A New One-Step Synthesis of Monobromocyclopropanes

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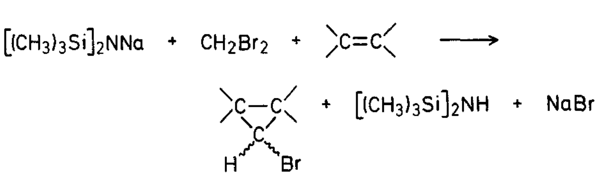
Dihalocyclopropanes and monochlorocyclopropanes can be conveniently prepared by known methods[1,2]. On the other hand, a convenient one-step procedure for the preparation of monobromocyclopropanes starting from olefins has hitherto not been reported[3,4]. The heretofore best method of synthesis of monobromocyclopropanes is the reaction of *gem*-dibromocyclopropanes with tributyltin hydride[5].

We here report a convenient new synthesis of bromocyclopropanes by reaction of olefins with dibromomethane and sodium bis-[trimethylsilyl]-amide in pentane.

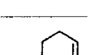
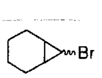
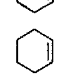
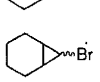
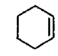
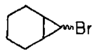
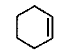
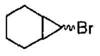
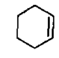
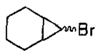
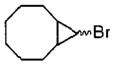
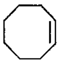
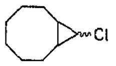
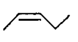
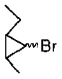
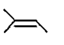
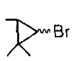
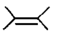
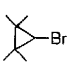
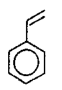
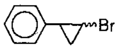
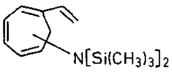
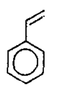
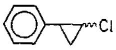
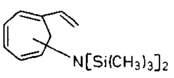


Alkali metal bis-[trimethylsilyl]-amides have been used in α-elimination reactions[6]. In contrast to alkyllithium, these nucleophilic agents generally undergo a hydrogen/metal exchange reaction with polyhalomethanes to give remarkably stable carbenoids[7] and thus may be used to advantage in our preparation of bromocyclopropanes. The results obtained under various conditions are listed in Table 1.

From the results listed in Table 1, the following conclusions may be drawn:

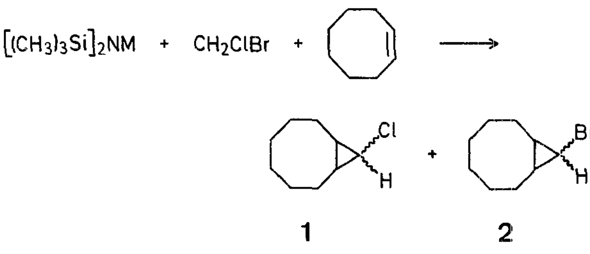
- the reaction temperature has little effect on the yields of product (cf. experiments 1–3);
- *sodium* bis-[trimethylsilyl]-amide gives the best results (experiments 1–6);
- with styrene (experiment 12), the reaction yields two types of product, resulting from addition both to olefinic and aromatic bonds; this result may be compared with the previously published[6] experiment 13;
- comparison of experiments 7 and 8 with 12 and 13 shows that the yields of chlorocyclopropanes are higher than those of the bromo analogs. For the synthesis of chlorocyclopropanes, our procedure seems indeed more interesting than the method involving butyllithium;
- experiment 7 shows a surprisingly high stereospecificity (also reported in Ref.[5]).

Table 1. Preparation of Monohalocyclopropanes from Olefins, Dihalomethanes, and Alkali Metal Bis-[trimethylsilyl]-amides

Experiment	Olefin	CH_2X_2	Amide of	Temperature	Products	Yield %	*cis/trans*
1		CH_2Br_2	Na	r. t.		40	1.5
2		CH_2Br_2	Na	0°		40	1.5
3		CH_2Br_2	Na	70°		30	1
4-5		CH_2Br_2	K	−30°; −10°		5	1.1
6		CH_2Br_2	Li	55°		30	1.3
7		CH_2Br_2	Na	r. t.		40	20
8		CH_2Cl_2	Na	r. t.		54	2.35
9		CH_2Br_2	Na	r. t.		30	3
10		CH_2Br_2	Na	r. t.		50	—
11		CH_2Br_2	Na	r. t.		45	
12		CH_2Br_2	Na	r. t.	 	25 6	—
13		CH_2Cl_2	Na	0°	 	40 11	2.12

The possibility of varying the alkali metal permits a systematic study of its influence on the behavior of the carbenoid intermediates towards olefins. As an example, the results obtained on carrying out the reaction with bromochloromethane and the bis-[trimethylsilyl]-amides of lithium, sodium, and potassium, respectively, are listed in Table 2.

Table 2. Products from the Reaction of Cyclooctene with Bromochloromethane and Alkali Metal Bis-[trimethylsilyl]-amides



Metal	Composition of Product (%)[a] 1	2
Li	87	13
Na	95	5
K	98	2

[a] by G.L.C. analysis

Competitive experiments and mechanistic studies will be presented in a forthcoming paper.

Synthesis of Monobromocyclopropanes; General Procedure:

In a three-neck flask, dibromomethane (18 g) is added dropwise with stirring to a mixture of sodium bis-[trimethylsilyl]-amide (18.3 g, 0.1 mol), olefin (0.3 mol), and dry pentane (50 ml). The mixture is held at room temperature (water bath) during the addition and for 2 additional hours. It is subsequently treated with water and extracted with ether. The extract is dried with sodium sulfate, and the product isolated by distillation.

The yields of monobromocyclopropanes are very low when $[(CH_3)_3Si]_2NNa, O(C_2H_5)_2$ is used. In this case it is necessary to warm the amide at 110° for 5 hr to remove the complexed ether.

With C_5-olefins it is difficult to separate the bromocyclopropanes from hexamethyldisilazane. In this case, the distillate is heated at reflux temperature with absolute methanol (0.3 mol) for 3 hr and is then distilled again.

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[5] D. Seyferth, H. Yamasaki, D.L. Alleston, J. Org. Chem. **28**, 703 (1963).

[6] B. Martel, E. Aly, J. Organomet. Chem. **29**, 61 (1971).

[7] B. Martel, J.M. Hiriart, Tetrahedron Lett. **1971**, 2737.

[8] Part of this work has been presented at the International Symposium on the Chemistry of Small-Ring Compounds and Activated Multiple Bonds, Louvain, September 13–16, 1971.