Observations on the Reductive Deoxygenation of Aryl and α,β-Unsaturated Carbonyl Compounds with Chlorotrimethylsilane and Zinc

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Reductive McMurry-type dicarbonyl coupling of certain aryl and α,β-unsaturated carbonyl compounds to give alkenes can be accomplished using chlorotrimethylsilane and zinc by a novel mechanism which does not involve pinacolic coupling and diol deoxygenation.

Some time ago, we reported a novel general method for the direct deoxygenation of a carbonyl compound to give an alkene involving reaction with chlorotrimethylsilane and zinc.[1] The essential mechanistic features of the reaction, which has subsequently been utilised by several groups,[2] are outlined in Scheme 1, and bear a direct resemblance to those of the Clemmensen reduction,[3] save that the penultimate organozinc carbenoid (2) does not undergo further reaction with silicon electrophiles. In view of the lower energy of the initial 'ketyl' type radicals (1) produced by single-electron transfer to aromatic and α,β-unsaturated carbonyl systems, it was therefore of interest to examine such systems with a view
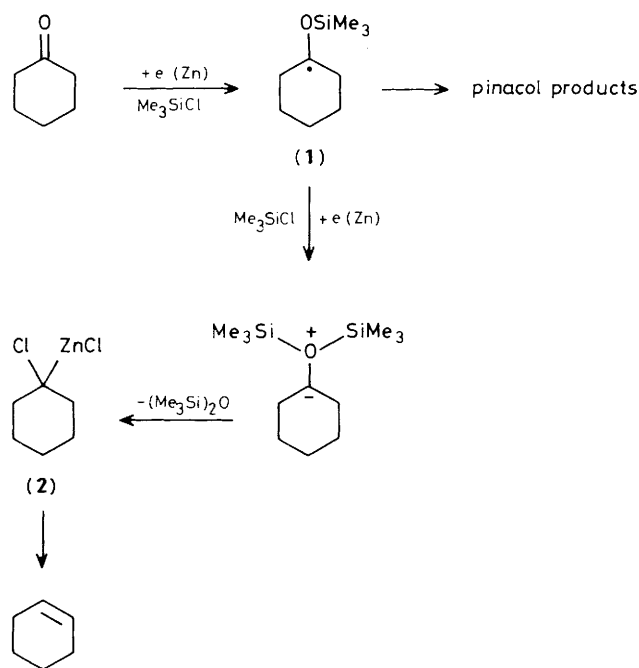
Scheme 1

to channelling the reaction pathway either towards pinacol type products or to carbenoid derived products *via* the key intermediates (1) and (2) respectively.

Initially we chose to study the behaviour of isophorone (3), which is known[4] to exhibit complex behaviour in the Clemmensen reduction. Simultaneous addition of the carbonyl compound and chlorotrimethylsilane to a stirred suspension of zinc dust in tetrahydrofuran at −30 °C led, after hydrolytic work-up, to isolation of the *meso* dimer (4) in low yield (15%). A similar result has recently been reported using single-electron transfer from organomanganese reagents[5] and conforms to the prediction that dimerisation will occur at the softer β-carbon atom.[6]

By contrast, however, reaction of the octalone (5) under similar conditions led to an excellent yield (85%) of the hydrocarbon 'dimer' (6), which may be formally derived by intermolecular coupling of two organozinc carbenoids, and is also obtained from (5) under McMurry-type coupling conditions using zinc and titanium trichloride.[7] Strong presumptive evidence for the s-*trans* geometry of the triene (6) comes from the u.v. spectrum, with λ_{max}. 309 nm; ε 43000. One possible explanation for the substrate dependent behaviour in this series is that the presence of additional geminal substituents on the γ carbon of the enone system inhibits dimerisation of the initial ambident siloxyallyl radical at the β-position and hence leads to reaction *via* the carbon atom of the original carbonyl group. Further support for this hypothesis comes from similar coupling reactions of 4,4-dimethylcyclohex-2-enone and cholest-4-en-3-one to afford the analogous oxygen-sensitive trienes (7) (23%) and (8) (43%) respectively.

We have also made a preliminary study of aromatic carbonyl compounds. Thus, reaction of α-tetralone (9) by slow addition of the carbonyl compound to an excess of chloro-trimethylsilane and zinc dust in ether at 0 °C gave 1,2-dihydronaphthalene (62%). Under such conditions efficient formation of the carbenoid without competing intermolecular reactions is understandably favoured. However, simultaneous addition of the carbonyl compound and chloro-trimethylsilane to zinc dust in tetrahydrofuran at −50 °C led
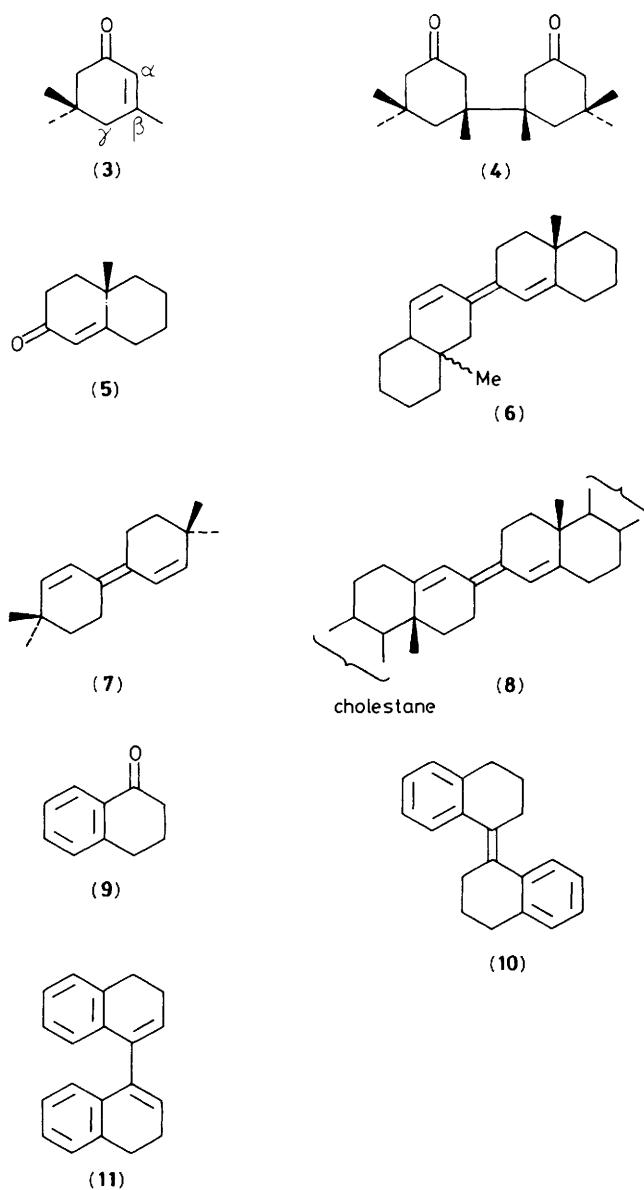
once again to isolation of a hydrocarbon fraction (20%) whose spectral properties are indicative of the dicarbonyl derived coupling compound (10). From the practical standpoint, it is important to stress that chlorotrimethylsilane must be rigorously free of hydrogen chloride. Thus, reaction of α-tetralone in protic chlorotrimethylsilane gave the symmetrical dehydro dimer (11) (75%) derived from pinacolic coupling and dehydration, whereas the bulk of the siloxy-centred carbon radical analogue presumably inhibits such a dimerisation. Reaction of benzaldehyde by the simultaneous addition method led, in similar fashion, to benzpinacol (50%) and a mixture of *cis*- and *trans*-stilbene (15%).

The mechanism of 'carbene dimer' formation in this series was of particular interest since a series of control experiments indicated that neither benzpinacol nor its silylated derivatives were a precursor of stilbene in these reactions. Clearly, the deoxygenative coupling reaction is not proceeding *via* the pinacol-type intermediates encountered in the use of low-valent tungsten[8] and titanium reagents.[7] Use of *trans*-stilbene epoxide as substrate, however, led to alkene formation (30%; *trans*:*cis* 83:17) and diphenylacetaldehyde (15%), the latter

presumably arising from zinc chloride-catalysed rearrangement. A reasonable pathway for the coupling reaction would therefore involve trapping of the intermediate organozinc carbenoid by a second molecule of carbonyl compound followed by subsequent deoxygenation of the resulting epoxide (Scheme 2).
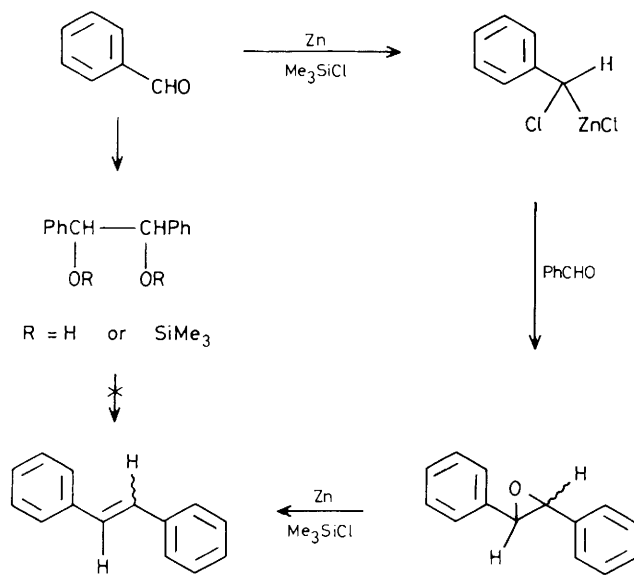
Scheme 2

Since the zinc–chlorotrimethylsilane reagent is compatible with sensitive ester and halogen functionality,[1] it therefore provides a mild complementary alternative to McMurry-type coupling in certain cases. On the basis of the mechanistic study described herein, improved methods for facilitating carbenoid generation, mitigating Lewis acid-induced epoxide ring-opening, and hence for improved inter- and intra-molecular dicarbonyl coupling and deoxygenation of epoxides are currently under investigation.

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