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A NEW SYNTHETIC METHOD OF [2.2]CYCLOPHANES[1]

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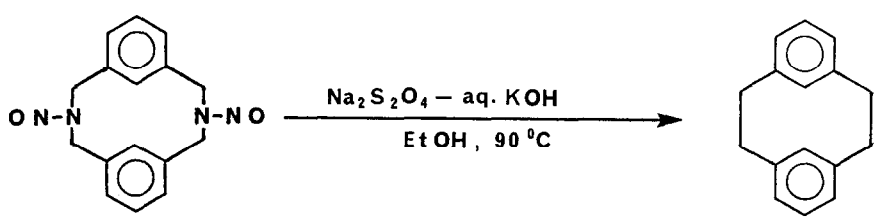
Diaza[3.3]cyclophanes were converted to the corresponding [2.2]cyclophanes via their N-nitroso derivatives by reductive extrusion of nitrogens. This reaction is simple, clean and mild, and may be an alternative synthetic way of [2.2]cyclophanes.

Many synthetic methods of [2.2]cyclophanes have been developed during the past twenty years.[2] Among them, synthetic routes via dithia[3.3]cyclophanes have been prevailing and efficient methods and many cyclophanes have been synthesized by this method.[2] In the course of the studies on azacyclophanes, we have developed a new method of constructing [2.2]cyclophanes from the corresponding diaza[3.3]cyclophanes.

Overberger[3] et al. reported generation of dibenzyls by reduction of N-nitrosodibenzylamines with sodium hydrosulfite in the presence of base. We applied the slightly modified Overberger's method to bis(N-nitrosoaza)-[3.3]cyclophanes. The reaction was very clean and [2.2]cyclophanes were main products. The syntheses of azacyclophanes as the starting materials were achieved by the previously reported method.[4]

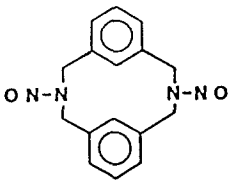
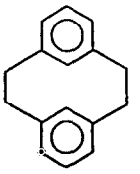
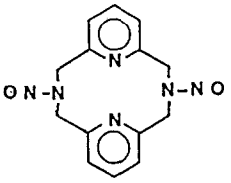
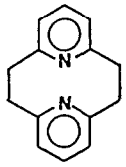
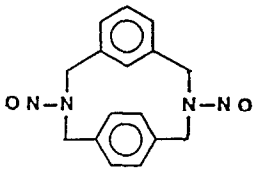
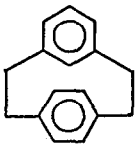
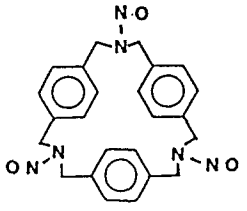
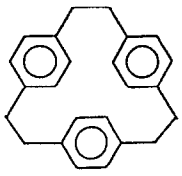
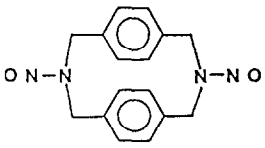
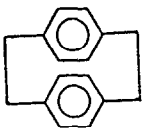
An example of the procedure is as follows and the yields of the [2.2]cyclophanes are listed in Table 1.

[2.2]Metacyclophane: A cold solution of $NaNO_2$(270mg, 1.6mmol) in 3ml of water was added to a solution of 2,11-diaza[3.3]metacyclophane(100mg, 0.42mmol) in 2ml of conc HCl and the mixture was left overnight at room temperature. Resultant precipitates were collected by filtration and dried in vacuo. The N-nitroso compound thus obtained(81mg, 0.27mmol) was dissolved into a mixture of 4N aq.KOH(5ml) and ethanol(5ml) and heated under reflux. Solid



sodium hydrosulfite(250mg, 0.14mmol) was added to this mixture. After 3 hrs, the mixture was poured into water and extracted with dichloromethane. Usual work up and sublimation(85°C/0.3mmHg) afforded 41.4mg(72.7%) of [2.2]metacyclophane as white crystals.

Table 1. Yields of [2.2]Cyclophanes[5]

N-Nitroso Der.	Product	Yield(%)	N-Nitroso Der.	Product	Yield(%)
		73			85
		68			19[6]
		29[6]			

The advantage of this procedure over the conventional sulfur-extrusion methods may reside in its mildness and simplicity.

References and Notes

1. Presented at the 54. Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1987; Abstr. No. 2IIIF 11.
2. F. Vögtle, "Cyclophanes I ", Ed., F. L. Boschke, Springer-Verlag, pp91-108, 1983.
3. C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, J. Am. Chem. Soc., 80, 3009(1958):C. G. Overberger and N.P. Marullo, ibid.,83, 1378(1961).
4. H. Takemura, M. Suenaga, K. Sakai, H. Kawachi, T. Shinmyozu, Y. Miyahara, and T. Inazu, J. Inclusion Phenom., 2, 207(1984).
5. Physical properties of these products were identical with those reported.
6. The low yields of cyclophanes resulted from low solubility of their N-nitroso derivatives in the solvent. During the course of the reactions, these N-nitroso derivatives were not dissolved in the solvent.

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