ADDITION OF ETHYLENE CHLOROHYDRIN

TO α -METHYLVINYL PHENYL ETHER

A.K. Gorban'

N.D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 4, pp. 759-760, April, 1960 Original article submitted August 19, 1959

As previous investigations have shown [1], the addition of ethylene chlorohydrin to vinyl alkyl ethers yields unsymmetrical β -chloroethyl alkyl acetals; when heated, the latter are symmetrized to form low-boiling dialkyl acetals and a high-boiling β , β -dichlorodiethyl acetal. Unsymmetrical β -chloroethyl phenyl acetal behaves similarly [2].

The author decided to extend this reaction to α -alkylvinyl aryl ethers [3] and achieved it with α -methylvinyl phenyl ether (I) with ethylene chlorohydrin (II).



Due to the high tendency of the β -chloroethylene phenyl ketal of acetone (III) to symmetrize, it could not be isolated and we obtained only one of its symmetrization products, the diphenyl ketal of acetone (IV), and also one of the decomposition products, phenol.



EXPERIMENTAL

To 10.0 g of ethylene chlorohydrin with b.p. $36-38^{\circ}$ (6 mm); n_D^{20} 1.4410, in a three-necked, round-bottomed flask with a thermometer, reflux condenser, and dropping funnel was added an equivalent amount (16.8 g) of α -methylvinyl phenyl ether with b.p. $48-50^{\circ}$ at 5 mm and n_D^{20} 1.5060. The α -methylvinyl phenyl ether was added to the ethylene chlorohydrin in the flask in 2 min and the temperature of the reaction mixture rose from 23 to 91°. The reaction mixture was stirred for a further hour, cooled, to room temperature, and vacuum distilled (26.2 g of product). We obtained the following fractions: I-with b.p. 77-84° (36 mm); n_D^{20} 1.4955; 7.5 g;IIwith b.p. 73-92° (7-5 mm); n_D^{20} 1.4938; 5.0 g; III-with b.p. 97-100° (5 mm); n_{20}^{20} 1.4768; 3.0 g; residue in distillation flask 7.2 g. The losses were 3.5 g.

Fraction I (7.5 g) with b.p. 77-84° (36 mm); n_D^{20} 1.4955, consisted of a mixture, difficult to separate, of the β , β '-dichlorodiethyl ketal of acetone (V), α -methylvinyl β -chloroethyl ether (VI), and the phenyl β -chloroethyl ketal of acetone (III).

Fraction II (5.01 g) with b.p. 73-92° (7-5 mm) and n_D^{20} 1.4938 was a mixture of α -methylvinyl β -chloroethyl ether (VI) and the β -chloroethyl phenyl ketal of acetone (III).

$$CH_{3}C \xrightarrow{OC_{6}H_{5}} CH_{2} = COCH_{2}CH_{2}CI + C_{6}H_{5}OH,$$

$$\downarrow CH_{3} CH_{2} = COCH_{2}CH_{2}CI + C_{6}H_{5}OH,$$

$$\downarrow CH_{3} (VI)$$

Fraction III (3.0 g) with b.p. 97-100° (5 mm); n_{12}^{29} 1.4768 contained the β , β '-dichlorodiethyl ketal of acetone (V). From the residue (7.2 g) we isolated 3.0 g (22% of theoretical) of the diphenyl ketal of acetone (IV) with b.p. 130° (4 mm); n_{12}^{29} 1.5500; d_4^{20} 1.0705. Found: C 78.81; 78.78; H 7.25; 7.18%; MR 67.92; C₁₅H₁₆O₂. Calculated: C 78.92; H 7.07%; MR 67.55. The physical constants agree with literature data [4]. A small amount of phenol crystals were collected during the isolation of the diphenyl ketal of acetone.

SUMMARY

1. The reaction of α -methylvinyl phenyl ether with ethylene chlorohydrin was studied.

2. An indirect method was developed for the synthesis of the diphenyl ketal of acetone from α -methylvinyl phenyl ether and ethylene chlorohydrin.

LITERATURE CITED

- 1. M.F. Shostakovskii, N.A. Gershtein, and A.K. Gorban', Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 212 (1949).
- 2. M.F. Shostakovskii, M.R. Kulibekov, and A.K. Gorban', Zhur, Obshch. Khim. 28, 2838 (1958).*
- 3. M.F. Shostakovskii, E.P. Gracheva, and N.K. Kul'bobskaya, Zhur. Obshch. Khim. 28, 1953 (1958).*
- 4. M.F. Shostakovskii, E.P. Gracheva, and N.K. Kul'bovskaya, Zhur. Obshch. Khim. 28, 2344 (1958).*

^{*} Original Russian pagination. See C.B. translation.