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CYCLOPENTADIENYL-ALUMINUM COMPOUNDS
I. THE REACTIONS OF CYCLOPENTADIENE WITH ALUMINUM ALKYLS*

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SUMMARY

The reactions of cyclopentadiene with aluminum alkyls were investigated. The metalation reaction occurs with formation of cyclopentadienyldiisobutylaluminum and is accompanied by side reactions. The facile addition of trialkylaluminum compounds to dicyclopentadiene is reported.

INTRODUCTION

The metalation reaction of cyclopentadiene has been carried out using metal alkyls, metal hydrides, or even metals, and represents a facile route to the ionic Group I and Group II metal cyclopentadienyls[1]. However, the metalation of cyclopentadiene with trialkylaluminum compounds has not been reported, and only a few organoaluminum compounds containing cyclopentadienyl groups have been mentioned in the literature[2-5].

The present paper reports on a study of the metalation of cyclopentadiene by various trialkylaluminum compounds. Side reactions were observed which led to a brief study of the addition reaction between dicyclopentadiene and aluminum alkyls[6]. The addition of the aluminum–carbon bond to the reactive double bond in dicyclopentadiene provides a facile synthesis of a class of secondary organoaluminum compounds. Such addition reactions are generally difficult to perform using internal olefins[7].

RESULTS AND DISCUSSION

Trialkylaluminum compounds do not react with cyclopentadiene in hydrocarbon solvents at room temperature. This was surprising since Grignard compounds, RMgX, react smoothly with cyclopentadiene to form RH and C_5H_5MgX[8]. Diisobutylaluminum hydride also appears to be unreactive toward this hydrocarbon at room temperature. No attempts were made to carry out the reaction in ether or other polar

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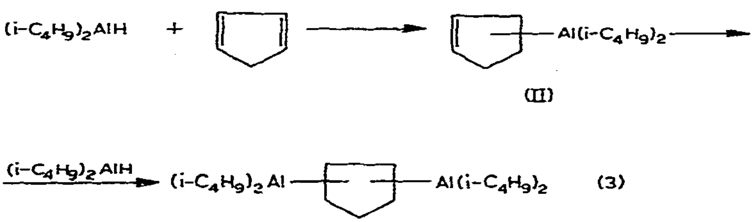
solvents because of the known instability of cyclopentadienylaluminum compounds in such solvents[5].

Since cyclopentadiene readily forms *endo*-dicyclopentadiene which is more reactive towards aluminum alkyls than is the monomer, it was necessary to minimize dimer formation. This was achieved by using a glass flow system in which gaseous cyclopentadiene diluted with nitrogen was preheated and passed through triisobutylaluminum at 150°–180°. Under these conditions a viscous reaction product was obtained from which cyclopentadienyldiisobutylaluminum(I) was isolated. Compound(I) was fully characterized and found to be identical with an authentic sample prepared by halogen interchange[4]. The metalation reaction is represented by equation (1):

$$AlR_3 + C_5H_6 \rightarrow \underset{(I)}{R_2AlC_5H_5} + RH \qquad (R = \text{isobutyl}) \qquad (1)$$

The principal reaction is accompanied by side reactions as revealed by analysis of the hydrolysis products. Besides hydrogen, cyclopentadiene and isobutane, the following were identified: cyclopentane, cyclopentene, bicyclopentyl and cyclopentylcyclopentene. The origin of these compounds can be rationalized by assuming the following side reactions [equations (2), (3)]:

$$(i\text{-}C_4H_9)_3Al \longrightarrow (i\text{-}C_4H_9)_2AlH + i\text{-}C_4H_8 \qquad (2)$$



(II)

(3)

(III)

Addition reactions similar to those in eqn. (2) have been reported using diborane[9]. The hydrolysis of (II) and (III) will give cyclopentene and cyclopentane. Further reaction of the organometallic adducts, *e.g.* (III), with cyclopentadiene can explain the presence of cyclopentylcyclopentene and bicyclopentane in the hydrolysis products.

The inability of trialkylaluminum compounds to metalate cyclopentadiene at moderate temperatures was unexpected in view of their known reactivity in protolytic reactions with compounds containing acidic hydrogen. However, it is noteworthy that indene is much more difficult to metalate than phenylacetylene with triphenylaluminum at elevated temperature[10].

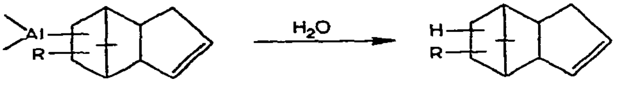
Reactions with endo-dicyclopentadiene

During the course of our metalation studies with cyclopentadiene it was discovered that the slowly formed *endo*-dicyclopentadiene (IV) reacts readily with trialkylaluminums at moderate temperatures. If the reaction temperature is raised to about 150° all three aluminum–carbon bonds can be utilized with a molar ratio of trialkylaluminum to (IV) of 1/3. This facile reaction allows the preparation of secondary organoaluminum compounds (V) according to eqn. (4):

(IV) (V) (4)

(R = alkyl; hydride)

The course of the addition was established by hydrolysis of the adducts (V) and analysis of the organic products (VI) [eqn. (5)]:



(V) (VI) (5)

Stereochemical aspects of the addition reaction were not investigated. No attempt was made to isolate the positional isomers or to resolve the possible stereoisomers of (VI).

It has been pointed out[7] that the addition reactions of trialkylaluminum compounds with internal olefins are generally quite slow and often are complicated because of side reactions. The facile and selective reaction with (IV) can be explained by the enhanced reactivity of the strained olefinic double bond of the bicycloheptene moiety. Practically no reaction takes place at the nonactivated double bond of the cyclopentene ring. A similar selectivity was observed with diisobutylaluminum hydride and (IV) at 60°.

EXPERIMENTAL

All reactions with organoaluminum compounds were carried out under a blanket of dry nitrogen. Cyclopentadiene was prepared by thermal depolymerization of (IV). *endo*-Dicyclopentadiene (IV) was prepared by slow dimerization of cyclopentadiene at room temperature. The trialkylaluminums used were obtained from commercial sources (Texas Alkyls or Ethyl Corp.). The elemental analyses, molecular weight determinations, iodine numbers, the analysis by mass spectroscopy, proton magnetic resonance and gas chromatography were carried out by the Analytical and Information Division, Esso Research and Eng. Co. Proton resonance spectra and integrations were recorded at ambient temperature using a Varian A-60 NMR spectrometer. Solutions were ca. 30 vol. % in CCl_4 with TMS as internal standard.

Reaction of triethylaluminum with cyclopentadiene

To 0.6 mole of the diene was added 0.18 mole of the aluminum compound at 0°. No gas evolution was observed on mixing or on warming to 60°. No reaction occurred, as evidenced by IR and ^{1}H NMR, except formation of (IV) from cyclopentadiene. Similar results were obtained using triisobutylaluminum.

Reaction of diisobutylaluminum hydride with cyclopentadiene

To a solution of 0.8 mole diisobutylaluminum hydride in 40 ml heptane was added 1.2 moles of freshly distilled cyclopentadiene. No gas evolution was observed.

IR and ^{1}H NMR spectra of the reaction mixture indicated that no reaction had occurred. The temperature then was raised to 60°. No gas evolution was detected. IR analysis indicated a gradual decrease in the intensity of the Al–H band (at 1770 cm^{-1}). After several hours reaction time the solvent was removed and the viscous organometallic residue was analysed for aluminum. (Found: Al, 10.6; $(i\text{-}C_4H_9)_2AlC_{10}H_{11}$ calcd.: Al, 9.9%.) Upon hydrolysis, 2 moles of gas were formed per mole of aluminum (93% isobutane, 7% hydrogen). Analysis of the liquid hydrolysis product by preparative GLC: 5% (IV), 95% monoolefinic hydrocarbon $C_{10}H_{14}$, m.p. 51.5°, b.p. 177°, identical with the known 5,6-dihydro-*endo*-dicyclopentadiene (VII) (reported m.p. 51°, b.p. 178°)[11].

Metalation of cyclopentadiene with triisobutylaluminum at 170°

A nitrogen stream containing gaseous cyclopentadiene was bubbled through a glass frit into a vessel containing 0.39 mole of triisobutylaluminum at 170° for 1 h. The viscous product was degassed under reduced pressure and analyzed. (Found: Al, 16.7%.) Hydrolysis of a sample gave 1.3 moles of gas per mole of aluminum (61% H_2, 39% isobutane). Vacuum distillation of the unhydrolysed product (0.001 mm/120° bath temperature) gave 25 g of distillate consisting of $(i\text{-}C_4H_9)_2AlC_5H_5$, triisobutylaluminum and little diisobutylaluminum hydride. From the distillate, 8.6 g of pure $(i\text{-}C_4H_9)_2AlC_5H_5$ was isolated using a combination of freezing and redistillation of the solid which crystallized. The ^{1}H NMR chemical shifts of $(i\text{-}C_4H_9)_2AlC_5H_5$ in benzene were identical with those reported[4]. (Found: Al, 13.1; calcd.: Al, 13.1%.) Hydrolysis followed by hydrocarbon analysis gave the correct ratio of isobutane to cyclopentadiene. Quantitative ^{1}H NMR analysis gave the correct ratio of cyclopentadienyl to isobutyl protons. M.p. 40–41° (uncorr.), b.p. 26°. at 0.04 mm and 60° bath temperature. The distillation residue was hydrolysed and the products analyzed: hydrogen, isobutane, cyclopentadiene, cyclopentane, bicyclopentyl, cyclopentylcyclopentene and traces of cyclopentene. A total of 19 mole % of triisobutylaluminum was converted to $(i\text{-}C_4H_9)_2AlC_5H_5$; the yield of purified $(i\text{-}C_4H_9)_2AlC_5H_5$ was 11%. No attempts were made to optimize the reaction.

Reaction of endo-dicyclopentadiene (IV) with triethylaluminum

Triethylaluminum, 0.18 mole, was treated with (IV), 0.6 mole, in a glass pressure bomb at 150° for 4 h. The viscous reaction product was stripped under reduced pressure to 150°. (Found: Al, 5.5. $Al(C_{12}H_{17})_3$ calcd.: Al, 5.3%.) Hydrolysis gave no ethane. The liquid hydrolysis product was distilled and analyzed (Table 1). Mass spectroscopic analysis indicated a molecular weight of 162 ($C_{12}H_{18}$ calcd.: 162).

GLC analysis (flame ionization detector, Carbowax capillary column) showed the product to consist of two compounds in a ratio 2.4/1, evidently isomers differing in the point of attachment of the ethyl group. Olefinic protons, δ 5.52 ppm, 2.0 H on the basis of $C_{12}H_{18}$ [(VI), $R = C_2H_5$]. IR bands at 3025 and 1607 cm^{-1} indicated the presence of $\geq$C–H and unsymmetrical $>$C=C$<$.

Reaction of endo-dicyclopentadiene (IV) with tri-n-butylaluminum

Tri-n-butylaluminum, 0.27 mole, and (IV), 0.79 mole, were heated at 100–130° for 5 h. After removal of unreacted starting material under reduced pressure, the viscous product was hydrolysed. Butane, 6.3. l, and a liquid product, 87 g, were obtained.

The high yield of butane indicates only 65% utilization of aluminum–carbon bonds. Separation of the liquid product by preparative GLC gave (VII) (12%) and monoolefinic hydrocarbon $C_{14}H_{22}$ (88%) (elemental analysis, Table 1). GLC analysis indicated the latter to consist of two compounds in a ratio 2.6/1. Olefinic protons, δ 5.53 ppm, 1.9 H on the basis of $C_{14}H_{22}$[(VI), R=n-C_4H_9]. IR bands at 3021 and 1605 cm^{-1} were indicative of a double bond.

TABLE 1

ANALYTICAL DATA FOR COMPOUNDS (VI)

R	Analysis found (calcd.) (%)		Mol.wt. found[a] (calcd.)	B.p. °C (mm)	Iodine number found (calcd.)
	C	H			
C_2H_5	88.80	10.60	167	82 (12)	146
	(88.90)	(11.10)	(162)		(157)
n-C_4H_9	88.38	11.62	186	82 (0.7)	132
	(88.42)	(11.56)	(190)		(133)

[a] The molecular weights were determined cryoscopically in p-bromotoluene.

^1H *NMR evidence for structure (VI)*

Integrated spectra of compounds (VI) (R=C_2H_5, R=n-C_4H_9) indicate the presence of two olefinic protons in each of the purified products. As shown in Table 2, their chemical shifts, δ 5.52-5.53 ppm, correspond closely to those assigned to the cyclopentene moiety of *endo*-dicyclopentadiene and its 5,6-dihydro derivative. No signals were observed for compounds (VI) in the region δ 5.9–6.1 ppm, which embraces assignments to olefinic protons in the bicycloheptene nucleus of the *endo*-dicyclopentadiene and in bicyclo[2.2.1]hept-2-ene and its various 2- and 7-substituted derivatives. Further evidence of the preservation of the cyclopentene moiety in compounds (VI) consists in a single-proton absorption at δ 2.95–2.98 ppm assignable to the allylic methine (C-3a) and another single proton absorption at δ 2.3–2.7 ppm assignable to the non-allylic methine (C-7a).

TABLE 2

NMR CHEMICAL SHIFTS[a] OF OLEFINIC PROTONS

Compound	Bicycloheptene nucleus	Cyclopentene moiety	Ref.
(VI), R=C_2H_5		5.52	[b]
(VI), R=n-C_4H_9		5.53	[b]
5,6-Dihydro-*endo*-dicyclopentadiene		5.50, 5.58	12
endo-Dicyclopentadiene[c]	5.92	5.45	12
3a,4,7,7a-Tetrahydroindene	5.76	5.57	[b]
Bicyclo[2.2.1]hept-2-ene (BCH)	5.92, 6.02		13
Various 2-subst. BCH	5.91–6.12		13, 14
Various 7-subst. BCH	5.91–6.07		15

[a] Ppm downfield from internal TMS. [b] Present work. [c] *endo*-3a,4,7,7a-Tetrahydro-4,7-methanoindene.

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