

Short Communication

Novel photodimerization of 2,3-dibromopropene

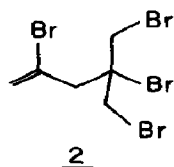
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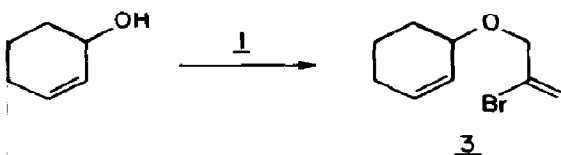
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1. Introduction

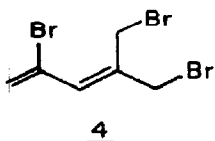
In the course of studying the Williamson ether synthesis using 2,3-dibromopropene (1), we found an unusual byproduct which we have identified as the tetrabromo dimer 2.



Our attempts to alkylate cyclohexenol using 1, under a variety of different reaction conditions [1], led only to recovered cyclohexenol and small amounts of desired ether 3. (A number of workers have cited problems with the alkylation of alkoxides using 2,3-dibromopropene [2]. Recently the alkylation of an alkoxide using 1 was reported [3].)



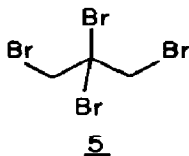
The structure of 2 was determined spectroscopically. Our assignment was further supported by the generation of diene 4 upon treatment of 2 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).



With the hope of improving the yield of 3 in the Williamson ether synthesis, we investigated the mechanism of formation of 2 from 1.

2. Results and discussion

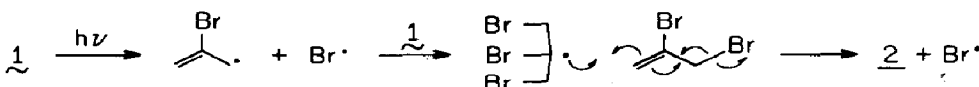
The formation of **2** is not catalyzed by bromide ion or bromine. Warming **1** in tetrahydrofuran (THF) with sodium bromide for 10 h led only to the recovery of 2,3-dibromopropene. Addition of a carbon tetrachloride (CCl₄) solution of bromine to a solution of **1** in CCl₄ resulted in the slow formation of the unstable tetrabromide **5** (proton nuclear magnetic resonance (¹H NMR) at 270 MHz, $\delta = 4.27$ (s)).



However, when **1** was warmed at 95 °C for 36 h, a dark oil was recovered [4]. Filtration of the crude reaction mixture through a plug of silica gel provided tetrabromide **2** in 60% yield. Bromide **2** also forms slowly in freshly distilled, neat 2,3-dibromopropene after several days (under nitrogen) in a flask on the benchtop. Tetrabromide **2** is also present in varying amounts in commercially available **1**.

With the previous observations in mind, we turned our attention to the possibility that **1** might be converted to **2** photochemically. Irradiation of **1** for 60 h using a 450 W medium pressure Hanovia lamp with a Pyrex filter resulted in the formation of **2** in 68% yield. The reaction proceeded to about 50% completion within 8 h. However, during the course of the reaction, the mixture became dark brown and apparently filtered out the light, causing the rate of the reaction to decrease significantly.

We rationalize that a light-induced homolysis of the allylic C-Br bond is responsible for initiating the reaction. Addition of the bromine atom to olefin **1** followed by reaction of the resulting tertiary radical with another equivalent of **1** and loss of a bromine atom accounts for the formation of **2** and the propagation of the chain reaction. Further investigations of the generality of this reaction are in progress.



Experimental details

3.1. General details

All reactions were carried out under an atmosphere of nitrogen. 2,3-Dibromopropene was distilled before use. THF was distilled from potassium using benzophenone as an indicator. Elemental analyses were performed by Galbraith Laboratories, Inc., Tennessee. IR spectra were recorded as chloroform solutions on a Perkin-Elmer 1320 IR spectrophotometer. ¹H NMR spectra were recorded in deuteriochloroform at 270 MHz on an IBM model

WP 270SY NMR spectrometer and chemical shifts are reported in parts per million relative to tetramethylsilane.

3.2. Tetrabromo dimer 2: photochemical reaction

2,3-Dibromopropene (1.1 g, 5.5 mmol, neat) was irradiated for 60 h at about 35 °C using a 450 W medium pressure lamp with a Pyrex filter. The resulting dark oil was filtered through a plug of silica gel using 25 vol.% ethyl acetate in hexane. Removal of the solvent from the filtrate, *in vacuo*, yielded 755 mg of 2 as an oil (68% yield) (see above). ¹H NMR: 5.94 (m, 1H), 5.78 (d, *J* = 2 Hz, 1H), 4.02 (d, *J* = 11 Hz, 1H), 3.94 (d, *J* = 11 Hz, 1H), 3.24 (s, 2H). IR: 1625, 1430, 1270, 1195, 1140, 970 and 910 cm⁻¹. The following analysis was obtained. Calculated for C₆H₈Br₄: C, 18.03%; H, 2.02%; Br, 79.96%. Found: C, 18.01%; H, 2.14%; Br, 80.22%. High resolution mass spectroscopy calculated for C₆H₈Br₄ *m/e* 399.7318, found *m/e* 399.7325.

3.3. Dimer 2: thermal reaction

2,3-Dibromopropene (530 mg, 2.65 mmol) was warmed neat at 95 - 105 °C for 36 h under a nitrogen atmosphere. The resulting brown oil was filtered as described above to yield 320 mg of 2 as an oil (60% yield).

3.4. Diene 4

To a solution of 110 mg (0.275 mmol) of dimer 2 in 3 ml of dry THF at 0 °C was slowly added 0.05 ml (0.33 mmol, 50 mg) of DBU. The resulting colorless solution was stirred for 2 h at 0 °C, diluted with ethyl acetate, washed with saturated aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* yielded an oil which was filtered through a plug of silica gel using 5 vol.% ethyl acetate in hexane. The solvent was evaporated from the filtrate, *in vacuo*, to yield 54 mg (60%) of 4 as an oil. (The low yield for the conversion of 2 to 4 is due to the apparent instability of 4 to the reaction conditions. The use of other bases did not improve the yield.) ¹H NMR: 6.25 (s, 1H), 5.98 (t, *J* = 2 Hz, 1H), 5.83 (d, *J* = 2 Hz, 1H), 4.28 (s, 2H), 4.13 (s, 2H).

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