A NEW REAGENT, Zn-ZnCl_-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-ZnCl₂-ROH.

It has long been known that Zn-AcOH is effective for the reduction of the double bond placed 1) 2) between two carbonyl groups. We found, however, that Zn-ZnCl₂-ROH 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 ($\underline{1}$), 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 ($\underline{8}$) and trans-anti ($\underline{9}$) 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., ${\rm H_{p}}$ of <u>8</u> is shielded by the phenyl ring on the position 3 of the opposite indenone ring, and its signal (6.67 τ) appeared at higher magnetic field than the signal of H_R of 9 (6.44 τ) did. Molecular models showed the presence of such the spacial relationship between $H_{\rm R}$ and the phenyl ring in <u>8</u>. 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 2 and 7 with Zn-ZnCl_-MeOD afforded 4-d2, and 8-d4 and 9-d4, respectively. Although the treatments of 4-d2, 8-d4, and 2-d4 with Zn-ZnCl2-EtOH did not cause any deuterium-hydrogen exchange, it is uncertain whether the reduction is concerned with keto-enol equilibrium or not.

| Olefin | ROH | Reaction time (h: | n Pr od uct r) | Yiel (%) | .d M | Mp °C) | τ _{CI} (CDC | H 1,) |
|---|--------|----------------------|---|-----------------------|------|-----------|-------------------------|-------------------|
| trans-1,2-Dibenzoylethylene | EtOH | 1 | 1,2-Dibenzoylethar | 1e 83 | | | | |
| Dimethyl maleate | EtOH | l | Dimethyl succinate | 95 | | | | |
| Dimethyl fumarate | EtOH | l | 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) |
| Ph ₂ ^C CN <u>1</u> Ph ₂ ^C CN | i-PrOH | 3 | $\frac{Ph_2C}{Ph_2C} \xrightarrow{H}_{CN} \frac{2}{Ph_2C}$ | 95 | 232 | | | 5.63 (s) |
| Ph Ph Ph 3 Ph 3 | EtOH | 1 | Ph H Ph H Ph H Ph tra | 71 5) ms | 229 | | 5.41 and (each d, | 6.24 J=2.4 Hz) |
| Fh CCO2Me 5 | EtOH | 2 | Ph H C=CPh2 CO2Me | <u>6</u> 74 | 161 | 4 | 5.30 and (each d, | 6.25 J=6 Hz) |
| $Ph \qquad Ph \qquad Ph \qquad O$ | EtOH | 2 | Ph H _A H Ph H H H H H A C | 33 <u>8</u> syn | 215 | (| 5.45 and (each d, | 6.67 J=4.5 Hz) |
| | | | ° H Ph | 2 33 | 192 | | 5.54 and (each d, | 6.44 J=4.5 Hz) |

a) Table 1. Reduction of Conjugated Double Bond with Zn-ZnCl_-ROH

a) A mixture of an olefin (1 g), Zn-powder (2 g), ZnCl₂ (2 g), and ROH (15-20 ml) was heated under reflux. Anhydrous ZnCl₂ was prepared by fusing commercially available ZnCl₂ on a pan.

References and Note

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