ORGANIC
LETTERS

2001
Vol. 3, No. 15
2375−2377

$LiCB_{11}Me_{12}$: A Catalyst for Pericyclic Rearrangements

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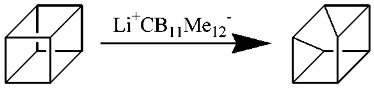
Received May 28, 2001

ABSTRACT



Benzene and 1,2-dichloroethane solutions of the Li^+ salt of the weakly coordinating anion $CB_{11}Me_{12}^-$ catalyze the rearrangement of cubane to cuneane, quadricyclane to norbornadiene, basketene to Nenitzescu's hydrocarbon, and diademane to triquinacene. The Claisen rearrangement of phenyl allyl ether is also strongly accelerated.

The lithium cation has been long recognized as an effective catalyst for pericyclic reactions. The catalysis of Diels−Alder reactions by solutions of $LiClO_4$ in Et_2O has received the most attention,[1−6] but the explosive nature of this reaction medium has been a concern. Lithium salts of many other anions have been used successfully as Lewis acid catalysts, including very weakly interacting ones, such as $LiCo(B_9C_2H_{11})_2$,[7] $LiB(Arf)_4$,[8] and $LiAl[(OC)Ph(CF_3)_2]_4$.[9] We now report remarkably high rates of rearrangements in solutions of $LiCB_{11}Me_{12}$ in benzene and 1,2-dichloroethane. Salts of the parent $CB_{11}H_{12}^-$ anion are easily prepared on large scale in two steps from $NaBH_4$, BF_3, and $CHCl_3$,[10] and its permethylation is facile and nearly quantitative.[11,12] The $CB_{11}Me_{12}^-$ salts of Li^+ and other cations, including chiral ones, therefore promise to be practical catalysts.

The $CB_{11}Me_{12}^-$ anion[11] is weakly coordinating and very lipophilic; this remarkable property can be further enhanced by the introduction of longer alkyl chains.[13] The lithium salt can be easily prepared[14] and dried by heating to 180 °C under reduced pressure. Under benchtop conditions, a saturated (300 g/L, 1.1 M) solution of $LiCB_{11}Me_{12}$ in benzene is

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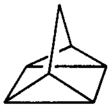
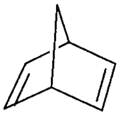
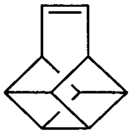
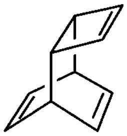
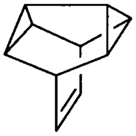
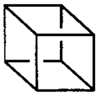
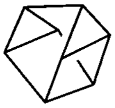
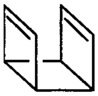
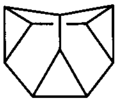
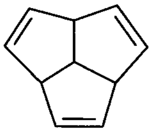
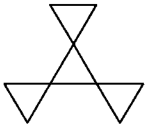
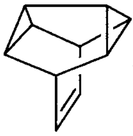
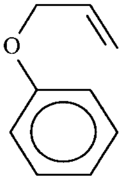
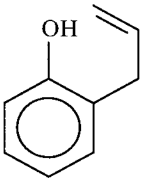
(14) By partitioning a solution of $CsCB_{11}Me_{12}$ in a 70/30 Et_2O/acetone mixture (10 g/L) against an aqueous solution of LiCl (15%). Quantitative conversion and yield are obtained upon 3 × 3 countercurrent extraction: three separate volumes of the organic phase (A, B, and C) are partitioned in five steps against three separate volumes of the aqueous phase (1, 2, 3): (i) C, B, A/1, 2, 3; (ii) C, B/1; A/2; 3; (iii) C/1, B/2, A/3; (iv) 1, C/2, B/3, A.; (v) 1, 2, C/3, B, A, where only the volumes joined by a slash are partitioned. The combined product-containing ether phases are evaporated to dryness, and the product is then dissolved in fresh, dry 70/30 Et_2O/acetone, leaving the insoluble salts behind.

10.1021/ol0161864 CCC: $20.00

Table 1. Some Reactions Catalyzed by $LiCB_{11}Me_{12}$[a]

reactant	$LiCB_{11}Me_{12}$		other examples	
	product	conditions, $t_{½}$	product, if any	conditions, $t_{½}$
		satd., C_6D_6,[b] 11 min satd., C_6D_6,[c] 100 h		5 M $LiClO_4$, Et_2O, 3 h
		dil., C_6D_6,[c] 15 h dil., 1,2-$C_2D_4Cl_2$,[c] 4.2 h		no cat., C_6D_6, 154 °C, 4 h
 [d]		satd., C_6D_6,[b] 90 °C, 6 h		Ag^+ [e]
		dil., 1,2-$C_2D_4Cl_2$,[c], 55 °C, 28 h		
 [f]	 [g]	satd., C_6D_6, 8 h[b]		Rh^+ gives diene Ag^+ gives cuneane[h]
		dil., 1,2-$C_2D_4Cl_2$,[c], 21 h		
 [i]		dil., 1,2-$C_2D_4Cl_2$,[c], 2.2 h		Ag^+ or H^+ [j]
		satd., C_6D_6,[b] < 5 min		
 [k]	no reaction	dil., 1,2-$C_2D_4Cl_2$,[c], 60 °C		
 [i]	no reaction	satd., C_6D_6,[b]		
		satd., C_6D_6,[b] 67 °C, 21 h[c]		no cat., 200 °C required
		dil., 1,2-$C_2D_4Cl_2$,[c] 75 °C, no reaction		5 M, $LiClO_4$, Et_2O, 67 °C, no reaction

[a] At 25 °C unless otherwise specified. $LiCB_{11}Me_{12}$ concentration: satd. = 300 g/L, dil. =10 g/L. Reactions were monitored by ^1H NMR and quantitated by integration. [b] Benchtop conditions. [c] Anhydrous conditions. [d] Nelsen, S. F.; Wolff, J. J.; Chang, H.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 7882. [e] Dauben, W. G.; Schallhorn, C. H.; Whalen, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 1446. Paquette, L. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 2584. [f] Eaton, P. E.; Cole, T. W. Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962, 3157. Eaton, P. E.; Nordari, N.; Tsanaktsidis, J.; Upadhyaya, S. *Synthesis* **1995**, 501. [g] Plus ~20% of an unidentified polymer. [h] Eaton, P. E.; Cassar, L.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 6367. Eaton, P. E.; Cassar, L.; Hudson, R. A.; Hwang, D. R. *J. Org. Chem.* **1976**, *41*, 1445. [i] Kaufmann, D.; Schallner, O.; Meyer, L.-U.; Fick, H.-H.; de Meijere, A. *Chem. Ber.* **1983**, *116*, 1377. [j] de Meijere, A.; Kaufmann, D.; Schallner, O. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 417. [k] Fitjer, L.; Conia, J.-M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 761. Beckhaus, H.-D.; Rüchardt, C.; Kozhushkov, S. I.; Belov, V. N.; Verevkin, S. P.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 11854 and references therein.

sufficiently electrically conducting to perform cyclic voltammetric measurements,[15] implying the presence of benzene-solvated dissociated Li^+ ions. The nature of the solvation is hinted at by the π-face interaction between Li^+ and an aromatic ring in the crystal of $LiCB_{11}Me_{12}$·toluene.[16] Upon dilution with benzene, this ionic liquid separates into two immiscible phases, one highly concentrated and conducting, the other dilute and nonconducting.[17]

It appeared to us that in this solution Li^+ ions would be even more active than those solvated by ether, regardless of which view[5,18] of the mechanism for catalysis by Li^+ is adopted. Indeed, at 67 °C under benchtop conditions, the

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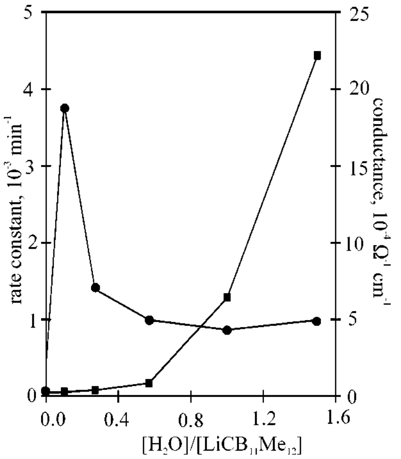

Figure 1. Rate constant (●) of the quadricyclane to norbornadiene rearrangement and conductance (■) as a function of water content in benzene saturated with $LiCB_{11}Me_{12}$.

Claisen rearrangement of phenyl allyl ether in a saturated benzene solution of $LiCB_{11}Me_{12}$ proceeded with a half-life of 21 h, but no reaction was detected in 5 M $LiClO_4/Et_2O$. The uncatalyzed reaction requires 200 °C.

This result prompted us to examine the rearrangement of several strained hydrocarbons devoid of any specific Lewis basic sites. Under benchtop conditions, most rearranged in saturated $LiCB_{11}Me_{12}/C_6H_6$ with remarkable ease (Table 1). The room-temperature isomerizations of quadricyclane to norbornadiene, of cubane to cuneane, and of diademane to triquinacene are particularly striking.

In the absence of special precautions, all solutions undoubtedly contained small amounts of water. These promote the catalysis strongly, and the half-lives listed in Table 1 have only semiquantitative significance.

The dramatic effect of moisture on the rate constant of the quadricyclane to norbornadiene rearrangement and on conductivity in saturated $LiCB_{11}Me_{12}/C_6H_6$ is illustrated in Figure 1. The very dry solution[19] is miscible with dry benzene and is a poor catalyst. The addition of up to 0.1 molecule of water per Li^+ ion greatly enhances catalysis, but further addition of water attenuates it. In contrast, increasing water content steadily increases conductivity. Solvation of Li^+ by water apparently favors the dissociation of the $LiCB_{11}Me_{12}$ tight ion pairs, but excessive hydration of dissociated Li^+ makes it a poorer catalyst. Only in the narrow region where there is sufficient water to favor the dissociation of the ion pairs, but not enough to attenuate the catalytic activity of Li^+, is $LiCB_{11}Me_{12}$ optimally active, and this fortunate situation appears to be approximated by standard benchtop conditions. It is unlikely that Brønsted acid derived from water is responsible for the catalysis, since the addition of a small amount[20] of LiOH to the $LiCB_{11}H_{12}$ has hardly any effect on the rate of quadricyclane rearrangement at 25 °C.

The results suggested an examination of other additives and solvents that might enhance ion pair dissociation but would not bind the Li^+ ion strongly. A cursory survey of dry solvents showed that solutions in 1,2-dichloroethane were especially effective. In an attempt to find out whether catalytic amounts of $LiCB_{11}Me_{12}$ would be sufficient, we examined a series of reactions with ~0.03 M $LiCB_{11}Me_{12}$ in $C_2D_4Cl_2$ under anhydrous conditions.[18] The quadricyclane to norbornadiene rearrangement proceeds with a half-life of 4.2 h at 25 °C. For comparison, in dry benzene, 0.03 M and saturated $LiCB_{11}Me_{12}$ catalyze the reaction with a half-life of tens of hours;[21] compare the 11 min observed with saturated benzene solutions under benchtop conditions. Table 1 compares the half-lives for isomerization of several other strained hydrocarbons in 1,2-$C_2D_4Cl_2$ with 0.03 M $LiCB_{11}Me_{12}$ under anhydrous conditions with literature data.

Some of the data in Table 1 contain mechanistic hints. The isomerizations of basketene suggest that the catalytic mechanism is distinct from that operating for transition metal induced rearrangements. Li^+ rearranges basketene to Nenitzescu's hydrocarbon, but Ag^+ rearranges it to snoutene. Because $LiCB_{11}Me_{12}$ does not catalyze the rearrangement of snoutene, this compound is not an intermediate in the former reaction. A similar difference is evident in the isomerization of cubane, which yields cuneane with Li^+ and tricyclo[4.2.0.0^{2,5}]octa-3,5-diene with Rh^+. Presumably, the transition metals form transient σ bonds to a carbon atom, while Li^+ is likely to rearrange strained hydrocarbons by Schleyer's[17] polarization mechanism.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9819179). S.M. is grateful to the Deutsche Forschungsgemeinschaft for a fellowship.

Supporting Information Available: Experimental details for conductivity measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] This behavior can be understood in terms of the general theory of ionic solutions of charged hard spheres in polarizable media: Friedman, H. L.; Larsen, B. *J. Chem. Phys.* **1979**, *70*, 92.

[18] Jiao, H. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11529.

[19] The $LiCB_{11}Me_{12}$ salt was dried (180 °C, 0.05 Torr, 8 h; at this point, ^1H NMR shows no water signal), and a small amount (4 mg) was transferred to each of a series of NMR tubes under an N_2 atmosphere in a Vacuum Atmospheres glovebox. The tubes were sealed by septa, removed from the glovebox, and dried again (180 °C, 0.05 Torr, 8 h). The solvent (400 μL), either 1,2-dichloroethane-d_4 or benzene-d_6, dried over CaH_2, was added by syringe. The substrate was added either under an Ar atmosphere or by syringe.

[20] LiOH (1%) was added to the aqueous LiCl solution used in the synthesis of $LiCB_{11}Me_{12}$.

[21] The half-lives for these slow reactions are less accurate as they could be affected by minute traces of water.