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A NEW REAGENT, Zn-$ZnCl_2$-ROH, FOR THE HYDROGENATION OF CONJUGATED DOUBLE BOND

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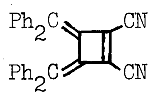
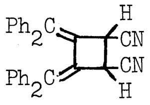
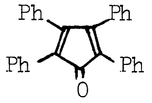
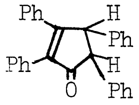
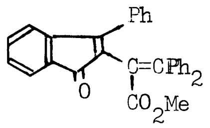
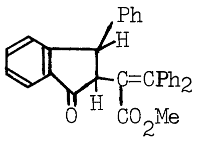
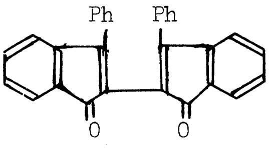
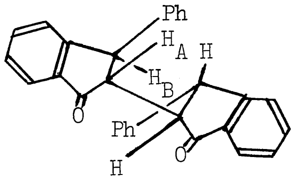
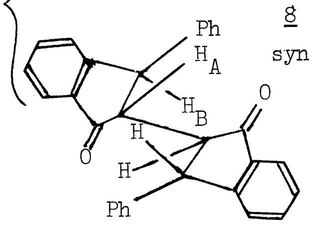
Not only the double bond placed between two carbonyl or cyano groups but also the double bonds of indenone and cyclopentadienone were easily hydrogenated by heating with Zn-$ZnCl_2$-ROH.

It has long been known that Zn-AcOH is effective for the reduction of the double bond placed between two carbonyl groups.1) We found, however, that Zn-$ZnCl_2$-ROH2) can be used for such a reduction under rather mild reaction conditions and is also effective for the reduction of the double bond of 1,2-dicyanoethylene, cyclopentadienone, and indenone.

Details of the reaction conditions and yields of the products are summarized in Table 1. The reduction of 1,2-dicyano-3,4-bis(diphenylmethylene)-1-cyclobutene (**1**), tetraphenylcyclopentadienone (**3**), and 2-(1-methoxycarbonyl-2,2-diphenylvinyl)-3-phenyl-2-inden-1-one (**5**) afforded the corresponding dihydro derivatives, **2**, trans-**4**, and **6**, respectively. Stereochemical relationship between the hydrogens in **2** and **6** was uncertain. The reduction of 2,2'-bi(1-oxo-3-phenylindenyl) (**7**) afforded two tetrahydro derivatives, to which trans-syn (**8**) and trans-anti (**9**) structures were tentatively assigned. Molecular models showed that cis-isomers of **8** and **9** would have serious steric repulsions. The syn and anti structures were assumed by means of the NMR spectral data, i. e., H_B of **8** is shielded by the phenyl ring on the position 3 of the opposite indanone ring, and its signal (6.67 τ) appeared at higher magnetic field than the signal of H_B of **9** (6.44 τ) did. Molecular models showed the presence of such the spacial relationship between H_B and the phenyl ring in **8**. The possibility that **8** and **9** are rotational isomers due to a restricted rotation around the 2-2' bond can be excluded, because the NMR spectra of them (o-dichlorobenzene) were not affected by raising temperature to 145 °C. It is clear that the hydrogen used for the reduction is that of hydroxyl group of ROH, because the reduction of **3** and **7** with Zn-$ZnCl_2$-MeOD afforded **4**-d_2, and **8**-d_4 and **9**-d_4, respectively. Although the treatments of **4**-d_2, **8**-d_4, and **9**-d_4 with Zn-$ZnCl_2$-EtOH did not cause any deuterium-hydrogen exchange, it is uncertain whether the reduction is concerned with keto-enol equilibrium3) or not.

Table 1. Reduction of Conjugated Double Bond with Zn-ZnCl$_2$-ROH[a)]

Olefin	ROH	Reaction time (hr)	Product	Yield (%)	Mp (°C)	τ_{CH} (CDCl$_3$)
trans-1,2-Dibenzoylethylene	EtOH	1	1,2-Dibenzoylethane	83		
Dimethyl maleate	EtOH	1	Dimethyl succinate	95		
Dimethyl fumarate	EtOH	1	Dimethyl succinate	95		
Fumaric acid	EtOH	2	Succinic acid	94		
trans-α,β-Dicyanostilbene	i-PrOH	3	meso-1,2-Dicyano-1,2-diphenylethane	71	235 (lit,[4)] 238)	4.80 (s)
 1	i-PrOH	3	 2	95	232	5.63 (s)
 3	EtOH	1	 4 trans[5)]	71	229	5.41 and 6.24 (each d, J=2.4 Hz)
 5	EtOH	2	 6	74	161	5.30 and 6.25 (each d, J=6 Hz)
 7	EtOH	2	 8 syn	33	215	5.45 and 6.67 (each d, J=4.5 Hz)
			 9 anti	33	192	5.54 and 6.44 (each d, J=4.5 Hz)

a) A mixture of an olefin (1 g), Zn-powder (2 g), ZnCl$_2$ (2 g), and ROH (15-20 ml) was heated under reflux. Anhydrous ZnCl$_2$ was prepared by fusing commercially available ZnCl$_2$ on a pan.

References and Note

1) A. Windaus, Chem. Ber., 39, 2249 (1906); K. Ohkata and T. Hanafusa, Bull. Chem. Soc. Jpn., 43, 2204 (1970).

2) It has been reported that this reagent is effective for a reductive cleavage of 1,2-dibenzoylcyclobutane into 1,4-dibenzoylbutane. J. Dekker, F. J. C. Martins, and J. A. Kruger, Tetrahedron Lett., 1975, 2489.

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