ADDITION OF HYDROGEN SELENIDE TO DIACETYLENIC KETONES

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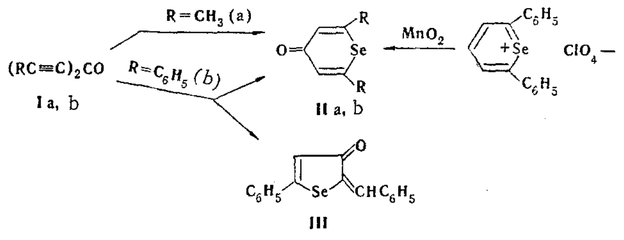
Up until now, selenopyrones were unknown. We have found that 2,5-heptadiyn-4-one (Ia) adds hydrogen selenide in the presence of bases to give 2,6-dimethyl-1-seleno-γ-pyrone (IIa). The addition of H_2Se to 1,5-diphenyl-1,4-pentadiyn-3-one (Ib) gives a mixture of 2,6-diphenyl-1-seleno-γ-pyrone (IIb) and 2-benzylidene-3-oxo-5-phenyl-2,3-dihydroseleno-phene (III), in yields of 17 and 28%, respectively.



A 0.3-ml sample of a 10% solution of triethylamine was added to a solution of 3 g (28 mmole) of ketone Ia ($R = CH_3$) in 30 ml of methanol, and H_2Se was bubbled into the mixture for 20 min in such a way that the temperature did not exceed 35°C. Half of the methanol was removed by vacuum distillation (with a water aspirator), and 25 ml of water was added. Selenopyrone IIa was crystallized from water to give 2.8 g (57%) of product. Vacuum sublimation gave colorless needles with mp 88-89°. UV spectrum, λ_{max}, nm (log ε): 236 (3.86), 310 (4.36). IR spectrum: 1625 cm^{-1}. PMR spectrum: singlets at 6.73 (2H) and 2.47 ppm (6H). Found, %: Se 42.0. C_7H_8OSe. Calculated, %: Se 42.2.

Hydrogen selenide was added as in the preceding experiment to 0.92 g (4 mmole) of ketone Ib. The resinous precipitate was extracted with 30 ml of boiling methanol, and the methanol solution was decanted and diluted with water. The reaction product was removed by filtration, dried, and dissolved in 100 ml of dry benzene, and hydrogen chloride was bubbled through the solution. The precipitated salt was removed by filtration and treated with aqueous sodium carbonate solution to give 0.21 g (17%) of selenopyrone IIb as yellowish needles with mp 145-146° [from benzene–cyclohexane (1 : 1)]. UV spectrum, λ_{max}, nm (log ε): 280 (4.22), 317 (4.27). IR spectrum: 1608 cm^{-1} (CO). PMR spectrum: singlet at 7.22 ppm (2H) and multiplet at 7.60 ppm (10H). Found, %: Se 25.5. $C_{17}H_{12}OSe$. Calculated, %: Se 25.4.

The benzene solution remaining after precipitation of the selenopyrone salt was washed with water and dried. The benzene was removed by distillation, and the residue was crystallized from benzene–cyclohexane (1 : 1) and twice from methanol to give 0.34 g (28%) of III as dark-yellow needles with mp 130-131°. UV spectrum, λ_{max}, nm (log ε): 338 (4.42), 438 (3.72). IR spectrum: 1660 cm^{-1} (CO). PMR spectrum: singlet at 6.98 (1H), multiplet at 7.58 (10H), and singlet at 8.05 ppm (1H). Found, %: 25.2 Se. $C_{17}H_{12}OSe$. Calculated, %: Se 25.4.

Compound IIb was also obtained by heating 0.395 g (1 mmole) of 2,6-diphenylselenopyrylium perchlorate and 1.9 g (20 mmole) of active manganese dioxide in 10 ml of acetonitrile for 10 min. The mixture was extracted with ether, and the extract was washed with water and dried. The ether was removed by distillation, and the residue was crystallized twice from benzene–cyclohexane (1 : 1) to give 0.096 g (32%) of a product that was identical to that described above.

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