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Preliminary communication

FORMATION OF CYCLOPROPANE RINGS VIA Zr—X (X = Cl, Br) γ-ELIMINATION

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Summary

(η-C_5H_5)$_2$Zr(Cl)H (I) reacts with 4-chlorocyclohexene and 4-bromocyclohexene to give moderate yields of bicyclo[3.1.0]hexane. Reaction of I with 4-chloropent-1-ene gives low yields of *cis*- and *trans*-1,2-dimethylcyclopropanes, 42% *trans*-pent-2-ene, and no *cis*-pent-2-ene. Reaction of I with 2-methyl-3-chloropropene gives 31% methylcyclopropane. Formation of these rings is believed to proceed by Zr—X (X = Cl, Br) γ-elimination. Side reactions include (1) Zr—X β-elimination to yield halogen-free olefins and (2) formation of halogen-free olefins by direct reduction of C—X by Zr—H.

It is known that (η-C_5H_5)$_2$Zr(Cl)H (I) reacts with olefins to form stable alkylzirconium complexes, (η-C_5H_5)$_2$Zr(Cl)R [1, 2]. This reaction involves either regiospecific addition of Zr—H to a terminal olefin or addition of Zr—H to an internal olefin followed by rapid rearrangement via reversible β-hydride elimination to place the Zr atom at the least hindered accessible position. Thus, reaction of I with either oct-1-ene or oct-4-ene forms complexes with the zirconium substituent at the end of the alkyl chain [2a]. It also is known that haloalkylmetallic complexes can undergo metal—halogen elimination to form olefins [3] or in some cases carbocyclic rings [4]. Earlier workers who studied the (η-C_5H_5)$_2$-Zr(Cl)R complexes have emphasized the utility and stereochemistry of Zr—R cleavages by electrophilic reagents [2]. We now report that (C_5H_5)$_2$Zr(Cl)H adds to olefins containing halogen. The addition is followed by decomposition to give cyclopropanes or olefinic products.

In the reaction of I with 4-chlorocyclohexene, which is representative of the reactions studied, 5.20 mmoles each of 1- and 4-chlorocyclohexene and 50 μl of benzene in C_6D_6 (2 ml total volume) were stirred for 61 h at 65°C (sealed tube, inert atmosphere). The reaction mixture was cooled and if the ^{1}H NMR spectrum of the completed reaction solution showed significant indication of residual alkylzirconium, the solution was hydrolyzed prior to analysis. The yields of organic products were determined by GLC and ^{1}H NMR. The products, yields, and reac-

TABLE 1

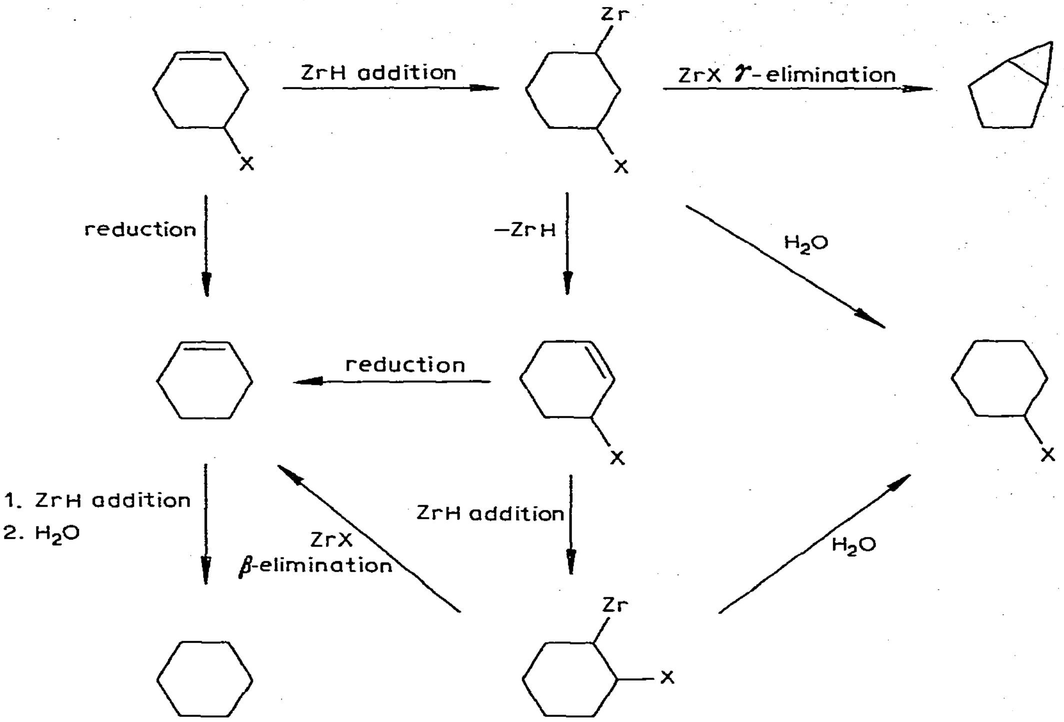
PRODUCTS FROM THE REACTION OF $(\eta\text{-}C_5H_5)_2Zr(Cl)H$ WITH OLEFINIC HALIDES

Reactant	Products, yield (%) (Determined by ^{1}H NMR)	Products, yield (%) (Determined by GLC)	Unreacted starting material (%) (Determined by GLC)	Reaction conditions
4-Chlorocyclohexene	Bicyclo[3.1.0]hexane (40) Cyclohexene (26)	Cyclohexane (5) Chlorocyclohexane (15)	8	61 h, 65°C (hydrolyzed)
4-Chlorocyclohexene	Bicyclo[3.1.0]hexane (35) Cyclohexene (39)	Cyclohexane (8) Chlorocyclohexane (2)	—	24 h, 85°C (hydrolyzed)
4-Bromocyclohexene	Bicyclo[3.1.0]hexane (18) Cyclohexene (40)	Cyclohexane (4) Bromocyclohexane (26)	10	90 h, 65°C (hydrolyzed)
4-Bromocyclohexene	Bicyclo[3.1.0]hexane (16) Cyclohexene (58)	Cyclohexane (9) Bromocyclohexane (5)	—	24 h, 85°C (hydrolyzed)
4-Chloropent-1-ene	Pent-2-ene (*trans* only) (42) *trans*-1,2-Dimethylcyclopropane (8) *cis*-1,2-Dimethyl cyclopropane (3)		—	65 h, 115°C
2-Methyl-3-chloropropene	2-Methylpropene (54) Methylcyclopropane (31)			50 h, 60°C
1-Chlorocyclohexene		Cyclohexene (14) Cyclohexane (20)	36	24 h, 85°C (hydrolyzed)
Chlorocyclohexane		Cyclohexane (96)	—	24 h, 85°C (hydrolyzed)
trans-1,4-Dichloro but-2-ene	1-Chlorobut-2-ene (29)		39	115 h, 75°C

tion conditions for the various experiments are summarized in Table 1.

In every case studied where X = Cl, the isolated yield of $(\eta\text{-}C_5H_5)_2ZrCl_2$ [5] was in the range 82—87%. Whenever possible, pure samples of volatile products were collected by GLC. The ^1H NMR spectra of all products are identical to those found in the literature or to those of authentic samples.

The proposed pathway for the reaction of I with 4-halocyclohexene is illustrated in Scheme 1.



Formation of bicyclo[3.1.0]hexane is believed to proceed by Zr—X γ-elimination, while formation of cyclohexene proceeds by Zr—X β-elimination and/or direct reduction of C—X by Zr—H. Product cyclohexene is susceptible to further addition of Zr—H to yield a cyclohexylzirconium complex, which, upon hydrolysis would give cyclohexane. The reaction of I with chlorocyclohexane to give cyclohexane demonstrated the feasibility of direct reduction of C—Cl by Zr—H*. The lower yield of bicyclo[3.1.0]hexane from 4-bromocyclohexene might be due to the facility of direct C—Br reduction.

The reaction of I with 1-chlorocyclohexene yielded no bicyclo[3.1.0]hexane. This is consistent with Zr—Cl β-elimination being favored over Zr—H β-elimination. Thus, after the Zr—H addition to the double bond in 1-chlorocyclohexene, either one or two Zr—H β-eliminations must precede Zr—Cl γ-elimination to give bicyclo[3.1.0]hexane. The Zr—H β-elimination would have to compete with Zr—Cl β-elimination, the latter giving cyclohexene. The faster rate of Pd—Cl

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*C—Cl reductions by M-H are common. See for example ref. 6a.
Reductions of CH_2Cl_2 to CH_3Cl and $CHCl_3$ to CH_2Cl by $(\eta\text{-}C_5H_5)Zr(Cl)H$ have also been observed [6b].

elimination compared with Pd—H β-elimination already has been demonstrated [3].

The reaction of I with 4-chloropent-1-ene gave *trans*-pent-2-ene but no *cis*-pent-2-ene. Formation of *trans*-pent-2-ene can occur from (1) Zr—X β-elimination and/or (2) reduction of formed 4-chloro-*trans*-pent-2-ene. Further explorations of effects of leaving groups and olefin stereochemistry on ring closure are in progress.

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