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Zinc-Promoted Reactions. 6. The Reduction of Diphenylcyclopropenone in Acidic Media.

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Abstract: The reduction of diphenylcyclopropenone with zinc was investigated under a variety of conditions. The product distribution can be explained in terms of a general mechanism for zinc-promoted reductions.

The zinc-promoted reduction of α,β-unsaturated ketones in acidic media has been reinvestigated recently [1] Diphenylcyclopropenone (**1**) is a peculiar member of this class of compounds. The reduction of **1** with metals like Na and Mg in non acidic media was reported to give only dimeric aromatic compounds.[2,3] Dimerization of diphenylcyclopropenyl radical anion, detected and characterised by EPR spectroscopy,[4] accounted for the product formation. The reduction of **1** with Zn in several acidic media is now reported, showing a quite different course of the reaction.

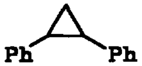
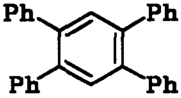
Results and Discussion

The reduction of **1** was investigated according to the Clemmensen procedure (7M HCl) and in anhydrous AcOH at the refluxing temperature, using an excess of amalgamated zinc. Experiments in AcOH were run also in the presence of anhydrous LiCl, HCl, and TFA. The results are reported in the Table. While significant differences in the product distribution were obtained in the various systems, the data show that practically no dimeric products were formed, with the exception of the small amounts of 1,2,4,5-tetraphenylbenzene, (**8**), obtained when the reaction was run in AcOH in the presence of anhydrous HCl or TFA

Radical species could not be detected by EPR spectroscopy unless a spin trapping agent was present [5] Accordingly, the assumption can be made that the first formed radical species might have a shorter life than the delocalized ketyl previously characterised by EPR. Their fast reduction in the acidic medium might prevent dimerization reactions

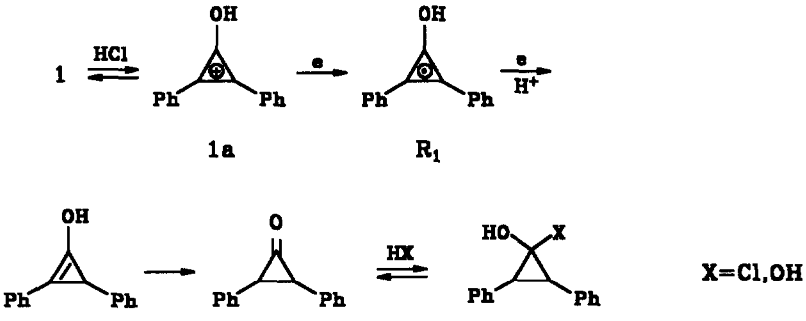
Under the strongly acidic Clemmensen procedure electron transfer from Zn to hydroxycyclopropenium cation **1a** may occur

TABLE. Products formed in the Zn(Hg) reduction of 1 in acidic media.[a]

Products[b]		Reaction systems				
		7M HCl	AcOH	AcOH/LiCl	AcOH/HCl	AcOH/TFA
$PhCH_2CH_2CH_2Ph$	2	59				
$PhCH{=}CHCH_2Ph$	3[c]	14		traces	6	7
$PhC(CH_3){=}CHPh$	4[c]	15			7	10
$PhCH(CH_3)CH_2Ph$	5	traces			traces	
	6[d]	10	7	52	24	53
$PhCH_2COCH_2Ph$	7		87	46	60	13
	8				traces	8
$PhCH{=}C(OAc)CH_2Ph$	9					4
$PhCH{=}C(OCOCF_3)CH_2Ph$	10					5

[a] Reaction conditions: 2 h at the refluxing temperature. Conversion: 94% in AcOH, 100% in the other systems. The yelds were determined by GC analysis. [b] Product distributions are in percentage. The data represent the average of two or more experiments. [c] Mixture of stereoisomers. [d] Trans/cis ratio: approximately 2:1, except in AcOH/LiCl which was 5:1.

The relatively high basicity of 1 has been measured.[6] The resulting cyclopropenyl radical R_1 is then converted into the 2,3-diphenylcyclopropanone (11) through the intermediacy of its enolic form



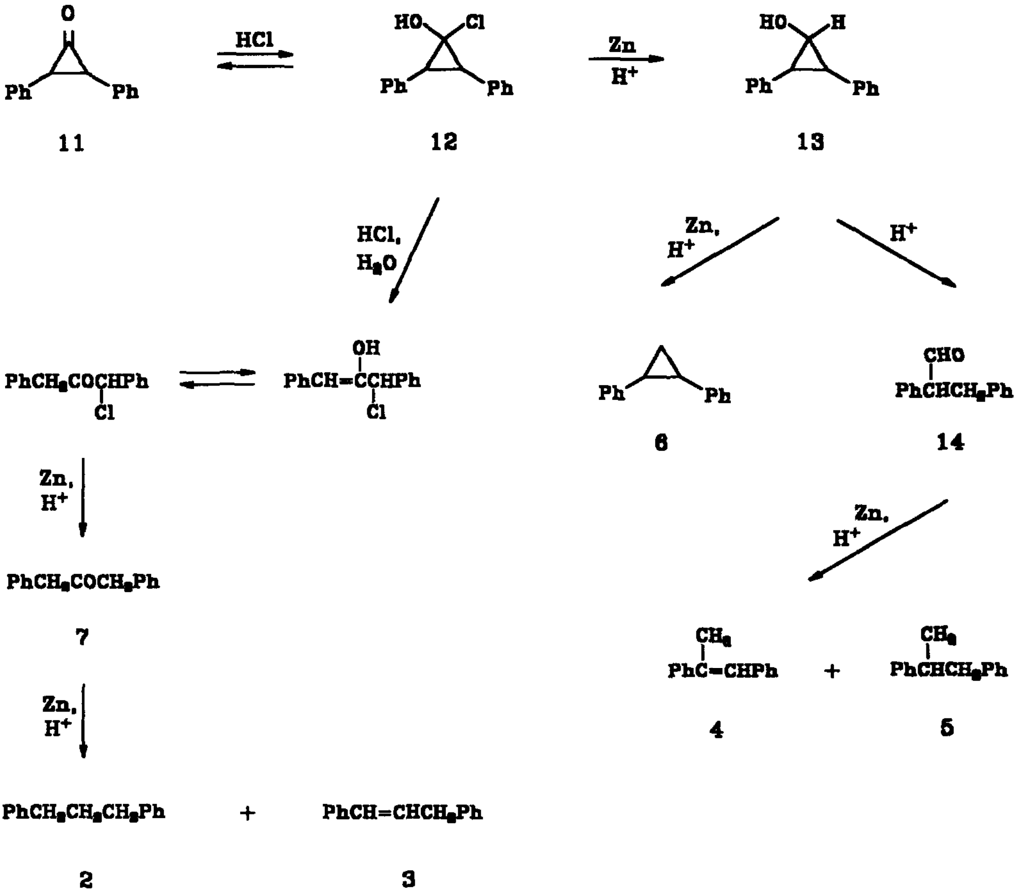
1a R1

11

Cyclopropanones are known to readily take up reagents like H_2O, HCl, and carboxylic acids, affording the corresponding carbonyl adduct.[7] Attempts to synthesise **11**, not yet described in the literature, failed so far However, there is little doubt that **11** or its HCl adduct **12**, is the precursor of **6**, a product formed in all the reactions, which was shown to resist zinc reduction under all the selected conditions. A precursor of **6** may be cyclopropanol **13**, as shown in the Scheme, which was detected in traces by GC/MS spectrometry in the crude reaction mixture.

The occurrence of 1,1-dichloro-2,3-diphenylcyclopropane as an intermediate, possibly originating from **12**, was excluded, since the Clemmensen reduction of this dichloride gave several products in the absence of **6** (see Experimental)

Scheme.



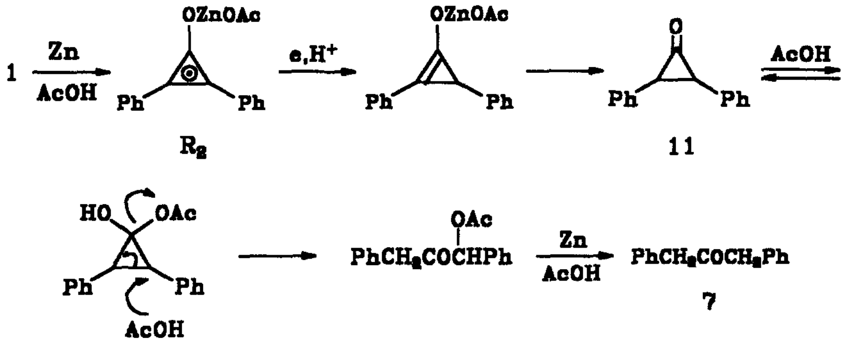
Cyclopropanone **11** may also be the precursor of acyclic hydrocarbons **2** and **3** In aqueous acidic media

HCl cyclopropanone adduct may undergo ring cleavage.[7] The cleavage of **12** requires nucleophilic attack by the external chloride to the benzylic carbon, the covalent chlorine acting as the leaving group.

Dehalogenation of an α-halo ketone under the conditions of the Clemmensen reduction is a known reaction [8] We have confirmed that ketone **7** undergoes the Clemmensen reduction affording a mixture of **2** and **3**.

The formation of branched hydrocarbons **4** and **5** may involve the intermediacy of 2,3-diphenylpropanal (**14**) originating from **13** through acid catalysed ring cleavage [9] A new synthesis of **14** was accomplished by treating the enamine of phenylacetaldehyde with benzyl bromide. When the Clemmensen reduction of **14** was performed without completing the reaction, **4** and **5** were obtained, along with the linear hydrocarbons **2** and **3** Thus **2** and **3** may derive also from aldehyde **14**

The reduction of **1** in neat AcOH followed a somewhat different course This can be ascribed to the first SET occurring from the metal to **1**, and not to its conjugated acid, due to the low protonating ability of the medium [10] The resulting radical R_2 may then undergo a second SET followed by protonation, ultimately affording cyclopropanone **11** A solvent carbonyl addition, followed by ring cleavage and reductive deacetoxylation of the intermediate α-acetoxy ketone, may account for the formation of **7**, the largely predominant product We have confirmed that **7** is practically unaffected by treatment with Zn in boiling AcOH The Zn/AcOH deacylation of α-acetoxy ketones was already reported [11]



The higher yields of **6** in the presence of LiCl, HCl, and TFA, were obtained at the expense of **7** In the presence of the above co-reagents, **11** might show a different reactivity in connection with the nature and the relative concentration of the corresponding carbonyl adduct

A more scattered product distribution in the presence of HCl or TFA, as compared with that in plain AcOH, was already observed in the zinc-promoted reduction of other ketones [12,13]

The minor amounts of enol esters **9** and **10** in the AcOH/TFA reduction of **1** can be ascribed to addition of AcOH or TFA to the carbonyl of **7**, followed by H_2O elimination

1,2,4,5-Tetraphenylbenzene (**8**), the only dimeric product formed in the zinc-promoted reduction of **1** in an acidic medium, has been previously obtained from the Zn/AcOH reduction of 1,3-diphenylpropenone.

Its formation was explained in terms of dimerization of 1,2-diphenylcyclopropenyl radical, followed by valence isomerization [1]

In conclusion, the zinc-promoted reduction of diphenylcyclopropenone may be understood in terms of the general mechanism already discussed for α,β-unsaturated as well as other carbonyl compounds.[12,13]

Experimental Section

The general procedure for the reductions was previously described [1,12] GC analyses were carried out with a Carlo Erba HRGC 5300 Mega Series apparatus on 30 m x 0 25 mm i d x 0.33 μm SPB-35 column. GC/MS analyses were performed with a VG quattro mass spectrometer on the same column. ^{1}H NMR spectra were recorded on a Bruker WP-80 spectrometer with $CDCl_3$ as the solvent HPLC analyses were performed with a Philips apparatus, equipped with a PU4020 UV detector on a 100 x 3 mm i.d., Lichrosorb Si 60 (7 μm) column. Isolation of the products were carried out by preparative HPLC on a 250 x 10 mm i d , Lichrosorb Si 60 (7 μm) column

Materials Anhydrous AcOH was prepared by refluxing (4h) 99 8% AcOH (Merck) with the calculated amount of Ac_2O (Merck) Stock solutions of approximately 0.3 M anhydrous HCl in AcOH were prepared by bubbling a HCl gas in the solvent. 99% TFA (Aldrich) was used, without further purification, in 5% concentration in AcOH Compounds **1** and **7** were commercial reagents (Aldrich) of 99% purity. Compounds **6**,[14] and 1,1-dichloro-2,3-diphenylcyclopropane[15] were prepared according to the literature

Product distribution analysis. Identification of the products and their distribution were accomplished by GC, NMR, and GC/MS analyses Compounds **2-4** and **6**,**7** were isolated in pure state by preparative HPLC Mass spectra of the products are given as supplementary material

Reduction of 1,3-diphenylpropan-2-one (7). The reductions were performed in various systems at the refluxing temperature for 2h The products were 70% **2**, 12% **3** and 2% 1,3-diphenylpropan-2-ol in 7 M HCl, 2% **2** and 2% **3** in neat AcOH, 2% **2** and 3% **3** in anhydrous AcOH/LiCl, 3% **2** and 3% **3** in anhydrous AcOH/HCl

Reduction of 2,2-dichloro-1,3-diphenylcyclopropane. The reduction performed with Zn/Hg in 7 M HCl for 2 h at reflux temperature gave 10% **3**, 50% **7** along with other minor products.

Synthesis of 2,3-diphenylpropanal (14). A solution of phenylethanal (12g Aldrich) and pyrrolidine (8g Aldrich) in anhydrous benzene (100 ml) was stirred for 2 h at room temperature in the presence of dry $CaCl_2$ (12g) and a trace of *p*-toluenesulfonic acid After filtration, benzyl bromide (17g Aldrich) was added and the reaction was kept 4 h at the refluxing temperature The solution was diluted with Et_2O and treated with 20% AcOH The organic layer was dried over Na_2SO_4 and the solvent removed Column chromatography over SiO_2 (elution with hexane-chloroform 3 1) gave the pure aldehyde (m p 52-54 °C; lit [16] 54 °C) in 50% yield

Reduction of 2,3-diphenylpropanal (14). The reduction performed with Zn/Hg in 7 M HCl for 2 h at the reflux temperature gave 2% **2**, 35% **3**, 9% **4**, 14% **5** and 40% 2,3-diphenylpropan-1-ol.

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Supplementary Material Available: Complete MS data for the products.

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