzene (40 ml) for 40 h under argon. The solvent was evaporated under reduced pressure. The residue was triturated with 10% aqueous hydrochloric acid (30 ml), the resulting solid was filtered off and recrystallized from a mixture of dichloromethane and acetone to give compound (**5**) (0.14 g, 46%), which was identical (i.r., m.p., R_F) with an authentic sample obtained as described above. Compound (**10**) (0.10 g, 32%) was obtained from the acidic mother liquor by alkalinization as described above.

12c*H*-4,8,12-*Trioxa*-4*H*,8*H*-*dibenzo*[cd,nm]*pyrene* (**15**).—A solution of compound (**10**) (0.25 g, 0.83 mmol) and triethylsilane (1 ml) in acetic acid (4.5 ml) was refluxed for 40 h under argon. The solvent was evaporated and the residue was triturated with ethanol to yield compound (**15**) (0.21 g, 89%), m.p. 280—300 °C (decomp.) [lit.,[8] 280—300 °C (decomp.)]; δ_H 4.83 (s, →C–H), 6.82 (d, *J* 8 Hz, 6 × ArH), 7.13 (t, *J* 8 Hz, 3 × ArH), practically identical with the spectrum described in the literature.[10]

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