NEW HYDROGENATING SYSTEMS FOR IONIC HYDROGENATION

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UDC 542.941.7-128:547.592.12:547.73

The hydride ion donor in ionic hydrogenation (IH) which has become common in preparative organic chemistry is most often triethylsilane [1]. A systematic search has been undertaken for new hydrogenating systems in order to expand the scope of IH.

In the present study, we found that ethyldichlorosilane (EDCS) may be used as the hydride ion donor. EDCS is an intermediate in the synthesis of triethylsilane. The presence of halogen atoms at silicon reduces the hydride lability of the hydrogen atom. Thus, the presence of a Lewis acid capable of cleaving the Si−H bond and increasing the concentration of carbocations is required for successful IH.

Olefins, alkyl halides, trifluoroacetate derivatives of alcohols, and 2-alkylthiophenes were found to react with EDCS by the action of $AlCl_3$ or $AlBr_3$. The reaction is complete in 2 h in CH_2Cl_2 at 20-40°C. We used p-toluenesulfonic acid (TSA) as the proton donor in the hydrogenation of olefins and thiophenes. The reagent ratios, reaction conditions, and hydrogenation product yields are given in Table 1.

Table 1 shows that 1-methylcyclohexene reacts with EDCS and TSA in the presence of an equimolar amount aluminum trihalide to form the hydrogenation product, methylcyclohexene in 65-75% yield after 2 h at 40°C. The yield is not changed by increasing the temperature or reaction time. This result likely stems from olefin polymerization occurring in the presence of the aluminum halide along with the major reaction

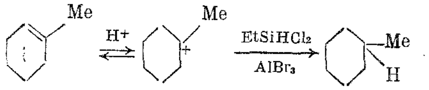

TABLE 1. Ethyldichlorosilane Hydride Ion Donor for Ionic Hydrogenation (2 h, CH_2Cl_2)

Substrate	$AlHal_3$	Reagent and reagent/substrate molar ratio			T., °C	Hydrogenation product	Yield, %
		EDCS	$AlHal_3$	TSA			
1-Methylcyclohexene	$AlBr_3$	2	1	1	40	Methylcyclohexane	75
	$AlCl_3$	2	1	1	40	"	65
Cyclohexene	$AlBr_3$	2	1	1	40	Cyclohexane	23
	$AlCl_3$	2	1	1	40	"	17
1-Chloro-1-methylcyclohexane	$AlBr_3$	2	0,25	0	20	Methylcyclohexane	92
	$AlCl_3$	2	0,25	0	20	"	94
Chlorocyclohexane	$AlBr_3$	2	0.25	0	20	Cyclohexane	45
	$AlCl_3$	2	0,25	0	20	"	40
Trifluoroacetate of 1-methylcyclohexane-1-ol	$AlBr_3$	2	0.5	0	20	Methylcyclohexane	81
	"	2	0,25	0	40	"	88
	$AlCl_3$	2	0,5	0	40	"	84
Trifluoroacetate of cyclohexanol	$AlBr_3$	2	0.5	0	20	Cyclohexane	10
	"	2	1	0	20	"	69
	$AlCl_3$	2	1	0	20	"	50
2-Ethylthiophene	$AlBr_3$	6	3	3	80*	2-Ethylthiophane	75

*10 h.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1322-1326, June, 1982. Original article submitted August 5, 1981.

TABLE 2. Aromatic Hydrocarbon Hydride Ion Donors in the Ionic Hydrogenation at 20°C in CH_2Cl_2

H-donor	Substrate	$AlHal_3$	Reagent and reagent/substrate ratio			Time, h	Hydrogenation product	Yield, %.
			H-donor	$AlHal_3$	TSA			
Cumene	1-Methylcyclohexene	$AlBr_3$	3	1	1	2*	Methylcyclohexane	34
	Trifluoroacetate of 1-methylcyclohexanol	$AlBr_3$	2	1	0	3	"	60
		$AlCl_3$	2	1	0	3		45
	1-Chloro-1-methylcyclohexane	$AlCl_3$	2	1	0	3	"	48
Dicumylmethane	1-Methylcyclohexene	$AlBr_3$	3	1	1	1*	"	53
		$AlBr_3$	3	1	0	2		40
		$AlCl_3$	3	1	2	2*		40
	Trifluoroacetate of 1-methylcyclohexanol	$AlBr_3$	2	1	0	2	"	80
		$AlCl_3$	2	1	0	3		77
	1-Chloro-1-methylcyclohexane	$AlBr_3$	2	1	0	2	"	80
		$AlCl_3$	2	1	0	3		80
p-Cymene	1-Methylcyclohexene	$AlCl_3$	2	2	1†	3.5	"	40
	Cyclohexene	$AlCl_3$	2	1	0,5†	3,5	Cyclohexane	10
1,3,5-Triisopropylbenzene	1-Methylcyclohexene	$AlCl_3$	2	1	0.5†	3.5	Methylcyclohexane	75
	Cyclohexene	$AlCl_3$	2	1	0.5†	3.5	Cyclohexane	8

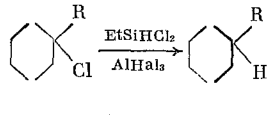
*40 °C.

†Gustavson complex $3PhCH_3 \cdot 2AlCl_3 \cdot HCl$.

High selectivity is one of the major features observed in IH using the $Et_3SiH-CF_3CO_2H$ system. Only compounds which form relatively stable tertiary carbocations enter the reaction. The concentration of these carbocations must be sufficient for reaction with the hydride ion donor [1]. Such selectivity is found also using the EDCS–TSA–$AlHal_3$ system, although to a reduced extent. Thus, an unbranched olefin such as cyclohexene is hydrogenated under the conditions described above but the yield of hydrogenation product does not exceed 25%. A similar drop in selectivity was observed previously in the hydrogenation of olefins by the $Et_3SiH-HCl-AlCl_3$ system [2]. The presence of a strong Lewis acid apparently so increases the concentration of the secondary carbocations formed under the reaction conditions from unbranched olefins that they become capable of completing the hydrogenation process. Thus, use of hydrogenation systems containing a Lewis acid permit an expansion of the scope of applicability of the IH method.

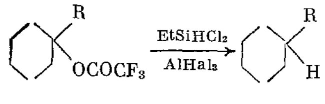
Use of EDCS in the presence of an aluminum halide gave hydrogenolysis of alkyl halides leading to saturated hydrocarbons. Thus, the tertiary alkyl halide, 1-chloro-1-methylcyclohexane is converted by EDCS in the presence of an aluminum halide to methyl cyclohexane with yields close to quantitative. The activity of $AlCl_3$ and $AlBr_3$ are virtually the same in this reaction (see Table 1).

The secondary alkyl halide, chlorocyclohexane is also hydrogenated by EDCS but the cyclohexane yield under the above conditions does not exceed 45%.



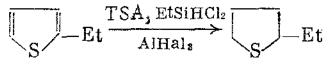
R = H, CH_3

Trifluoroacetate derivatives of alcohols readily react with EDCS in the presence of an aluminum halide. The trifluoroacetate group is replaced by hydrogen and a saturated hydrocarbon is formed. Thus, the trifluoroacetate derivative of 1-methyl-1-cyclohexanol in the presence of a catalytic amount of aluminum halide is converted to methylcyclohexane in 80–88% yield depending on the reaction conditions (see Table 1). The trifluoroacetate derivative of the secondary alcohol, cyclohexanol, is hydrogenated by EDCS to cyclohexane though good yields require the presence of an equimolar amount of aluminum halide.



R = H, CH_3

Great interest lies in our discovery of the possible use of EDCS for the hydrogenation of thiophene derivatives. The reaction is carried out at 80°C and leads to the corresponding thiophane in high yields (see Table 1).



Ipatieff et al. [3] reported that the alkylation of alkylbenzenes by olefins in sulfuric or hydrofluoric acid gives saturated hydrocarbons. These authors attributed this finding to the transfer of a hydride ion from the alkylbenzene to the carbocation formed from the olefin under the reaction conditions.

We have found that aromatic hydrocarbons with a branched alkyl substituent in the presence of an aluminum halide also may be used as hydride ion donors in the IH reaction and hydrogenolysis. Cumene, dicumylmethane, p-cymene, and 1,3,5-triisopropylbenzene were used for this study. The reaction was run at 20-40°C for 2-3.5 h in Ch_2Cl_2 or toluene. In the case of olefin hydrogenation, TSA or gaseous HCl was used as the proton donor. The results are given in Table 2 which shows that the best hydride ion donor for olefin hydrogenation is triisopropylbenzene. Thus, use of this donor for 1-methylcyclohexene gives methylcyclohexane in 75% yield. Use of dicumylmethane gives methylcyclohexane from 1-methylcyclohexene in 55% yield.

Olefin hydrogenation proceeds more selectively when using C–H hydride ion donors than in the case of EDCS. For example, cyclohexene forms cyclohexane under the conditions studied in 10% yield.

It is interesting to note that olefin hydrogenation also proceeds in the absence of a protic acid, though in yields not exceeding 40%. In this case, the proton donor is probably the carbocation formed from the aromatic hydrocarbon with branched hydrocarbon chain or loss of a hydride ion from this compound.

As in the case of Et_3SiH and Et_3SiHCl_2, the use of cumene and the other aromatic hydrocarbons studied in the presence of an aluminum halide permits replacement of the trifluoroacetate group in trifluoroacetate derivatives of alcohols and of the halogen atom in alkyl halides by hydrogen. The reaction leads to the formation of saturated hydrocarbons in 60-80% yields (see Table 2).

Thus, aromatic hydrocarbons with a tertiary carbon atom in their side-chain in the presence of aluminum halide may be used to obtain saturated hydrocarbons from olefins, alkyl halides, and trifluoroacetate derivatives of alcohols.

EXPERIMENTAL

A sample of 1-methylcyclohexene was prepared from cyclohexanone according to Zelinsky [4] and a sample of 1-chloro-1-methylcyclohexane was obtained from 1-methylcyclohexene was prepared according to Mousseron et al. [5]. The trifluoroacetate derivative of 1-methylcyclohexanol was prepared according to our previous procedure [6]. A sample of ethylthiophene was prepared by the reduction of acetothienone [7]. A sample of $AlCl_3$ was purified by sublimation in an argon atmosphere.

The qualitative and quantitative analyses of the reaction mixtures were carried out by gas-liquid chromatography on a Khrom-3 chromatograph with a katharometer detector, and helium gas carrier.

Stainless steel columns were used: 1) 3.5 m × 6 mm packed with 10% PEGA on 0.2-0.3 mm BLK Ribosorb, 2) 2.5 m × 6 mm packed with 5% SE-30 on 0.16-0.22 mm Chromatone N-AW-HMDS, and 3) 2.5 m × 6 mm packed with 15% carbowax 20M on 0.16-0.20 mm Chromatone N-AW-DMCS. The temperature was 65-130°C. The hydrogenation products were identified relative to known samples. The product yields were found using an internal standard with correction factors. Octane, nonane, and tridecane served as internal standards. The hydrogenation was carried out by one of the methods described below. The reagent ratios and reaction conditions are given in Tables 1 and 2.

Method A. The hydrogenation of 1-chloro-1-methylcyclohexane by EDCS in the presence of $AlCl_3$. A sample of 0.170 g substrate was placed in a flask equipped with a reflux condenser. The flask was cooled with dry ice–acetone and 0.332 g EDCS, 2.5 ml CH_2Cl_2, and 0.043 g $AlCl_3$ were added. The cooling was stopped and the reaction mixture was maintained for 2 h at ~20°C with magnetic stirring. Then, the mixture was decomposed by water with cooling and the internal standard was added. The aqueous layer was removed and extracted with CH_2Cl_2. The combined organic layer was dried with $MgSO_4$ and analyzed. The methylcyclohexane yield was 94%.

Method B. Hydrogenation of 2-ethylthiophene by EDCS and TSA in the presence of $AlBr_3$. A sample of 0.112 g ethylthiophene was added to an ampule cooled with dry ice–acetone and 0.772 g EDCS and 0.515 g TSA were added. Then, 3 ml CH_2Cl_2 and 0.798 g $AlBr_3$ were introduced. The ampule was sealed, placed in a controlled-temperature bath, and maintained for 8 h at 80°C. Then, the ampule was cooled, opened, and the mixture was decomposed with water using dry ice–acetone cooling. The internal standard (tridecane) was then added. Further work-up as described for Method A gave a 75% yield of 2-ethylthiophene.

Method C. Hydrogenation of 1-methylcyclohexene by 1,3,5-triisopropylbenzene and Gustavson complex. A sample of 0.935 g $AlCl_3$ was added to a two-necked flask equipped with a reflux condenser and gas inlet tube and then 1.1 ml (10.6 mmole) toluene was added. HCl was introduced at 20°C and stirred for 30 min. Then, the flask was cooled with dry ice–acetone and 0.675 g 1-methylcyclohexene, 0.868 g triisopropylbenzene, and 3 ml toluene were added. The mixture was maintained for 3.5 h at ~20°C. The flask was then cooled, the mixture was decomposed with water, and the internal standard (nonane) was added. Further treatment as described in Method A yielded 85% methylcyclohexane.

CONCLUSIONS

Ethyldichlorosilane and alkylisopropylbenzenes in the presence of aluminum halides are hydride ion donors in the ionic hydrogenation of olefins, alkyl halides, and trifluoroacetate derivatives of alcohols.

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NEW DATA ON THE STEREOCHEMISTRY OF THE REARRANGEMENT OF THE CARANE SYSTEM TO THE 1-METHYL-4-ISOPROPYLBICYCLO[3.1.0]HEXANE SYSTEM

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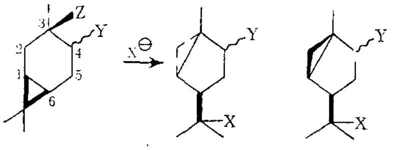
UDC 541.63:542.952.1:547.597.1

3,4-Disubstituted caranes (I) in a number of reactions undergo rearrangement with intramolecular 1,3-transannular participation of the cyclopropane ring (CPR). The steric precondition for the rearrangement is cis arrangement of the CPR and the leaving group at the C-3 reaction site [1]. As result, derivatives of 1-methyl-4-isopropylbicyclo[3.1.0]hexanes are formed:



(I) (II) (III)

Two stereochemical pathways for the rearrangement leading to products with different stereochemistry may be proposed: a) retention of configuration of the reaction site leads to the formation of products with trans orientation of the reformed CPR and isopropyl group in (II) and b) inversion of configuration of the reaction site

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1327-1333, June, 1982. Original article submitted July 16, 1981.

0568-5230/82/3106-1182$07.50