[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Organic Peroxides. VI. Allyl Hydroperoxide[1]

BY STANLEY DYKSTRA AND HARRY S. MOSHER

RECEIVED OCTOBER 31, 1956

Allyl hydroperoxide has been prepared in purified form by the reaction of allyl methanesulfonate with hydrogen peroxide and methanolic potassium hydroxide. This is the first member of the series of allylic type hydroperoxides which are the primary intermediates in the air oxidation of unsaturated compounds. Allyl hydroperoxide detonates on heating and decomposes on prolonged exposure to light at room temperature but is relatively stable in the cold and dark.

Although the preparation of allylic hydroperoxides by the air oxidation of olefinic compounds is a very common and important reaction, the parent compound of this series, allyl hydroperoxide, has never been reported. However, it has been postulated as an unstable intermediate[2] in the industrially important vapor phase oxidation of propylene.

The direct synthesis and isolation of allyl hydroperoxide in a purified state has now been achieved by the action of hydrogen peroxide on allyl methane sulfonate by the method of Williams and Mosher.[3] Although the usual procedure[3] gave solutions indicating allyl hydroperoxide yields of 30–40% as measured by titration, considerable difficulty was experienced in isolation and purification because of its unstable nature. It underwent slow decomposition at 40–60° with the formation of an explosive polymeric residue. It detonated when heated rapidly in a capillary tube. The distilled but impure product, which was known to contain at least water and hydrogen peroxide, was very sensitive to light. Exposure to artificial room illumination for only ten minutes resulted in extensive destruction in some of the impure samples of allyl hydroperoxide as evidenced by the appearance of a carbonyl band at $5.95\ \mu$ in the infrared spectrum. Because of the decomposition of these crude preparations in the presence of light and heat, the preparation and purification of allyl hydroperoxide was conducted entirely in Pyrex low actinic glassware in the presence of artificial illumination from a photographic red light; initial purification was accomplished by evaporative distillation below 20°; final purification was by gas–liquid partition chromotography.[4] Samples so purified did not show this rapid decomposition on exposure to light.

The sensitivity to light must be dependent upon impurities and cannot be the result of enhanced absorption and photodissociation since the ultraviolet absorption spectrum of allyl hydroperoxide (log ϵ 0 at 312 mμ) shows only a slight bathochromic shift from that of n-butyl hydroperoxide (log ϵ 0 at 302 mμ) which is stable to ordinary light. Thus the amount of light which will pass through a Pyrex flask and be absorbed by allyl hydroperoxide must be extremely small.

Allyl hydroperoxide is extremely irritating to the mucous membrane of the nose. Even the slightest contact with the skin causes a prolonged burning sensation and blisters which persist for approximately one week. It detonates when heated, but it cannot be detonated by striking with a hammer, grinding in a porcelain mortar, or by grinding between ground glass plates. When placed on a few grains of anhydrous potassium carbonate, there is slight warming followed by a detonation after three to five minutes. When dropped on anhydrous barium oxide, an immediate detonation takes place.

The allyl hydroperoxide was characterized by carbon hydrogen analysis, active oxygen determination, infrared and ultraviolet spectra, positive reaction to bromine in carbon tetrachloride, solubility in cold dilute sodium hydroxide solution and reduction to propanol.

The starting material, allyl methanesulfonate, could not be made by the procedure of Sekera and Marvel.[5] The method which Hahn and Walter[6] developed for the preparation of allyl phenylsulfonate was also unsatisfactory, although it did result in a 20% yield of allyl methanesulfonate. The treatment of methanesulfonyl chloride and allyl alcohol in ether solution with powdered potassium hydroxide also gave very low yields. These findings correspond to those reported by Raphael and Sondheimer[7] in the preparation of 2-octyne-1-methanesulfonate. However, by the slow addition of methanesulfonyl chloride to an allyl alcohol–ether solution of sodium alloxide, yields up to 68% of allyl methanesulfonate were finally achieved.

Experimental

Allyl Methanesulfonate.—Sodium, 6.9 g. (0.3 mole), was allowed to dissolve in anhydrous allyl alcohol, 100 g., and the resulting solution was diluted with 100 ml. of anhydrous ether. This solution was cooled to 0° and rapidly stirred while methanesulfonyl chloride, 36 g. (0.31 mole), dissolved in 200 ml. of anhydrous ether, was added over a 2-hr. period. The reaction mixture was held at about −5° for 2 hr. and allowed to warm to room temperature overnight. The salt was removed by filtration, the filtrate was evaporated under 20 mm. pressure and the residue was distilled over a little potassium carbonate; b.p. 70–75° (3 mm.), 28 g. (68.5%), n^{20}_{D} 1.4414.

Anal. Calcd. for $C_4H_8O_3S$: C, 35.30; H, 5.92. Found: C, 35.39; H, 5.78.

Lower yields were obtained when the allyl alcohol was not freshly distilled or when the methanesulfonyl chloride was added too rapidly with inefficient stirring. Yields from 55 to 68% were consistently obtained by the above procedure.

Allyl Hydroperoxide.—The following procedure was con-

---

[1] (a) Presented before the 126th Meeting of the American Chemical Society, New York, N. Y., Sept., 1954. (b) Previous paper in the series, *Anal. Chem.*, **27**, 517 (1955).

[2] V. Y. Shtern and S. S. Polynak, *Doklady Akad. Nauk, U.S.S.R.*, **85**, 161 (1952); *C. A.*, **46**, 9397 (1952).

[3] H. R. Williams and H. S. Mosher, THIS JOURNAL, **76**, 2984, 2987 (1954).

[4] M. Dimbat, P. E. Porter and F. H. Stross, *Anal. Chem.*, **28**, 90 (1956).

[5] V. C. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 345 (1933).

[6] F. T. Hahn and H. Walter, *Ber.*, **54B**, 1531 (1921).

[7] R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 2100 (1950).

ducted in Pyrex, low actinic, glassware in a room illuminated with a red photographic light bulb. Care was taken so that the reaction mixture never came into contact with metal such as nickel from a spatula, iron or rust from a metal stirrer, etc. At any point where the allyl hydroperoxide was being heated or concentrated by evaporation, the apparatus was surrounded by a safety shield and sand bags.

Allyl methanesulfonate, 10.8 g. (0.08 mole), was dissolved in methanol, 30 ml., and 30% reagent grade hydrogen peroxide, 44 g. (0.44 mole), was added after the temperature had reached 0° by cooling with an external ice–salt-bath. While the temperature was kept at 0°, 50% potassium hydroxide solution, 10.1 g. (0.09 mole), was added slowly dropwise with vigorous stirring over a fifteen-minute period. The mixture was stirred for 1 hr. at 0° and then allowed to warm to 20° over a 2-hr. period. The reaction mixture was cooled to 0°, made strongly basic with 50% potassium hydroxide solution, 10.1 g., and subjected to vacuum evaporation at 15° or below until 30 g. of distillate had been collected in the Dry Ice trap. Most of the methanol, some water and a small amount of hydrogen peroxide were removed by this latter operation. Care was taken to ensure that the concentration did not go beyond this point. The residue was extracted with two 15-ml. portions of ether to remove any non-volatile neutral substances and then neutralized at 0° with 15% hydrochloric acid to *p*H 6. The resulting solution was extracted with four 20-ml. portions of peroxide-free ether and the ether extracts were dried over anhydrous sodium sulfate. This ether solution contained 0.06 mole of total peroxide by titration.[8]

The major portion of the ether was removed below 15° at 150 mm. pressure through a 12-inch column packed with Pyrex helices. The residue was then evaporatively distilled at room temperature or below by progressively lowering the pressure to 6 mm. The fractions were collected in a series of traps kept at 0, −20 and −75°. The residue was about 0.5 g.[9] Each fraction was qualitatively analyzed by gas–liquid partition chromatography.[10] The −75° trap contained ether with only a trace of any allyl hydroperoxide. The −20° trap contained 0.93 g. which was estimated to be contaminated with a total of about 35% of water and hydrogen peroxide.[11] The contents of the 0° trap, 1.95 g., showed the presence of about 20% hydrogen peroxide and/or water by gas–liquid partition chromatography. The water and hydrogen peroxide could not be distinguished from each other on this particular column,[10] but both came off together far ahead of the allyl hydroperoxide peak. From 250 mg. of this cut was isolated 110 mg. of purified allyl hydroperoxide. Isolation was accomplished by passing the exit gases through a micro trap cooled in Dry Ice, during the time that the allyl hydroperoxide was exiting from the tube.[12]

This 110 mg. was again passed through the gas chromatography column. The partitionogram indicated only a trace of impurities.[13] The isolated allyl hydroperoxide, 58 mg., $n^{20}{}_{D}$ 1.4200, was analyzed.[14]

Anal. Calcd. for $C_3H_6O_2$: C, 48.61; H, 8.16; O, 43.23; active oxygen, 21.58. Found: C, 47.87; H, 8.52; O, 43.61 (by difference); active oxygen (determined by titration[8]), 20.8%.

The infrared spectrum of a thin film showed a broad band at 3.0 μ characteristic of the O–H bond of the hydroperoxide molecule. There was moderate absorption at 6.15 μ characteristic of the double bond. This sample showed no discrete absorption at 5.8–6.0 μ indicating the absence of carbonyl impurities. There were strong peaks at 3.5, 7.09, 7.48, 10.12 (shoulder at 9.90), 10.74 and 12.28 μ. All primary hydroperoxides have shown this latter band.[1b] Weaker bands occurred at 5.38, 8.00, 8.70 and 11.64 μ. The latter is at the position assigned to the O–O stretching frequency of the peroxide bond.[1b]

Acknowledgment.—We are grateful to the California Research Corporation for a grant which made this investigation possible.

---

(8) C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

(9) The amount of residue varied from slight, as in this experiment, to 3 g. if the distillation had been carried out slowly at a bath temperature of 50°. In every case this residue would detonate if a drop was heated in a test-tube over a free flame. Three drops were sufficient to shatter completely an eight-inch Pyrex test-tube. The explosive nature of this residue was lost slowly on standing. In one of the earlier experiments when the distillation was complete but the distillation flask containing the residue was still in an oil-bath at approximately 110°, a detonation occurred which completely destroyed the apparatus. The decomposition of allyl hydroperoxide and the nature of this polymer will be studied further.

(10) The column was a 100 × 0.6 cm. Pyrex tube packed with 60 mesh fire brick.[4] The fire brick had been digested with hydrochloric acid, followed by ammonium hydroxide treatment and thoroughly leached with distilled water, then dried and impregnated with G.E. SF-81 (40) silicone oil. The column was run at 38°, 8 p.s.i. with a helium through-put of 205 ml. min. Under these conditions the retention time for ether was 1.0 min., for allyl alcohol was 1.9 min., for benzene was 5.0 min. and for allyl hydroperoxide was 7.3 min. The samples were injected with an all-glass capillary pipet. The high flow rate was employed so that the temperature could be kept below 40°.

(11) Several previous experiments indicated that the water could not be separated satisfactorily by simple distillation. Successive dryings over anhydrous copper sulfate appeared to be the most efficient way to dry the product but led to extensive decomposition. Therefore anhydrous sodium sulfate was used as the drying agent although it did not appear to be too effective.

(12) Because of the very high flow rate of helium carrier gas during these isolations,[10] the recovery was very poor. On several calibration runs under approximately the same conditions, using allyl alcohol as a standard compound, a recovery of 45 to 50% was realized.

(13) The fact that a second passage of the main fraction through the gas–liquid partition chromatography column gave a partitionogram which indicated only traces of impurities establishes that insignificant decomposition of the allyl hydroperoxide was taking place on the column under the conditions used.[10]

(14) Carbon and hydrogen analyses by Microchemical Specialties Co., Berkeley, Calif. The samples were evaporated slowly and no unusual decomposition was observed during the combustion.

STANFORD, CALIF.