

Formation of Cyclo-octyne by Pyrolysis of Cyclo-octeno-1,2,3-selenadiazole

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Summary The reaction of cyclo-octanone semicarbazone (2) with SeO_2 leads to cyclo-octeno-1,2,3-selenadiazole (3) from which, on heating to 170–220°, cyclo-octyne (5), the lowest stable cycloalkyne, can be prepared in good yields.

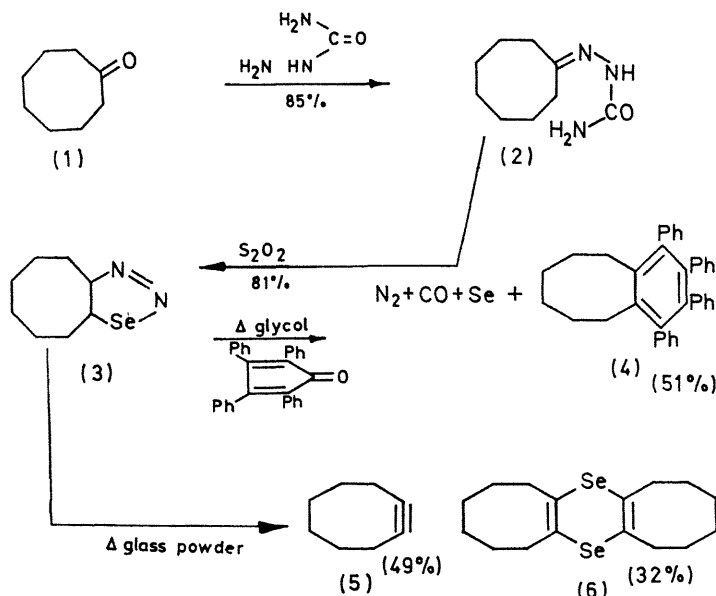
DURING our investigations of the thermolytic and photolytic behaviour of cyclo-octyne in the presence of TiCl_4 ,¹ with $\text{Fe}(\text{CO})_5$,² and $\text{Mo}(\text{CO})_6$, respectively, we carried out the

following methods of cyclo-octyne formation: bromination and dehydrobromination of cyclo-octene (total yield 9%)³ and the preparation and oxidation of cyclo-octanedione bis-hydrazone^{4,5} or of 1-aminocyclo-octeno-1,2,3-triazole⁶ starting from cyclo-octanone (total yield 3 and 15% respectively). In a search for a novel synthesis providing higher yields we investigated the photodecomposition of cyclo-octanedionebis-toluene-*p*-sulphonylhydrazone.⁶

We now report our work on the pyrolysis of cyclo-octeno-1,2,3-selenadiazole, which can be prepared similarly to the known aromatic substituted 1,2,3-selenadiazoles.^{7,8} For this purpose cyclo-octanone was treated in boiling absolute alcohol with semicarbazide acetate. The cyclo-octanone semicarbazone was oxidized as a suspension in dioxan with an excess of SeO_2 in a saturated aqueous solution. Ring closure leads to the required cyclo-octeno-1,2,3-selenadiazole, which can be purified by chromatography on silica gel or by careful distillation at 0.5×10^{-3} mm (b.p. 99–101°). Pyrolysis of cyclo-octeno-1,2,3-selenadiazole in glycol in the presence of tetraphenylcyclopentadienone leads to the elimination of N_2 and Se and formation of the corresponding cyclo-octyne adduct (4). Pyrolysis at 170–220° on glass powder yields 49% cyclo-octyne, which can be distilled under reduced pressure in a current of nitrogen into a cooled trap. In the residue compound $\text{C}_{16}\text{H}_{24}\text{Se}_2$ remains: this probably has the structure (6). Starting with cyclo-octanone (1) the total yield of cyclo-octyne is 34%.

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