View Article Online / Journal Homepage / Table of Contents for this issue

Triarylcarbenium Salts Highly Reducible by Primary Alcohols

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The carbenium salts [Ph{2,6-$(MeO)_2C_6H_3$}$_2$C]X (X = ClO_4, BF_4), prepared from Ph[2,6-$(MeO)_2C_6H_3]_2COH$ and a slight excess of acid in propan-2-ol, have been reduced in primary alcohol or methanol much faster than the related triarylcarbenium salts to give Ph[2,6-$(MeO)_2C_6H_3]_2CH$ and the aldehyde.

Owing to the steric and electronic effect of methoxy groups, 2,6-dimethoxyphenyl derivatives often exhibit unusual physical and chemical properties.[1,2] Tris-2,6-dimethoxyphenylmethanol [2,6-$(MeO)_2C_6H_3]_3COH$ **1a** has long been known to be far more basic than triphenylmethanol,[2a,b] but the properties of the carbenium salt **2a** in alcohols have not been studied.[2c,f,g] It is expected that the methoxy groups at the 2,6-positions are electronically in favour of carbenium ion formation, [eqn. (1)], which sterically hinders the reactions with bulky substrates [eqn. (2)].[3] We report here that (2-$MeOC_6H_4$)[2,6-$(MeO)_2C_6H_3]_2COH$ **1b** and Ph[2,6-$(MeO)_2C_6H_3]_2COH$ **1c** also form stable carbenium salts **2b** and **2c** and that **2c** reacts in primary alcohols and methanol much faster than the related salts **2a** and **2b**.

$$\underset{\mathbf{1}}{Ar_3C\text{-}OH} + H^+ \rightleftharpoons \underset{\mathbf{2}}{[Ar_3C]^+} + H_2O \qquad (1)$$

$$\mathbf{2} + RCH_2OH \rightarrow \underset{\mathbf{3}}{Ar_3C\text{-}H} + RCHO + H^+ \qquad (2)$$

Ar_3 = **a**: [2,6-$(MeO)_2C_6H_3]_3$,
b: (2-$MeOC_6H_4$)[2,6-$(MeO)_2C_6H_3]_2$,
c: Ph[2,6-$(MeO)_2C_6H_3]_2$,
d: [2,5-$(MeO)_2C_6H_3]_3$,
e: Ph_2[2,6-$(MeO)_2C_6H_3$]

The light-yellow crystals of **1a**[2a,e] dissolve in alcohols to form purple (methanol), light-purple (ethanol), or colourless (propan-2-ol) solutions; they form a purple suspension in water. These properties suggest the facile formation of the carbenium ion **2a** in equilibrium even in neutral conditions. In fact, the colour of the solutions deepened on bubbling with CO_2. Dark-purple crystals of **2a**† were obtained from propan-

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† *Characterization of new compounds*: NMR spectra recorded in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer; IR spectra recorded for Nujol mull using Shimadzu FTIR-4200 spectrometer; UV spectra recorded using Shimadzu UV-160 spectrophotometer. **2a** (X = ClO_4):[2f] dark-purple crystals; m.p. 188–189 °C (from propan-2-ol); IR ν/cm^{-1} 1100 (ClO_4); ^{1}H NMR: δ 7.60 (3 H, t, J 8 Hz, 4-H), 6.54 (6 H, d, J 8 Hz, 3,5-H), 3.60 (18 H, s, OMe); ^{13}C NMR: δ 162.8 (2,6-C), 142.5 (4-C), 105.1 (3,5-C), 57.0 (OMe) (the C$^+$ peak was too weak to be observed); UV/nm 525 (log ε, 4.24).

For **2b** (X = ClO_4): dark-purple crystals; m.p. 150–152 °C (from propan-2-ol); IR ν/cm^{-1} 1100 (ClO_4); ^{1}H NMR: δ 7.70 (1 H, overlapped), 7.69 (2 H, overlapped), 7.10–6.97 (3 H, m), 6.59 (4 H, d), 3.78 (3 H, s), 3.58 (12 H, s); ^{13}C NMR: δ 185.7 (C$^+$), 163.0, 162.9, 143.7, 141.9, 136.6, 134.2, 124.6, 121.9, 111.7, 105.1, 56.8, 56.7; UV/nm 438 (sh), 532 (log ε, 4.24).

For **2c** (X = ClO_4): dark-purple crystals; m.p. 152–155 °C; IR ν/cm^{-1} 1100 (ClO_4); ^{1}H NMR: δ 7.83 (2 H, t), 7.75 (1 H, tt), 7.53–7.42 (4 H, m), 6.66 (4 H, d), 3.57 (12 H, s); ^{13}C NMR: δ 192.1 (C$^+$), 163.9, 145.9, 144.7, 137.2, 134.7, 129.2, 124.9(1-C), 105.6, 56.9; UV/nm 479 (log ε, 4.37), 525 (sh). Satisfactory elemental analysis were obtained for **2a**, **2b** and **2c**. **1a**,[2a] **1b**, **1c**,[2e] **1d**, **1e**,[2e] **3a**,[2d] **3b**, **3c**, and **3e** were also similarly fully characterized.

2-ol solution by adding only a slight excess of perchloric acid or tetrafluoroboric acid. These salts **2a** are quite stable even in hot propan-2-ol (60 °C, 12 h). However, in hot methanol or ethanol containing a slight excess of perchloric acid, **1a** reacted to give mixtures of **2a** and the reduced compound $[2,6\text{-}(MeO)_2C_6H_3]_3CH$ **3a**[2c,d] in a variety of ratios depending on the reaction conditions (*e.g.* 39 : 61 in EtOH at 50 °C in 2 h).

Both **1b** and **1c** also reacted immediately on mixing with a slight excess of acid ($HClO_4$, HBF_4, H_2SO_4, HNO_3, HCl, or CF_3CO_2H) in propan-2-ol to give dark-purple solutions, and crystals of the carbenium salts **2b**† and **2c**† (X = ClO_4, BF_4) were obtained on cooling the solutions at −30 °C in quantitative yields. In acidic methanol and ethanol, **1b** and **1c** also reacted at room temp. to give dark-purple solutions, followed by the formation of colourless crystals of **3b** (24 h) and **3c** (less than 2 h) in 85–95% yields; **2b** and **2c** reacted similarly in these alcohols.

When a solution of **2c** in *n*-butanol was heated to reflux, *n*-butanol was found to be the sole byproduct as detected by GC and UV. Analogous treatment of **2c** in propan-2-ol gave acetone in 80% yield as confirmed by UV and by the formation of the 2,4-dinitrophenylhydrazone.

Both $[2,5\text{-}(MeO)_2C_6H_3]_3COH$ **1d** and $Ph_2[2,6\text{-}(MeO)_2C_6H_3]COH$ **1e** were much less reactive in acidic methanol and ethanol than **1c**. However, **1d** was more reactive in these alcohols than **1e** giving **3d** in quantitative yield (50 °C in less than 2 h), while **1e** was more reactive in propan-2-ol than **1d** giving **3e** in quantitative yield (50 °C in 12 h).

The consumption rates of carbenium salts in these alcohols were measured by UV and they followed pseudo-first-order kinetics for **2a–c**. The reaction in ethanol at 25 °C was several times faster ($t_{1/2}$ = 18 h for **2a**, 23 min for **2b**, 2 min for **2c**) than in methanol ($t_{1/2}$ = *ca.* 72 h for **2a**, 80 min for **2b**, 20 min for **2c**). It was also found that for **1c** in acidic methanol the rate was affected little by the type of acid ($HClO_4$, HBF_4, HCl, H_2SO_4, HNO_3) or by the amount of perchloric acid between 1.2–5.0 equiv.

It is worth noting here that the usage of acid must be avoided to neutralize the reaction mixture during the preparation of these triarylmethanols using organolithium reagent.[2,4] Preliminary results obtained show that a variety of organic compounds including diethyl ether and tetrahydrofuran are easily reduced by **1c** or **2c**.

This work was supported by the Grant-in-Aid for Scientific Research No. 04555207 from the Ministry of Education, Science and Culture and partially by Shorai Foundation for Science and Technology.

Received, 21st June 1993; Com. 3/03560C

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