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A Simple Synthetic Method of [2.2]Cyclophanes by Lanthanoid-Mediated Coupling of Bis(bromomethyl)benzenes

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The coupling of bis(bromomethyl)benzenes with iodized samarium, cerium or Misch metal gives [2.2]cyclophanes in satisfactory yields in a short time.

A variety of methods for the preparation of [2.2]cyclophanes are known up to date.[1)] Among all, direct coupling of bis(bromomethyl)benzenes with sodium or sodium-tetraphenylethylene is the simplest, but gives a very low yield. We have developed a simple method giving satisfactory yields of [2.2]cyclophanes by lanthanoid-mediated coupling of bis(bromomethyl)benzenes.

Previously, Kagan et al.[2)] reported the SmI_2-mediated coupling of benzyl bromide to 1,2-diphenylethane. Amalgamated cerium also promotes the same coupling.[3)] We applied this method to bis(bromomethyl)benzenes.

In our experiments, low-valent iodides (LnI_2) of samarium, cerium and Misch metal (Mm) were used as the coupling agents. In a general procedure, bis(bromomethyl)benzene (1 mmol) in Na-dried THF (8 ml) was added to LnI_2[4)] (2 - 10 mmol) in Na-dried THF (8 ml) under nitrogen at room temperature. After stirring for 5 - 60 min, an internal standard for GC analysis, if required, was added, and the mixture was worked up in the usual manner.[2)] Distribution and identification of the products were determined by GC using authentic samples. In a few cases, the main products were isolated by preparative TLC.

Tables 1 and 2 summarize the results for 1,3- and 1,4-bis(bromomethyl)benzenes, respectively. All the reactions give, apart from [2.2]cyclophane (2), xylene (3), monobromoxylene (4), bis(methylphenyl)ethane (5) and/or bis(bromomethylphenyl)ethane (6) and unidentified by-products. In Table 1, the highest yield (44%) of metacyclophane 2 is attained with 2 mmol of MmI_2 per 1 mmol of substrate. In a more diluted solution (0.6 mmol of MmI_2, 0.3 mmol of substrate, 16 ml of THF), reduction products 3 and 5 are formed in higher proportions to 2. Reaction performed on 10-mmol scale (23 mmol of MmI_2, 10 mmol of substrate, 150 ml of THF) gave 2 in 38% isolated yield. In Table 2, the highest yield (22%) of paracyclophane 2 is attained with 10 mmol of MmI_2. The yields are much higher than those by the sodium-mediated coupling.

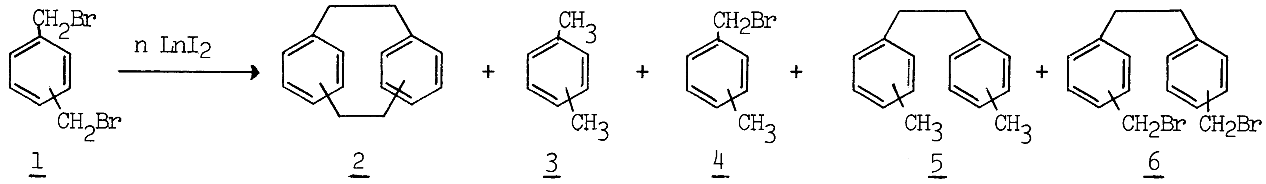

Table 1. Results for the coupling of 1,3-bis(bromomethyl)benzene

LnI_2	n[a)]	Time/min	Product distribution/%[b)]							
			1	2	3	4	5	6	7[c)]	8[c)]
MmI_2	2	60	-	44.5(35)	5.9	-	10.7	-	28.1	5.2
	2[d)]	60	23.5	23.2	6.7	-	9.3	14.4	4.2	-
CeI_2	5	60	12.8	15.2	2.5	0.5	4.2	47.1(36)		
SmI_2	2	5	-	19.5	16.0	-	17.3	-		

a) Mole ratio of LnI_2 to substrate. b) Parentheses denotes isolated yields after recrystallization from hexane. c) Unidentified products having much longer retention times, as detected by GC. d) Used substrate (0.3 mmol) in THF (8 ml).

Table 2. Results for the coupling of 1,4-bis(bromomethyl)benzene

LnI_2	n[a)]	Time/min	Product distribution/%[b)]						
			1	2	3	4	5	6	9[c)]
MmI_2	5	60	37.9	12.0	0.1	0.2	7.7	27.1	5.7
	10	60	-	22.2(18)	0.6	-	1.7	-	34.6
CeI_2	5	60	6.3	7.3	-	-	11.5	64.6	1.9
	10	60	7.0	10.8	-	-	-	49.8	3.1
SmI_2	5	10	-	8.2	1.2	-	32.1	-	47.3

a) - c) See those in Table 1.

References

1) V. Boekelheide, "Cyclophanes I," ed by F. Vögtle, Splinger-Verlag, Berlin (1983), p. 91.

2) P. Girard, J. L. Namy, and H. B. Kagan, J. Am. Chem. Soc., 102, 2693 (1980).

3) T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka, and M. Yokoyama, J. Org. Chem., 49, 3904 (1984).

4) Ingots of samarium (Rare Metallic Co. Ltd.) and of Misch metal (an alloy of Ce 49%, La 29%, Nd 15%, Pr 3.9%, Fe 1.2%, Sm 1.0%, and others 0.8%, Santoku Kinzoku Kogyo Co.) were scraped to a ca. 50 mesh powder with a rasp under nitrogen just before use. The cerium used was a 20 mesh powder storaged in mineral oil (Rare Metallic Co. Ltd.) and was washed with hexane. Dark brown solutions of CeI_2 and MmI_2 (2 mmol) in THF (8 ml) were prepared by treating the Ce (2.2 mmol) and the Mm powder (320 mg, an amount corresponding to 2.2 mmol of Ce) in THF (5 ml) with a catalytic amount of iodine, followed by adding diiodoethane (2 mmol) in THF (3 ml). The composition of the resulting iodides was tentatively assumed on the stoichiometric basis[2)] to be CeI_2 and MmI_2. A dark blue solution of SmI_2 (2 mmol) in THF (8 ml) was prepared in a similar way, but without iodine pretreatment.

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