

Addition Reaction of some Rare-earth Metals to Unsaturated Compounds in Ethers

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Abstract

The reaction of rare-earth metals such as cerium, neodymium, samarium and ytterbium with unsaturated hydrocarbons and aromatic ketones having various electronic affinities was investigated. Ytterbium is the most reactive. The cleavage of the carbon-carbon bonds and carbon-oxygen bonds by ytterbium and samarium is also described.

Introduction

In two preceding papers [1 - 2] we have shown that rare-earth metals, in a similar way to alkali and alkaline earth metals, add to aromatic ketones or hydrocarbons in ether to give intensely colored insoluble compounds which have been characterized by reaction with some electrophiles.

In this paper we describe an attempt to make a semiquantitative classification of the reactivity of cerium, neodymium, samarium, ytterbium and some other metals with respect to various unsaturated compounds and to correlate these reactivities with the reduction potentials of organic compounds.

The interaction of unsaturated hydrocarbons with lanthanides had previously been investigated by other techniques: Nd(butadiene)₃ and Sm(butadiene)₃ by metal vaporization [3], (COT)₂Ce* and (COT)₃Ce₂ by reacting COT with Ce(OiPr)₄ and AlEt₃ [4], (COT)Yb by reacting the metal in liquid ammonia [5]; (COT)Sm, starting from SmI₂ and the potassium salt of COT [6]; Ln(COT)2THF Ln(COT)₂ Ln = Nd, Ce, by metal vaporization [7]. More recently naphthalene was reacted with thin films of various metals, obtained by vaporization [8].

Experimental

Two mmol of the metal powder (Aldrich; 40 mesh) were transferred by glove box into a Schlenk flask fitted with a serum cap and containing a magnetic bar. The conditioning oil was eventually washed out three times with 1 ml of pentane. The metal was

then activated for 2 h at room temperature with 1 ml of a solution containing 0.1 mmol of 1,2-diiodoethane in 1,2-dimethoxyethane (DME). Then the flask was cooled to -20 °C and filled with 0.5 mmol of the organic compound in 4 ml of DME (metal/organic compound 4:1). Following an additional 2 h reaction time, the flask was warmed to room temperature and the mixture stirred overnight. The adduct was then protolyzed and the organic part was isolated, analyzed by ¹H NMR and VPC or HPLC with an internal standard to determine quantitatively the conversion of the starting material.

Results and Discussion

Table 1 shows various organic substrates we selected to cover a wide range of electron affinities, but with small differences between each compound and which we have arranged by decreasing half-wave reduction potentials for the first electron [9]. On the other hand, among the fourteen lanthanides we chose ytterbium because of its well-known reducing power and its capacity for being dissolved in liquid ammonia [10], samarium because of its common use in organic synthesis [11] and cerium and neodymium as being representative of the earlier lanthanides (and for their low cost).

The reactivities are defined as the conversion rate of the starting materials after a standard procedure (see 'Experimental'). Due to the undefined state of the metallic surface and to poor stirring of the reaction medium, some variations in the conversions are frequently observed. Hence our results are more conveniently represented by 'stars'

With a few exceptions, the chemical reduction by lanthanides fits into standard electrochemical reduction potentials for the first half-wave. This is reminiscent of the quantitative reduction of aromatic hydrocarbons by sodium-biphenyl as reported by Hoijtink *et al.* [12], but in our case we are far from the standard conditions (insolubility of the adducts).

After protolysis most of the hydrocarbons considered here produce dihydroderivatives (i.e. dianionic intermediate species) as can be observed by reaction with alkali metals or by polarographic

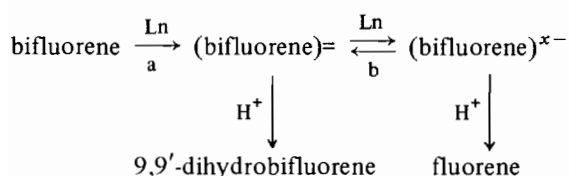
*COT: cyclooctatetraene.

TABLE 1. Rare-earth metals and electrochemical series of some organic compounds

Run	Organic substrates	First half-wave reduction potential (V) ^a	Rare-earth metals ^b				Main products
			Ce	Nd	Sm	Yb	
1	1,3-Butadiene	2.4			0	*	1- and 2-butenes
2	Pyridine	2.59			0		
3	Naphthalene	2.50			0	0	
4	Phenanthrene	2.44			0	*	9,10-dihydrophenanthrene
5	1,1-Diphenylethylene	2.30			0	*	1,1-diphenylethane
6	Chrysene	2.27			0	*	5,6-dihydrochrysene
7	Fluorene	2.12			0		
8	Pyrene	2.06			0		
9	Tetraphenylethylene	2.02			**		tetraphenylethane
10	1,4-Diphenylbutadiene	2.00	*	0	**	**	1,4-diphenylbutene (mixed isomers)
11	Anthracene	1.94	*	0	**	**	9,10-dihydroanthracene
12	Benzophenone	1.79	**	**	**	**	see ref. 2
13	Cyclooctatetraene	1.62	**	0	**	**	
14	Tetracyclene	1.49			*		di- and tetrahydrodecalene
15	Chalcone	1.44		**	**	**	see ref. 2
16	Benzil	1.16		*	*	*	see ref. 2
17	Δ 9:9'-Bifluorene	1.00		*	**	**	see Table 2
18	Fluorenone	0.87		**	**	**	see ref. 2

^aStandard calomel electrode. ^b0, no conversion and no coloration; *, conversion rate = 0.05 to 0.95; **, conversion rate > 0.95.

reduction. However in our standard conditions, reacting Δ 9:9'-bifluorene (bifluorene) with samarium or ytterbium provides not only 9,9'-dihydrobifluorene but also fluorene which is the product of the reductive cleavage of the carbon-carbon bonds. The formation of this latter product is observed only in the presence of an excess of metal (Table 2, exp. 2 and 3). In experiment 3 samarium and bifluorene were first reacted in a 4:1 molar ratio for one day. Then a sufficient amount of bifluorene was added to obtain a 1:2 molar ratio. After hydrolysis a distribution similar to the one in experiment 2 was observed. Thus step 'b', Scheme 1 is reversible.



(Ln = Sm, Yb)

Scheme 1.

Table 2 also gives the behavior of bifluorene with gadolinium and neodymium (quite similar results), erbium (no reaction) and magnesium as a reference. In our standard conditions none of these metals causes the cleavage of the double bonds.

As described previously [2] ketones produce mixtures of pinacols (one electron reduction) and alcohols (two electron reduction). However samarium and ytterbium, under standard conditions, also pro-

TABLE 2. Reduction of Δ 9:9'-bifluorene by some rare-earth metals

Run	Metal	Metal:hydrocarbon molar ratio	Products (wt.%) (NMR)		
			BF ^a	DHBF ^b	Fluorene
1	Yb	4:1		85	15
2	Sm	1:2	58	42	
3	Sm	4:1		80	20
		then 1:2	70	30	
4	Nd	4:1	68	32	
5	Gd	4:1	60	40	
6	Er	4:1	100		
7	Mg	4:1	30	70	

^aBF = bifluorene.

^bDHBF = dihydrobifluorene.

mote the cleavage of the oxygen-carbon bonds of ketones having low reduction potential, such as fluorenone and benzil. In this latter case 1,2-diphenylethane, the product of a formally eight-electron reduction forms. However the reactivities based on conversion rates, as shown in Table 1, have to be considered carefully. Otherwise they could depend on the reduction state of the substrate, therefore on the metal:substrate molar ratio.

A common intermediate is probably responsible for the cleavage of the carbon-carbon and carbon-oxygen bonds.

In any case, ytterbium proves to be the most powerful reducing agent, followed by samarium. The

reactivity of other lanthanides clearly depends on the organic substrate, i.e. hydrocarbons or ketones and must be related to its capacity, or not, to stabilize a one-electron reduction state; it depends also on the stable oxidation states of the metals.

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