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Uranium iodides as catalysts for Diels–Alder reactions

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Abstract

Uranium triiodide is found to be an efficient Lewis acid catalyst for various Diels–Alder reactions which are performed in mild conditions and with low amounts of catalysts. The replacement of an iodide by a dihydrobis(pyrazolyl)borate ligand does not increase activity or selectivity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

By the use of Lewis acids as catalysts, Diels–Alder reactions are performed in higher rates and with better selectivities than thermal reactions [1]. Besides the metal halides commonly used as promotors, it has been recently reported that several metal triflates including transition metals [2,3], bismuth [4], lanthanides or scandium triflates and bis((perfluoroalkyl)-sulfonyl)amides [5–8] possess high activity for the catalysis of Diels–Alder reactions. In the course of our investigations, we have found that lanthanide iodides as Lewis acids catalyze a wide range of reactions [9]. Samarium diiodide is a precatalyst especially for reactions such as enolisation of carbonyl coumpounds [10] or Mukaiyama Michael aldol tandem reactions [11] which have not been described with lanthanide triflates.

With the aim of examining the influence of the low valency of the precatalyst on catalytic reactions, we had previously undertaken a comparative study of divalent samarium iodide and trivalent uranium derivatives [12,13]. We showed that UI_3 and $U(OAr)_3$ [$Ar = 2,4,6$-$Me_3C_6H_2$] can be used for the catalysis of Mukaiyama aldol reactions as well as samarium diiodide [14]. We now report that trivalent uranium iodides are the precursors of catalysts for a variety of Diels–Alder reactions as we precedently described for samarium diiodide [15].

2. Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. THF was distilled from sodium benzophenone ketyl and degassed im-

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mediately prior to use. CH_2Cl_2 was distilled from CaH_2 and degassed immediately prior to use. All the substrates were distilled and degassed before use. Brucker AM 250, and AM 200 NMR spectrometers, operating at 250 and 200 MHz were used for the NMR spectra.

2.1. Preparation of catalysts

$UI_3(THF)_4$ has been prepared by reacting freshly amalgamated «oxide-free» uranium turnings with freshly sublimed iodine in THF [16]. The addition of iodine has to be done slowly and the temperature must be maintained at −10°C, until all the iodine is added, to avoid the ring opening of the THF [16–18]. After some time, the mixture is warmed up to room temperature and the reaction progresses for 10–12 h [16]. $[U\{H_2B(3\text{-tBu,5Me-pz})_2\}I_2(THF)_2]$ has been obtained by reacting $UI_3(THF)_4$ with the potassium salt of the ligand in THF, as previously described [19].

2.2. General procedure for catalytic reactions

To a suspension of the catalyst in CH_2Cl_2 (10 ml) were successively added 6 mmol of cyclopentadiene and 2 mmol of the dienophile. The reaction mixture was stirred at room temperature and the reaction time was determined by GC using cyclododecane as an internal standard. The reaction mixture was hydrolyzed, extracted with ether and dried over $MgSO_4$. After evaporation of the solvent the products were purified by chromatography on silica gel with pentane/ether mixtures.

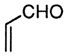
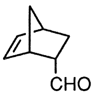
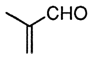
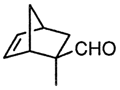
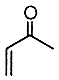
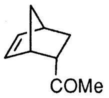
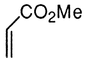
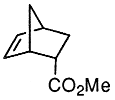
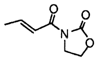
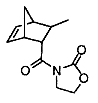
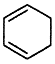
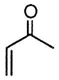
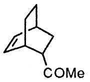
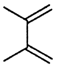
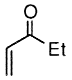
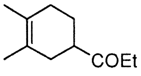
3. Results

We have found that $UI_3(THF)_4$ **1** [16] catalyzes various cycloaddition reactions of cyclic and acyclic dienes with α,β-unsaturated carbonyl compounds as dienophiles. Reactions are performed in CH_2Cl_2 or THF at room temperature and lead to the adducts in moderate to good yields as indicated in Table 1. The catalytic activity of $UI_2L(THF)_2$ ($L = [H_2B(3\text{-}t\text{-Bu,5-Me-pz})_2]$) **2** [19] is also examined in some cases.

The cycloadditions of cyclopentadiene with α,β-unsaturated aldehydes or ketones are very rapid in CH_2Cl_2 and THF with both catalysts **1** and **2** (entries 1–9). With $UI_3(THF)_4$ a very low catalyst ratio (1 mol%) can be used without decreasing the rate and the yield of the reactions. The cycloaddition of a less reactive dienophile such as methyl acrylate with cyclopentadiene is much faster in the non-coordinating solvent (entries 10 and 11). The selectivity in adduct *endo* is higher in CH_2Cl_2 than in THF (see entries 7, 8 and 10, 11). With less reactive dienes as cyclohexadiene and 2,3-dimethylbutadiene we have only tested the activity of the catalysts in methylene chloride: by the use of 5 mol% $UI_3(THF)_4$ the adducts were isolated in moderate yields. Substitution of one iodide by the dihydrobis(polypyrazolyl)borate ligand leads to a decrease in the activity of the uranium catalyst. For the cycloadditions of methacrolein or methylvinyl ketone on cyclopentadiene, the adducts were obtained in methylene choride with similar rates, yields, and selectivity with both catalysts (compare entries 4, 6 and 7, 9). Yet for the reaction of cyclohexadiene with methyl vinyl ketone, using 5 mol% of catalyst **2**, only traces of adducts were obtained (entry 14) as for the reaction of 2,3-dimethylbutadiene with ethyl vinyl ketone (entry 16).

Recently, Garrigues et al. explored the activity of bismuth triflate and bismuth chloride as Diels–Alder catalysts [4] and compared their activity to those of other Lewis acids such as $Sc(OTf)_3$, $Yb(fod)_3$, $[TiCp_2^*(OTf)_2(H_2O)]$ and $[ZrCp_2^*(OTf)_2(H_2O)]$. Bismuth triflate is the most efficient; as in all the reactions, 1 mol% of catalyst is used and the reactions are the fastest. By comparison, $UI_3(THF)_4$ is less active than bismuth triflate but shows an activity similar to that of other catalyts indicated above or to a cationic zirconocene complex [20] and even higher in the case of the Diels–Alder reactions

Table 1
Diels–Alder reactions catalyzed by uranium iodides

Entry	Diene	Dienophile	Catalyst[a]	Solvent	t (h)	Major product	*Endo*/*exo*[d]	Yield
1			$UI_3(THF)_4$[a]	CH_2Cl_2	0.08		73/27	95[e]
2			$UI_3(THF)_4$[b]	CH_2Cl_2	0.08		72/28	86[f]
3			$UI_3(THF)_4$[a]	THF	0.08		70/30	100[e]
4			$UI_3(THF)_4$[b]	CH_2Cl_2	0.08		14/86	67[f]
5			$UI_3(THF)_4$[a]	THF	0.08		10/90	85[e]
6			$UI_2L(THF)_2$[a,c]	CH_2Cl_2	0.16		11/89	63[e]
7			$UI_3(THF)_4$[b]	CH_2Cl_2	0.08		82/18	61[f]
8			$UI_3(THF)_4$[a]	THF	0.08		70/30	64[f]
9			$UI_2L(THF)_2$[a,c]	CH_2Cl_2	0.08		84/16	75[e]
10			$UI_3(THF)_4$[a]	CH_2Cl_2	1		95/5	77[f]
11			$UI_3(THF)_4$[a]	THF	14		78/22	79[e]
12			$UI_3(THF)_4$[b]	CH_2Cl_2	4		87/13	52[f]
13			$UI_3(THF)_4$[a]	CH_2Cl_2	2		100/0	70[e]
14			$UI_2L(THF)_2$[a,c]	CH_2Cl_2	20			<10[e]
15			$UI_3(THF)_4$[a]	CH_2Cl_2	4			58[f]
16			$UI_2L(THF)_2$[a,c]	CH_2Cl_2	20			<10[e]

[a] 5% mol catalyst. [b] 1% mol catalyst. [c] $L = [H_2B(3tBu,5Me - pz)^2]$. [d] Ratio determined by GC/MS. [e] Yields % based on weight and ^1H NMR of the crude product. [f] Yields % after chromatography.

of cyclopentadiene, which are very rapidly performed with 1 mol% of $UI_3(THF)_4$.

It is worth noting that $UI_3(THF)_4$ is far more efficient than lanthanide triflates employed in

10–20 mol% for the catalysis of the addition of cyclopentadiene on methyl vinyl ketone [5]. The reactions of cyclopentadiene with *N*-crotonoyloxazolidinone catalyzed by lanthanum, yttrium or ytterbium triflates coordinated by tetraglyme [6] are much slower (21 h–60 h) than using **1** (3 h). The comparison of trivalent uranium and divalent samarium iodides indicates a higher activity for the former. In the same conditions, reactions are faster with $UI_3(THF)_4$ than with $SmI_2(THF)_2$: 1 h vs. 24 h for the reaction of methyl acrylate with cyclopentadiene [15] and 4 h vs. 24 h for the reaction of *N*-crotonoyloxazolidinone with cyclopentadiene [21].

The catalytic activity of uranium triiodide for hetero-Diels–Alder reactions has also been examined. In presence of 5 mol% of $UI_3(THF)_4$, the addition products of a silyloxydiene (Danishefsky diene) on an aldehyde or an imine are obtained at room temperature within a short reaction time. The desired pyrone is obtained after acid treatment in the case of benzaldehyde and isolated directly from the reaction mixture for the imine. For the aza Diels–Alder reaction, uranium triiodide is more active than ytterbium triflate, which is used in higher amounts (10%) and with a longer reaction time [22], but less active than $Bi(OTf)_3$ [23], or $In(OTf)_3$, whose high activity for hetero Diels–Alder reactions has been recently reported [24].

We think that the active species is tetravalent as a change of colour is observed after the addition of the dienophile to $UI_3(THF)_4$ in THF and the colour is maintained until the end of the reaction. When the catalytic reaction was studied in CH_2Cl_2, the active species is also U(IV), but in this case the U(IV) is formed due to an oxidative addition of the solvent. The green colour of the reaction mixture indicates the presence of tetravalent uranium, allowing us to conclude that uranium triiodide is only a precatalyst as we previously found for samarium diiodide. The evaluation of UI_4 as a catalyst in this type of reactions would be interesting and may clarify the mechanism. However, the preparation of this material is hard [25,26] and its solubility is limited in the most common solvents (insoluble in CH_2Cl_2 and soluble in THF with formation of iodobutoxides) [17,18].

In the case of Mukaiyama aldol reactions catalyzed by uranium triiodide, we have found that the rates of the reactions in THF were higher than in CH_2Cl_2 [12]. These differences in the effect of the solvent for aldol and Diels–Alder reactions are in fact explained by a difference in the structure of the catalyst. The trivalent uranium iodide used for the aldol reactions of formula UI_3 was prepared by a high temperature method and had no coordinated solvent [12]. It is probably in a polymeric form and is less active in a non-coordinating solvent. Differently, $UI_3(THF)_4$ prepared in solution is monomeric and more active in CH_2Cl_2.

4. Conclusion

$UI_3(THF)_4$ is an efficient Lewis acid catalyst for Diels–Alder reactions since short reaction times and small amounts of catalyst are required (1 mol%). Moreover, it possesses a higher activity than samarium diiodide and other lanthanide-based catalysts. The use of the complex $[UH_2B(3\text{-}t\text{-Bu,5-Me-pz})_2I_2(THF)_2]$ has shown that the replacement of one iodide by a dihydrobis(pyrazolyl)borate decreases the activity and does not increase the selectivity.

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