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SYNTHESIS OF [2.2]CYCLOPHANES BY PHOTODESELENATIVE RINGCONTRACTION[1)]

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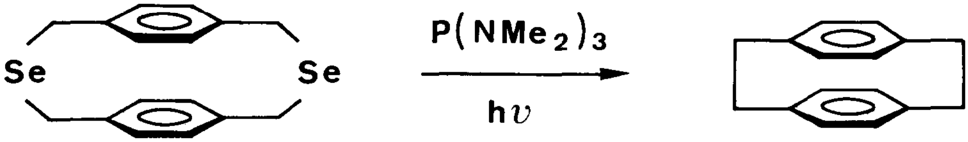
Summary: Several cyclophanes were prepared by photodeselenation of diselena[3.3]cyclophanes with hexamethylphosphorous triamide in excellent yields, compared with the other chalcogen-atom extrusion methods.

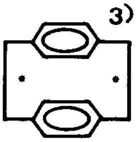
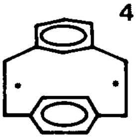
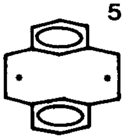
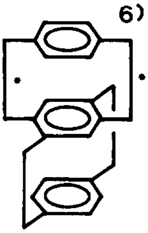
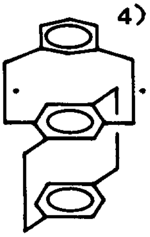
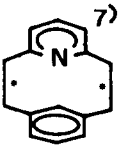
In the preceding paper of this series, we reported the synthesis of diselena[3.3]cyclophanes by a reductive coupling of bisselenocyanates with dihalides and the following deselenation using Stevens rearrangement-hydrogenolysis or flash pyrolysis to give [2.2]cyclophanes.[1)] We wish to report a more facile, general synthesis of [2.2]cyclophane system by photodeselenative ringcontraction of the diselenacyclophanes, compared with the two deselenation methods abovestated.



Among a variety of phosphorus reagents, hexamethylphosphorous triamide, $P(NMe_2)_3$, was found to be a good reagent for the photodeselenation reaction just as trialkyl phosphite for the photodesulfurization[2)] of dithiacyclophanes. On irradiation of a solution of diselenacyclophane (50 mg) and excess hexamethylphosphorous triamide (ca. 1 g) in THF (30-50 ml) with a 400W high pressure mercury lamp under nitrogen bubbling, the desired cyclophanes shown in Table were easily separated by the usual work-up. The structures of the cyclophanes were identified by comparison of PMR, MS, and other spectra with the authentic samples.

The table shows that the yields of cyclophanes **1** - **6** by the photodeselenation are much higher than those by both Stevens rearrangement-hydrogenolysis

Table. Yields of [2.2]Cyclophanes and Irradiation Times

	 3)5)	 4)	 5)	 6)	 4)	 7)
Product	**1**	**2**	**3**	**4**	**5**	**6**
Yield(%) a)	**93**	**53** c)	**48**	**80**	**51**	**25**
hν(hr) b)	**4.5**	**20**	**16**	**23**	**47**	**22**

* New C-C bonds by photodeselenation. a) Isolated yields. b) Irradiation time. c) A by-product, monoselenacyclophane of 14% yield.

and flash pyrolysis of diselenacyclophanes,1) the photodesulfurization of the corresponding dithiacyclophanes,3,4) and thermal desulfonation of cyclic disulfones.5) Consequently it should be emphasized that the present method is obviously preferred over all of chalcogen-atom extrusion methods so far studied for [2.2]cyclophane synthesis, since the intermediate diselena[3.3]cyclophanes are easily prepared in fairly good yields.

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