Regio- and Stereo-specific Reduction of Conjugated and Non-conjugated Triple Bonds by Activated Zinc Powder

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Regio- as well as stereo-specific reductions of a wide variety of acetylenic derivatives have been carried out in absolute ethanol with zinc powder activated with 1,2-dibromoethane, and with zinc powder activated successively with dibromoethane and copper(I) bromide, the first reagent being less powerful and more selective than the second one.

Although there are several reports concerning the reduction of acetylenic compounds with powdered zinc to the corresponding alkenes (mostly Z-isomers), the published procedures give little experimental information.[1,2] The published data do not give a good impression of the scope of this reduction.

We have carried out reductions with a wide variety of acetylenic compounds (for an example with an allene see ref. 3), using two kinds of zinc powder which are differently activated. Zinc powder activated by successive reaction with 1,2-dibromoethane and lithium dibromocuprate, $LiCuBr_2$ (in tetrahydrofuran, THF) (indicated as $Zn/Cu–C_2H_4Br_2$), appeared to have a greater reducing ability than zinc powder activated only with dibromoethane ($Zn–C_2H_4Br_2$).

Short interaction (addition at 30 °C, allowing the temperature to rise, then heating for 5 min at 80 °C) in absolute ethanol (40 ml) between $Zn–C_2H_4Br_2$ [from Zn (30 g) and dibromoethane (8 g)] and the diynes (0.15 mol) $HC{\equiv}CC{\equiv}CC_6H_{13}$, $Me_3SiC{\equiv}CC{\equiv}CC_6H_{13}$, $MeC{\equiv}CC{\equiv}CCH(OEt)_2$, $MeC{\equiv}C\text{-}C{\equiv}C[CH_2]_4OH$, $EtC{\equiv}CC{\equiv}CEt$, or $BuC{\equiv}CC{\equiv}CCH_2OCH(Me)\text{-}OEt$ gave† the enynes $H_2C{=}CHC{\equiv}CC_6H_{13}$, Z-$Me_3SiC{\equiv}CCH{=}CHC_6H_{13}$, Z-$MeC{\equiv}CCH{=}CHCH(OEt)_2$, Z-$MeC{\equiv}CCH{=}CH[CH_2]_4OH$, Z-$EtC{\equiv}CCH{=}CHEt$, and Z-$BuC{\equiv}CCH{=}CHCH_2OCH(Me)OEt$ respectively, in at least 70% isolated yields.

These reductions show some interesting features which seem useful for organic syntheses. In the first place $Zn–C_2H_4Br_2$ is highly selective, only one of the two triple bonds being reduced; Morris *et al.*[2] in their reduction of $C_6H_{13}C{\equiv}CC{\equiv}C[CH_2]_7CO_2Me$ with iron powder in aqueous propanol could detect at best 16% of the enyne ester Z-$C_6H_{13}C{\equiv}CCH{=}CH[CH_2]_7CO_2Me$, the main products being *Z,Z*- and *Z,E*-$C_6H_{13}CH{=}CHCH{=}CH[CH_2]_7CO_2Me$. The protective property of the Me_3Si-group opens up the possibility of synthesizing Z-3,1-enynes from 1,3-diynes (Scheme 1).

$$HC{\equiv}CC{\equiv}CR \xrightarrow[Me_3SiCl]{EtMgBr} Me_3SiC{\equiv}CC{\equiv}CR \xrightarrow{Zn–C_2H_4Br_2} Me_3SiC{\equiv}CCH{=}CHR \xrightarrow[MeOH]{NaOH} HC{\equiv}C\text{–}CH{=}CHR$$

Scheme 1

The reduction of heterosubstituted diynes appears to be regiospecific, the triple bond nearest to the substituent being reduced.[2]

A further useful property of $Zn–C_2H_4Br_2$ is that it discriminates between conjugated and non-conjugated terminal triple bonds. Thus phenylacetylene, 2-thienylacetylene, and 1-ethynylcyclohexene were reduced to styrene, 2-vinylthiophene, and 1-vinylcyclohexene respectively (1 h reflux in absolute ethanol, 0.10 molar scale, 25 g of Zn, activated with 6—7 g of dibromoethane) in 80—90% yields (after distillation), whereas non-1-yne remained unchanged. Sulphur in thiophene does not seem to have a poisoning effect, and even the enyne sulphide Z-$HC{\equiv}CCH{=}CHSEt$ was converted into Z-$H_2C{=}CHCH{=}CHSEt$ (45 min reflux, 0.10 molar scale, 35 g of Zn) in 90% yield.

The zinc–copper couple as prepared by us‡ is a much more

† The zinc powder was filtered off, and then rinsed with 96% EtOH. The filtrate was poured into a solution of KOH (25 g) in water (300 ml) (or a 1 M aqueous solution of HCl in the case of the silicon derivative) and the products were extracted with diethyl ether.

‡ Zinc (40 g) and absolute ethanol (50 ml) were first refluxed with dibromoethane (10 g) until evolution of ethene had stopped. A solution of CuBr (10 g) and anhydrous LiBr (12 g) in THF (3 ml) was then added at 40—50 °C.

powerful reducing reagent. It enabled us to convert the following compounds into the *Z*-alkene or *Z,Z*-alkadiene derivatives: $EtOCH_2C{\equiv}CCH_2OEt$, $Et_2NCH_2C{\equiv}CCH_2NEt_2$, $EtC{\equiv}CCH_2CH_2OH$, $BuC{\equiv}CCH_2OH$, $H_2C{=}CHC{\equiv}C{-}CH_2CH_2OH$, Z-$HC{\equiv}CCH{=}CH[CH_2]_4OH$, $MeC{\equiv}CC{\equiv}C{-}[CH_2]_4OH$, $EtC{\equiv}CC{\equiv}CEt$, $BuC{\equiv}CC{\equiv}CCH_2OCH(Me)OEt$, $HC{\equiv}C[CH_2]_4C{\equiv}CH$, $BuC{\equiv}CCH_2OEt$, and $Me_3SiC{\equiv}CCH_2C{\equiv}CH$ (only the terminal triple bond was reduced in the last case). Generally after a refluxing time of 1—1.5 h, taking 0.15 mol of substrate and 40 g of Zn, the conversions were complete. Alcohols and amines were reduced more easily than ethers. The sulphide $EtC{\equiv}CCH_2SEt$ was not reduced at all under these conditions.

Interestingly we observed a sharp decrease with increasing number of CH_2 groups in the reduction rates of $RC{\equiv}C[CH_2]_nOH$ and $RC{\equiv}C[CH_2]_nNEt_2$. For $n = 1$ or 2 the acetylenes were completely reduced under the above mentioned conditions, but in the case of $n = 4$ maximally 15—20% reduction had taken place and with $n = 8$ at best 5—10%.

The hydrocarbon $MeC{\equiv}CC_6H_{13}$ could not be reduced with our reagents. All these experimental facts indicate that OH, NR_2, and OR groups particularly assist in the adsorption of the $C{\equiv}C$ onto the metal surface, presumably because these groups can co-ordinate with zinc. This co-ordinative assistance may be, of course, more efficient if there is only a short distance between the triple bond and the hetero-substituent (entropy effect).

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References

1 S. G. Morris, S. F. Herb, P. Magidman, and F. E. Luddy, *J. Am. Oil Chem. Soc.*, 1972, **49**, 92; B. S. Rabinovitch and F. S. Looney, *J. Am. Chem. Soc.*, 1953, **75**, 2052; F. Näf, R. Decorzant, W. Thommen, B. Willhalm, and G. Ohloff, *Helv. Chim. Acta*, 1975, **58**, 1016; W. Oppolzer, G. Fehr, and J. Warneke, *ibid.*, 1977, **60**, 48; B. L. Sondengam, G. Charles, and T. M. Akam, *Tetrahedron Lett.*, 1980, 1069; A. J. Clarke and L. Crombie, *Chem. Ind. (London)*, 1957, 143; Houben-Weyl, 'Methoden der Organische Chemie,' 4e Auflage, Band V/1b, 583, 790, Georg Thieme Verlag, Stuttgart, 1972.

2 S. G. Morris, S. F. Herb, P. Magidman, and F. E. Luddy, *J. Am. Oil Chem. Soc.*, 1972, **49**, 505.

3 L. Brandsma and H. D. Verkruijsse, 'Synthesis of Acetylenes, Allenes and Cumulenes,' Elsevier, Amsterdam, New York, 1981.