Carbocationic Cyclisations and Hydroxylations initiated by Dehalogenation of Terminally Unsaturated α-Bromo-ketones

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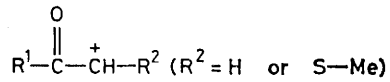
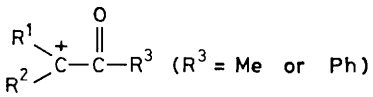
Action of $Ag^+SbF_6^-$ on the linear terminally unsaturated α-bromoketones (**3**)—(**5**) leads, *via* the oxonium salts (**12**)—(**14**), to the regio- and stereo-specifically substituted cyclohexanols (**6**)—(**8**).

In intramolecular reactions of olefinic π-bonds to produce cyclohexanones useful intermediates, equivalent to an acyl carbenium cation (**1**), have been obtained either from the appropriate protonated diazomethyl methyl ketone[1] or, more recently, by the Pummerer reaction from β-keto methyl sulphoxides.[2]

We show here the use of the acyl carbenium ion equivalents (**2**)† formed by dehalogenation of the title compounds. Cyclic acyl compounds are easily obtained in this way.

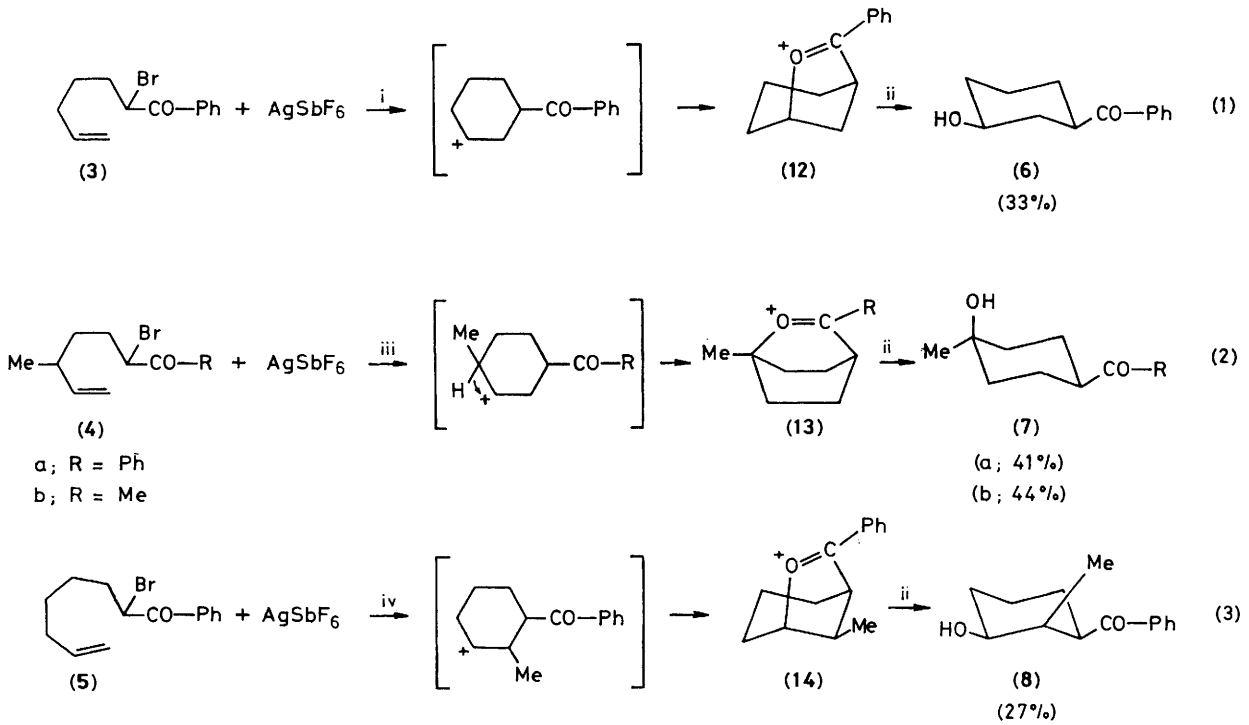


(1)

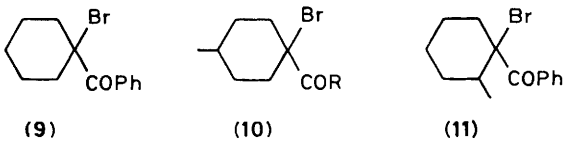


(2)

† The main reactions of such activated carbenium ions are described in ref. 4.



Scheme 1. *Reagents and conditions:* i, CH_2Cl_2, reflux, 46 h; ii, $NaHCO_3$, H_2O; iii, CH_2Cl_2, reflux, 18 h for (**4a**); CH_2Cl_2, room temp., 21 h for (**4b**); iv, isolated complex (neat), 100 °C, 1 h.



When 1.2 mol. equiv. of $Ag^+SbF_6^-$ was added to compounds (**3**)—(**5**)‡ in CH_2Cl_2 solution complexes precipitated immediately.§ Treatment of these complexes as in Scheme 1, hydrolysis, and the usual work-up, led to the products (**6**)—(**8**) following preparative t.l.c.¶ They were identified by comparison with authentic samples which had been obtained by dehalogenation of (**9**), (**10**), and (**11**) respectively.[3]

The structures and the stereochemistry of the hydroxyketones (**6**), (**7**), and (**8**) can only be explained by the formation of oxonium salts, (**12**), (**13**), and (**14**), respectively; their hydrolysis implies the formation of a transient hemi-acetal.[4]

The carbenium ions, precursors of the oxonium salts, can be formed either directly by cyclisation [equation (1)] or by this cyclisation followed by a hydride shift [equation (2)]. In the case of equation (3) a more reasonable mechanism involves a preliminary migration of the double bond followed by cyclisation.

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‡ Synthesised by alkylation of the appropriate terminally unsaturated bromides with ethyl benzoylacetate or ethyl acetoacetate sodium enolates, hydrolysis, and decarboxylation, bromination with phenyltrimethylammonium tribromide, and chromatography on a Florisil column.

§ The stocheiometry of the complexes seems to be 1 : 1 [Ag^+ : compounds (**3**)—(**5**)] since the yields of isolated complexes (filtration) are 90—95% for this stoicheiometry.

¶ Most of the other products are oligomers (not analysed).

References

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