α′-Bromination of α,β-Unsaturated Ketones by an Electrochemical Procedure

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A novel and straightforward method to accomplish regioselective α′-bromination of α,β-unsaturated ketones, in which a substrate–CF_3CO_2H–CuBr–Et_4NOTs–MeCN system is subjected to electrolysis with variable current density, is described.

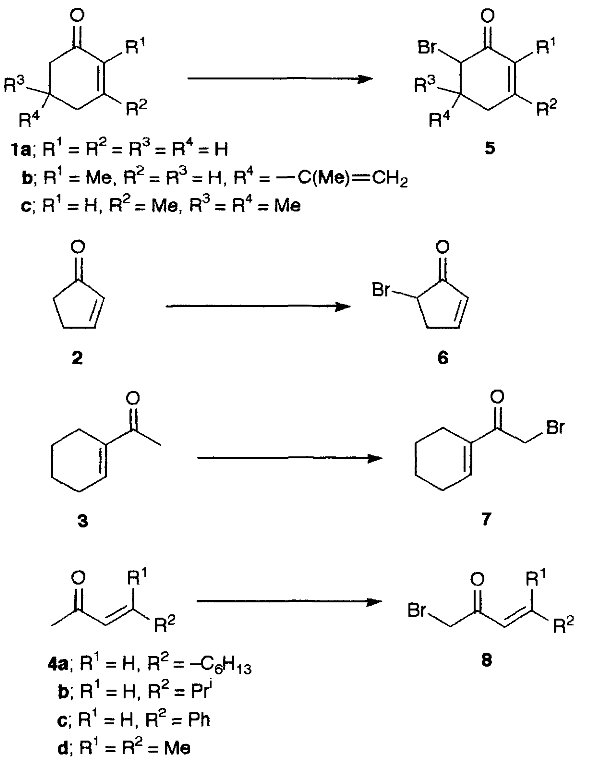
A variety of methods have been proposed for α-halogenation of ketones. However, the introduction of a halogen atom into an α′-position of α,β-unsaturated ketones has been difficult except for some special cases[1] since halogenation of a carbon–carbon double bond[2] or a γ-allylic position[3] takes place preferentially. Although an electrochemical oxidation of halides has been reported to be the most effective procedure for the introduction of a halogen atom into some groups[4] including α-halogenation of simple ketones,[5] no investigation has been performed as with α,β-unsaturated ketones, to our knowledge. In this article, we report the electrochemical procedure to bring about regioselective α′-bromination of α,β-unsaturated ketones.

A solution of cyclohex-2-en-1-one **1a** (2 mmol), copper(I)

Table 1 Electrolytic bromination of α,β-unsaturated ketones[a]

Substrate	Product (yield/%)[b]
1a	**5a** (80)
1b	**5b** (78)
1c	**5c** (77)
2	**6** (68)
3	**7** (74)
4a	**8a** (73)
4b	**8b** (70)
4c	**8c** (82)
4d	**8d** (67)

[a] All compounds showed satisfactory ^{1}H and ^{13}C NMR, IR and mass spectra. [b] Isolated yields.



1a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = {-}C(Me){=}CH_2$
c; $R^1 = H$, $R^2 = Me$, $R^3 = R^4 = Me$

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2 **6**

3 **7**

4a; $R^1 = H$, $R^2 = {-}C_6H_{13}$
b; $R^1 = H$, $R^2 = Pr^i$
c; $R^1 = H$, $R^2 = Ph$
d; $R^1 = R^2 = Me$

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bromide (4 mmol), trifluoroacetic acid (8 mmol) and tetraethylammonium tosylate (0.2 mol dm^{-3}) in acetonitrile (10 ml) was subjected to electrolysis using carbon rod electrodes in an undivided cell. After 20 F mol^{-1} of electricity had been passed at a constant current (15 mA cm^{-2}), 6-bromocyclohex-2-en-1-one **5a** was obtained in 80% yield *via* purification by PLC. α′-Bromination of various α,β-unsaturated ketones was accomplished using the same reaction conditions as shown in Table 1. It is characteristic that, in the electroreaction of carvone **1b**, bromination was performed only at the 6-position to form **5b** and the isolated carbon–carbon double bond group including its adjacent position was inert in the electrolysis course.

The electrolysis with acids other than trifluoroacetic acid (*e.g.* hydrochloric acid, acetic acid, or sulphuric acid) or in the absence of an acid did not lead to selective α′-bromination. Active methylene compounds such as α-substituted acetoacetates have been reported to undergo α-halogenation by electrolysis in the presence of sodium methoxide as an enolizing reagent.[6] The bases such as potassium *tert*-butoxide or 2-pyrrolidinone,[7] however, failed to perform the electrochemical α′-bromination of α,β-unsaturated ketones. A current density affected susceptibly of the reaction course as revealed by the result that cyclopent-2-en-1-one **2** afforded 2-bromocyclopent-2-en-1-one (49%) along with 5-bromocyclopent-2-en-1-one **6** (25%) by electrolysis at 30 mA cm^{-2} while electrolysis at 15 mA cm^{-2} formed only **6**.

Brominating reagents other than copper(I) bromide were examined. Electrolysis using Et_4NBr furnished **6** in 60% yield from **2**, while affording no bromination product from **4a**. NaBr in a MeCN–H_2O system did not perform the electrochemical bromination. Electrolysis in the presence of bromine effected only bromination of a carbon–carbon double bond.

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