Trityl Cation as a Leaving Group in Electrophilic Vinylic Substitution

By **Zvi Rappoport** * and **Ilan Schnabel**, Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

On treating 1,1-di-*p*-methoxyphenyl-3,3,3-triphenylpropene with bromine or acid, trityl cation is cleaved with the fromation of 1,1-di-*p*-methoxyphenylethylene derivatives. With chlorine, vinylic substitution occurs.

An uncommon leaving group in electrophilic aromatic substitution is the trityl cation which is cleaved from tetra-arylmethanes by the action of strong acids (HI or H_2SO_4).[1] It is also formed in acetic–sulphuric acid mixtures from the compounds $Ph_3C{\cdot}CHX_2$ ($X = CN$, CO_2R, or $CONH_2$) probably *via* their tautomers, *e.g.*, $Ph_3C{\cdot}CX{=}C(OH){\cdot}OR$ or $Ph_3C{\cdot}CX{=}C{=}NH$.[2] We have found now that a trityl cation can be displaced in electrophilic vinylic substitution by bromine or by a proton.

Reaction of 1,1-di-*p*-methoxyphenyl-3,3,3-triphenylpropene (1)[3] with bromine in carbon tetrachloride results in discharge of the colour, but neither the expected 1,2-dibromide (2) nor the vinyl bromide (3) were formed. The products isolated after aqueous work-up are 1,1-di-*p*-methoxyphenyl-2,2-dibromoethylene (4)[4] and triphenylmethanol (6). Chromatography of the anhydrous reaction mixture gave a fraction with an n.m.r. singlet corresponding to that of triphenylmethyl bromide (5). In another experiment 1,1,4,4-tetra-*p*-methoxyphenylbutadiene (7)[5] was isolated in addition to compounds (1) and (6) [equation (1)]. Attempts to direct the reaction into formation of the vinyl bromide (3) by bromination in the presence of sodium hydroxide or triethylamine resulted only in a lower yield of compound (4). Similarly neither compound (2) or (3) could be detected when the reaction was interrupted after shorter reaction times.

The reaction is best explained as a bromodetritylation,

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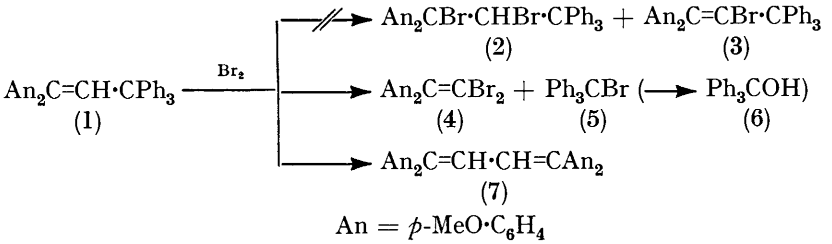

$$\underset{(1)}{\mathrm{An_2C{=}CH{\cdot}CPh_3}} \xrightarrow{\mathrm{Br_2}} \left| \begin{array}{l} \not\longrightarrow \underset{(2)}{\mathrm{An_2CBr{\cdot}CHBr{\cdot}CPh_3}} + \underset{(3)}{\mathrm{An_2C{=}CBr{\cdot}CPh_3}} \\ \longrightarrow \underset{(4)}{\mathrm{An_2C{=}CBr_2}} + \underset{(5)}{\mathrm{Ph_3CBr}}\ (\longrightarrow \underset{(6)}{\mathrm{Ph_3COH}}) \\ \longrightarrow \underset{(7)}{\mathrm{An_2C{=}CH{\cdot}CH{=}CAn_2}} \end{array}\right. \qquad (1)$$

$\mathrm{An} = p\text{-}\mathrm{MeO{\cdot}C_6H_4}$

i.e. in the present case as an electrophilic vinylic substitution of trityl by bromine. The primary electrophilic attack of bromine on the double-bond of compound (1) leads to the carbonium ion (8), which then expels the trityl cation. The latter captures the bromide ion, forming compound (5), which gives compound (6) by hydrolysis, while the 1,1-di-*p*-methoxyphenyl-2-bromoethylene is rapidly brominated by bromine to form compound (4) [equation (2)]. Formation of the butadiene (7) by reaction of the 1,1-di-*p*-methoxyphenyl-2-bromoethylene with 1,1-di-*p*-methoxyphenylethylene is known [5] and a similar reaction of compound (1) with 1,1-di-*p*-methoxyphenyl-2-bromoethylene seems plausible.

$$\begin{tikzcd} \mathrm{An_2C{=}CH{\cdot}CPh_3} \arrow[r, "\mathrm{Br_2}"] & {} & & & \\ \underset{(8)}{\mathrm{An_2\overset{+}{C}{-}CHBr{\cdot}CPh_3}} \arrow[r] & \mathrm{Ph_3C^+} \arrow[d] & + & \mathrm{An_2C{=}CHBr} \arrow[d] & (2) \\ & (5) & & (4) & \end{tikzcd}$$

Since addition to (8) to form (2) or expulsion of a proton to give (3) do not seem to compete with trityl expulsion, the main driving force for the reaction is probably the relief of steric strain in the crowded ion (8), which is best achieved by elimination of the bulky trityl cation. Indeed, the reaction of the ethylene (9) [which is less crowded than (1)] with bromine gives the 1,2-dibromide and a rearranged bromide [equation (3)] [6]

$$\underset{(9)}{\mathrm{Ph_3C{\cdot}CH{=}CH_2}} \xrightarrow{\mathrm{Br_2}} \mathrm{Ph_3C{\cdot}CHBr{\cdot}CH_2Br} + \mathrm{Ph_2C{=}C(Ph){\cdot}CH_2Br} \qquad (3)$$

while $\mathrm{IN_3}$ and INCO give with compound (9) only rearranged products,[7] and no trityl group is eliminated. Such additions of electrophiles to compound (9) probably occur on the terminal methylene group.

It is, therefore, surprising that the reaction of compound (1) with chlorine gave a compound with analysis and n.m.r. proton count consistent with the chlorine analogue of compound (3). Even though the $\mathrm{An_2\overset{+}{C}{\cdot}CHCl{\cdot}CPh_3}$ cation is the most stable among the possible isomers, it is possible that the product isolated contains some isomeric rearrangement products [*e.g.* $\mathrm{AnCCl{=}C(An)CPh_3}$] since the aromatic region in the n.m.r. shows a more complicated multiplet than that of (1). No $\mathrm{An_2CCl{\cdot}CPh{=}CPh_2}$ can be present in the product since it would undergo rapid ethanolysis, and no ethoxy-signals were observed in the n.m.r. of the material which was crystallized from ethanol.

The reaction of compound (1) with two other electrophiles, mercuric acetate and proton was studied briefly. While mercuric acetate reacts with 1,1-diphenylethylene in methanol with the formation of $\mathrm{Ph_2C(OMe){\cdot}CH_2HgOAc}$,[8] compound (1) was recovered unchanged from its reaction with $\mathrm{Hg(OAc)_2}$ in ethanol.

When compound (1) was dissolved in acetic acid containing 4% of sulphuric acid, the solution turned yellow immediately and three absorption maxima at 406, 429, and 516 nm developed. The first two maxima correspond to those of the trityl cation in sulphuric–acetic acid mixtures,[2,9] while the third corresponds to a maximum which is obtained on dissolving 1,1-di-*p*-methoxyphenylethylene in the same mixture. The apparent low value of ε (2150) for the absorption at 516 nm in a solution of 4% sulphuric acid in acetic acid is in line with *ca.* 3% protonation to form the ion (10). In water half protonation is obtained only at *ca.* 45% sulphuric acid.[10] The value of ε at 516 nm for compound (10) in water is 74,000.

The reaction of compound (1) is again an electrophilic protodetritylation, but under these conditions the trityl cation is stable as such, while the di-*p*-methoxyphenylethylene is protonated to give the cation (10) [equation (4)].

$$\mathrm{An_2C{=}CH{\cdot}CPh_3} \xrightarrow{\mathrm{H^+}} \mathrm{Ph_3C^+} + \mathrm{An_2C{=}CH_2} \xrightarrow{\mathrm{H^+}} \underset{(10)}{\mathrm{An_2\overset{+}{C}{-}CH_3}} \qquad (4)$$

The kinetics gave the same results when followed either at 406 or at 516 nm. Based on the calculated infinity (100% cleavage) the first-order rate coefficient decreases slowly with time, but calculated for process with 84% decomposition at equilibrium, 10^4k_1 (at room temperature) is $8{\cdot}4 \pm 0{\cdot}8\ \mathrm{s^{-1}}$. The reaction is thus faster than the protodetritylations of $\mathrm{Ph_3C{\cdot}CHX_2}$ ($\mathrm{X = CN, CO_2R, \text{or } CONH_2}$).[2]

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EXPERIMENTAL

N.m.r. data are given as τ values for tetramethylsilane as internal standard, and were measured with a 60 MHz (Varian T-60) instrument.

1,1-*Di*-p-*methoxyphenyl*-3,3,3-*triphenylpropene* (1), m.p. 137—138° was prepared from 1,1-di-*p*-methoxyphenylethylene and triphenylmethyl bromide according to Tadros *et al.*;[3] τ $(CDCl_3)$ 6·33 (3H, s, MeO), 6·20 (3H, s, MeO), 2·82 (15H, broad s, Ph_3C), 2·60—3·77 (8H, m. 2*p*-methoxyphenyl).

Bromination of Compound (1).—(*a*) To compound (1) (43 g, 99 mmol) in ether (300 ml) an equimolar amount of bromine solution in ether was added at room temperature with stirring. The red solution was stirred for additional 15 min and then washed with dilute aqueous sodium hydroxide, dried, and evaporated. The oil was crystallized from ethanol to give unchanged compound (1), triphenylmethanol (30%) (m.p. 164°, singlet at τ 2·9), and 1,1,4,4-tetra-*p*-methoxyphenylbutadiene (30%), m.p. 206°, $\lambda_{max.}$ (EtOH) 264 (log ε 4·36), 358 nm (4·55); τ $(CDCl_3)$ 6·22 (6H, s, 2MeO), 6·13 (6H, s, 2MeO), and 2·72—3·34 (18H, m, 4 *p*-methoxyphenyl + 2 vinyl-H) [lit.,[5] m.p. 206—207°, $\lambda_{max.}$ (EtOH) (from graph), 268 (log ε 4·5) and 364 nm (4·6)].

(*b*) To compound (1) (0·5 g, 1 mmol) in carbon tetrachloride (50 ml) an equimolar amount of bromine in carbon tetrachloride was added at room temperature. The red mixture turned pale yellow after 48 h, and the solvent was evaporated. The mixture was chromatographed on silica with benzene–light petroleum mixtures as eluants. A fraction which was eluted with 60% benzene was rechromatographed to give a solid, m.p. 92° (from ethanol); τ 6·20 (3H, s, MeO) and 2·65, 2·80, 3·03, and 3·18 (4H, q, *p*-methoxyphenyl). The n.m.r. is identical with that of 1,1-di-*p*-methoxyphenyl-2,2-dibromoethylene.[4] Its yield is 54% as judged by the ratio of signals at τ 6·33 and 6·20. Another fraction showed only a singlet at τ 2·70, which is at a position identical to that of authentic compound (5).

(*c*) In three different experiments an equimolar amount of bromine was added to compound (1) (100 mg) in carbon tetrachloride (10 ml). The solvent was evaporated after 45 min, 75 min, and 6 days at room temperature, giving respectively 33, 36, and 54% of compound (4).

Bromination of Compound (1) *in the Presence of Base*.—(*a*) The ethylene (1) (1 mmol) and sodium hydroxide (1 mmol) were dissolved in ethanol (80 ml) and bromine (1 mmol) in carbon tetrachloride (20 ml) was added without shaking. After 24 h, the mixture was poured into water, extracted with ether, washed, dried, and the solvent was evaporated. The n.m.r. was similar to that obtained in the absence of base. The use of six-molar excess of KOH and similar work-up after 3 days gave an oil (with similar n.m.r. spectrum) which yielded compound (4) in 20%. On cooling a solution of the oil in ethanol a few crystals of compound (1) separated.

(*b*) Bromine (1 mmol) and triethylamine (1 mmol) in carbon tetrachloride (100 ml) were added to compound (1) (0·5 g, 1 mmol) in carbon tetrachloride (100 ml). One fraction was worked-up after 2 h, to give 17% of compound (4) (identified by n.m.r. spectroscopy). Another fraction was poured into dilute HCl and then worked-up. Chromatography of the combined fractions on silica with light petroleum–benzene gave successively compound (1) as the main compound (isolated), triphenylmethanol [isolated, m.p. and mixed m.p. 164°, two singlets at τ 6·62 (OH) and 2·9 (Ph)], and triphenylmethyl bromide (identified by the singlet at τ 2·70).

1,1-*Di*-p-*methoxyphenyl*-2-*chloro*-3,3,3-*triphenylpropene*.—To compound (1) (1·72 g, 3·58 mmol) in carbon tetrachloride (100 ml) a saturated solution of chlorine in carbon tetrachloride (30 ml) was added in portions. The mixture turned violet, but the colour disappeared after a few seconds, and reappeared on addition of a new portion of the chlorine solution. When the addition was complete the violet colour failed to appear. The yellow solution was stirred at 40° for 30 min; the solvent was evaporated and the oil was refluxed for 10 min in ethanol. The solid obtained was recrystallized (EtOH) to give 1·48 g (80%) of white needles, m.p. 141—142° of 1,1-di-*p*-methoxyphenyl-2-chloro-3,3,3-triphenylpropene. Its i.r. is similar to that of compound (1), except for a strong absorption at 633 cm^{-1}; τ $(CDCl_3)$ 6·37 (3H, s, MeO), 6·23 (3H, s, MeO), and 2·80—3·77 (23H, aromatic) (Found: C, 81·4; H, 5·6; Cl, 7·4. Calc. for $C_{35}H_{29}ClO_2$: C, 81·3; H, 5·65; Cl, 6·85%).

Reaction of Compound (1) *with Mercuric Acetate*.—To a hot solution of compound (1) (0·5 g, 1 mmol) in ethanol (300 ml), mercury(II) acetate (0·27 g, 1 mmol) in ethanol (200 ml) was added. The mixture was stirred for 18 h and then the solvent was evaporated. The residual oil was dissolved in carbon tetrachloride and filtered. The n.m.r. is identical with that of compound (1).

Reaction of Compound (1) *in Acetic–Sulphuric Acid*.—Sulphuric acid (1 ml) was added to compound (1) (2·2 mg) in acetic acid (25 ml) and the mixture was stirred vigorously. The solution turned yellow and three maxima at 406, 429, and 516 nm developed. After 2 h the apparent ε at 516 nm is 2150. The progress of the reaction was followed at 406 and at 516 nm. Using the calculated infinity 10^4k_1 values were 8·2, 6·7, 5·3, and 4·1 s^{-1} at 4, 8, 18, and 66 min, respectively. Using 84% reaction for the infinity value, the corresponding 10^4k_1 are 10, 8·1, 7·9, and 7·6 s^{-1}, respectively.

In an independent experiment, 1,1-di-*p*-methoxyphenylethylene (1·5 mg) was dissolved in a mixture of acetic acid (25 ml) and sulphuric acid (1 ml). An absorption maximum at 516 nm (with apparent ε of 2150) appears.

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