Cerium(IV)-Oxidation with a Dual Oxidant System; Reaction of Some Arylmethanols

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Although the oxidizing power of the cerium(IV) ion is well recognized[1], application of cerium(IV)-oxidation to organic synthesis has been scanty, due to the large quantities of reagents being required. To alleviate this burden we investigated systems in which catalytic amounts of cerium(IV) salts are added, and during oxidation of organic substrates, the cerium(IV) species is continously replenished by the action of a lighter, cheaper multi-electron oxidant.

Table. Oxidation of Arylmethanols with $Ce^{4\oplus}/BrO_3^{\ominus}$

Alcohol	Carbonyl compound	Yield[a] [%]	b.p[b] (or m.p.)	Lit.[c] b.p. (or m.p.)
$C_6H_5—CH_2—OH$	$C_6H_5—CHO$	90	177–180°	178.1°
$4-H_3C—C_6H_4—CH_2—OH$	$4-H_3C—C_6H_4—CHO$	92	202–204°	204–205°
$4-O_2N—C_6H_4—CH_2—OH$	$4-O_2N—C_6H_4—CHO$	75	(103–105°)	(106°)
$C_6H_5—CH(CH_3)—OH$	$C_6H_5—CO—CH_3$	86	200–203°	202°
$(C_6H_5)_2CH—OH$	$(C_6H_5)_2CO$	83	(45–48°)	(48.1°)

[a] Yield of isolated product of >95% purity as determined by T.L.C. (all reactions were carried out under nitrogen).

[b] B.p. refer to bath temperatures.

[c] *Handbook of Chemistry and Physics*, CRC Press, Cleveland, U.S.A.

The Belousov-Zhabotinskii reaction[2] forms the basis of our present work. In this process Ce(IV) is reduced by bromomalonic acid, but the resulting Ce(III) ion is reoxidized by the bromate ion. Thus, it should be possible to effect Ce(IV)-oxidation of organic compounds with the $Ce^{4\oplus}/BrO_3^{\ominus}$ couple, while omitting malonic acid which is the reducing agent in the Belousov-Zhabotinskii reaction. We now wish to describe the successful oxidation of benzylic alcohols to the corresponding carbonyl products[3].

As stoichiometric Ce(IV)-oxidation of benzylic alcohols often represents the method of choice[3] for such transformation, our improved procedure would make it even more attractive on a preparative scale. From our experience, the purity and yield of the product from this catalytic process are comparable to that of the stoichiometric reaction. Aqueous acetonitrile appears to be a good compromise as a solvent between water and aqueous acetic acid with respect to experimental simplicity and dissolving power.

$$Ar—CH_2—OH \xrightarrow[-\,H^{\oplus}]{Ce(IV)/BrO_3^{\ominus}} Ar—CHO$$

It should be emphasized that bromate ion is not capable of oxidizing arylmethanols. The oxidation reported herein must be mediated by cerium(IV) species.

Oxidation of Arylmethanols with Catalytic Amounts of Ce(IV) Salts; General Procedure:

A stirred mixture of a benzyl alcohol (5 mmol), sodium bromate (755 mg, 5 mmol), ammonium cerium(IV) nitrate (28 mg, 0.05 mmol) in aqueous acetonitrile (7:3 v/v, 10 ml) is heated at 80° under nitrogen for 3 h. The cooled mixture is poured into water (40 ml) and extracted with benzene (2 × 20 ml). The dried extracts are evaporated and distilled or recrystallized. Identification of the product is by comparison with authentic sample (from commercial sources).

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