DESELENATION OF DISELENACYCLOPHANES — A NEW SYNTHETIC METHOD OF [2.2]CYCLOPHANES—¹⁾

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Summary: Several diselena[3.3]cyclophanes were prepared by coupling of bisselenocyanates and bis(bromomethyl)benzenes in good yields. The benzyne Stevens rearrangement-Raney Ni hydrogenolysis method gave good yields of double- and triple-layered cyclophanes from the diselenides, though the flash pyrolysis method gave them in low yields.

Previously we reported the synthesis of bibenzyl and its related compounds such as [2.2]paracyclophane by flash pyrolysis of acyclic diselenides in good yields.^{2,3} In the present paper, we now report a new synthetic method of a series of cyclic diselenides, diselenacyclophanes 1-6 and the corresponding deselenated products, double- and triple-layered cyclophanes 7-12, by benzyne Stevens rearrangement-hydrogenolysis or direct flash pyrolysis of the cyclic diselenides.

Compared with a facile synthesis of dithiacyclophanes by alkaline coupling of dithiol with dibromide,⁴⁾ the corresponding diselenacyclophanes have been afforded by a similar way in low yields because the reaction of an oxygen-reactive component, diselenol or its dianion gave hardly separable diselenide-polymer as well as the desired coupling product.⁵⁾ We recently described that substituted dibenzyl selenides were generally obtained by coupling of the corresponding benzyl selenocyanates with substituted benzyl halides in the presence of sodium



borohydride in 80-95% yields.²⁾ This coupling procedure under reductive conditions was applied to the synthesis of diselenacyclophanes 1-6 from bisselenocyanates and bis(bromomethyl)benzenes using a high dilution technique. A series of diselenacyclophanes containing triple-layered ones were obtained in excellent yields as shown in Table 1.⁶⁾ Diselena[3.3]metacyclophane 1, for example, was afforded in a good yield of more than ten times than that (7%) reported before.⁵⁾ Furthermore, this new method is convenient to prepare unsymmetrical diselenacyclophanes as well as symmetric ones, compared with a use of the preceding method for symmetric ones alone,³⁾ and very easy to purify the products because of the formation of no tedious polymer.

Sulfur extrusion reaction of dithia[3.3]cyclophanes was brought about by the

Table 1. Yields and properties of diselena[3.3]cyclophanes			
Diselenide ^{a)}	Yield(%)	mp (°C)	¹ H-NMR (&,CDC1 ₃ ,100MHz)
≤ Se	85	120-122 ⁵⁾	7.04(m),6.46(s)
Se Y	05	colorless prisms	3.78(s)
	01	168-170	6.87-7.16(m), 6.98(s),5.61(s),
Se Se	18	colorless needles	3.94(s),3.57(s)
- <u></u> 2			
Se Se	73	214-215 colorless prisms	6.84(s),3.89(s)
→ ○ → 3			
		182-184	6.72-7.02(m),
Se Se	68	pale yellow prisms	6.57,6.37(A ₂ B ₂ m), 5.96(s),5.33(s),
$\boldsymbol{\boldsymbol{\triangleleft}}$			2.39-3.97(m)
4			
Se / Se		177-179	6.67,6.63(A ₂ B ₂ m),
	74	colorless prisms	5.75(s),
5			2.42-3.92(m)
			7.15-7.35(m),
	93	168.5-169.5 colorless prisms	7.06(s), 6.89-6.97(m).
, se → 6			3.99(s),3.91(s)

 a) All of diselenacyclophanes show satisfactory elemental analysis and MS spectrum.

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Stevens rearrangement and Raney nickel hydrogenolysis to give a series of [2.2]cyclophanes 7,11) Analogously selenium extrusion from diselena[3.3]cvclophane to give [2.2]cyclophane was carried out by two methods (A and B) as follows. (A) Benzvne-Hydrogenolysis: Into a solution of diselenacyclophane (] mmo]) and isoamyl nitrite (2 q) in 1.2-dichloroethane (20 ml), a solution of anthranilic acid (4 mmol, 2 equiv.) in 1,2-dichloroethane (20 ml) was dropwisely added with vigorous stirring at reflux for more than 4 h under nitrogen. After removal of the solvent, the residue was chromatographed on silica gel with CCl $_{\scriptscriptstyle A}$ to yield a pale yellow solid or semi-solid. A suspension of the product and Raney Ni (W-2, 1 g) in ethanol (50 ml) was stirred at gently reflux for 17-23 h under hydrogen. Worked up the mixture, a semi-solid obtained was chromatographed on silica gel with hexane-benzene to give cyclophane in an overall yield shown in Table 2. The structure of each cyclophane was identified by comparison of its MS and 1 H-NMR spectra with those of authentic sample. (B) Flash Pyrolysis: Using the pyrolytic apparatus and conditions previously described.³⁾ the diselena[3,3]cyclophanes were thermally deselenated under a reduced pressure (3-5 mmHg) to give the corresponding [2.2]cyclophanes as shown in Table 2.



Table 2. Yields(%) of cyclophanes by (A) benzyne-hydrogenolysis and (B) flash pyrolysis

The table reveals that the benzyne-hydrogenolysis method is superior to the direct extrusion method by flash pyrolysis and the yields are comparable to those of the transformation of the corresponding disulfides into cyclophanes by benzyne-hydrogenolysis method. On the other hand, the benzyne method with diselenide is preferred for the synthesis of triple-layered cyclophane 10, compared to the disulfide benzyne method (12%).¹¹⁾ Consequently, the benzyne Stevens rearrangement-hydrogenolysis for deselenation is a useful synthetic way to prepare double- and triple-layered cyclophanes. Further applications of this method are now in progress.

References and Notes

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