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SHORT COMMUNICATIONS

Photoinitiated Reaction of Carboxylic Acids with Oxiranes

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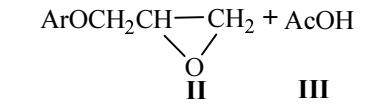
Polycarboxylic acids are used as hardener of epoxy resins operating only at high temperature in the presence of catalysts [1].

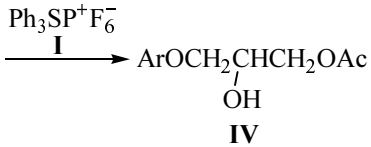
A study of photopolymerization of a mixture of epoxy resins with methacrylic acid (or its derivatives) at room temperature in the presence of triphenylsulfonium hexafluorophosphate $Ph_3S^+PF_6^-$ **I** was performed earlier [2, 3]. This compound initiated a ionic polymerization of the epoxy component and radical polymerization of the acrylate derivative [4]. At the same time it was presumed basing on the analysis of IR spectra and on consumption rates of each reagent that at this temperature a reaction occurred between epoxy and carboxy groups [2, 3].

To test this assumption we studied at UV irradiation in the presence of the above photoinitiator **I** a model reaction between monomer compounds: cresyl glycidyl ether **II**, used as active diluent for epoxy resins, and acetic acid **III**. The reaction was carried out at the epoxide **II** – acid **III** ratio and initiator **I** concentration used in [2, 3].

For the sake of comparison ether **II** was subjected to acetylation with acid **III** under generally used conditions: in the presence of a tertiary amine and at heating [5].



II **III**



IV

Ar = *o*-, *m*-MeC_6H_4.

Under photoinitiation 1-acetoxy-2-hydroxy-3-cresoxypropane **IV** was isolated in high yield as confirmed by ^{1}H NMR and IR spectroscopy.

The properties and spectral characteristics of compound **IV** were fully identical to those of the substance obtained by acetylation of ether **I** at heating. It should be noted that irradiation of the above mixture for several hours in the absence of photoinitiator **I** did not result in formation of compound **IV**; only the acidity of the medium somewhat increased. Apparently the formation of compound **IV** is catalyzed by products of photodegradation of the initiator, either cation-radical $Ph_2S^{+\cdot}$ or acid HPF_6 [4]. However the mechanism of their operation requires a special study.

Thus using UV irradiation and photoinitiators of radical and ionic polymerization of type **I** it is possible to perform the reaction between oxiranes and carboxylic acids at room temperature.

Cresyl glycidyl ether **II** (mixture of *ortho*- and *meta*-isomers) (Production Certificate ТУ 6 05-214-152-77) was distilled in a vacuum just before use. Epoxy groups content, %: found 25.91, calculated 26.23. Glacial acetic acid and triethylamine, both of "chemically pure" grade, were purified by distillation. Triphenylsulfonium hexafluorophosphate **I** was synthesized by procedure [6], mp 210–211°C (from aqueous methanol).

1-Acetoxy-2-hydroxy-3-cresoxypropane (IV). (a) A mixture of 17.3 g (0.11 mol) of ether **II**, 12.7 g (0.21 mol) of acid **III**, and 0.52 g of photoinitiator **I** was charged into a glass cell 0.5 cm thick tightly covered with a quartz lid, optically transparent for UV radiation of 254 nm wavelength. The reaction mixture was kept at constant temperature 25°C, and after irradiation for 1.5 h from a distance of 30 cm it was subjected to vacuum distillation to obtain 19.8 g (66%) of clear colorless liquid boiling at 170–175°C (14 mm Hg.), n_D^{20} 1.4561. IR spectrum, ν, cm^{-1}: 1110 (COC), 1230 (COC), 1610 (benzene ring), 1700 (C=C), 3400 (OH). ^{1}H NMR spectrum,

δ, ppm: 2.11 s [3H, $CH_3C(O)$], 2.30 s (3H, CH_3), 2.66 s (1H, OH), 3.80–4.30 m (5H, CH_2CHCH_2), 6.70–6.80 m, 7.07–7.18 (4H, C_6H_4).

(b) A reaction mixture containing 20.5 g (0.25 mol) of ether **II**, 15.0 g (0.12 mol) of acid **III**, and 1.1 g of triethylamine was heated at 100°C for 2.5 h, then it was washed with distilled water till neutral washings. The residue was distilled in a vacuum. We obtained 25.7 g (70%) of colorless liquid with bp. 170–175°C (14 mm Hg), n_D^{20} 1.4560. IR and ^{1}H NMR spectra of this compound are identical to those of compound obtained by procedure (a).

UV irradiation was carried with a mercury quartz lamp DRT-1000 with light intensity 9.2 W m^{-2} and wavelength 200–360 nm. IR spectrum was recorded on spectrophotometer UR-20 from mulls in mineral oil, ^{1}H NMR spectrum was registered on spectrometer Varian VXR-300 at operating frequency 299.943 MHz in deuterochloroform, internal reference TMS.

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