

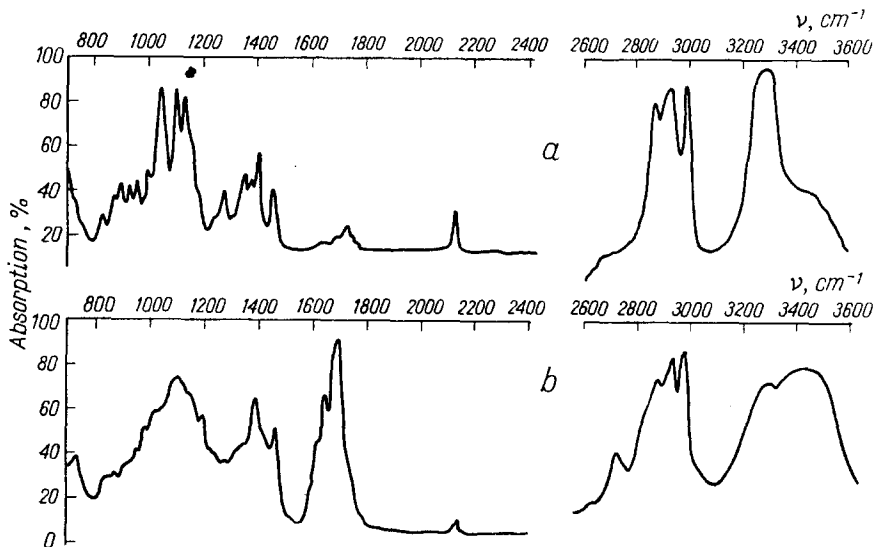
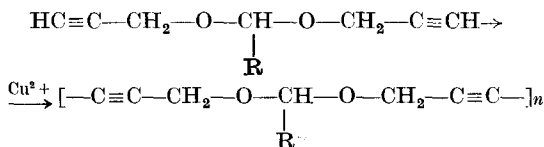
THE PREPARATION OF POLYETHERS BY OXIDATIVE POLYDEHYDROCONDENSATION OF DIPROPARGYL ACETALS*†

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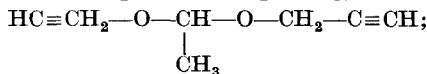
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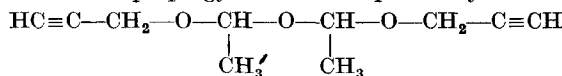
IN PREVIOUS communications [1-3] we have reported the use of the oxidative polydehydrocondensation of dipropargyl ethers and esters for the preparation of polyethers and polyesters. We also extended this reaction to the preparation of polyacetals according to the scheme:



Infrared spectra: *a*—dipropargyl acetal



b—dipropargyl acetal from paraldehyde



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† Communication IV in the series "The synthesis and study of polymers containing acetylenic bonds in the chain".

In the present paper an account is given of the synthesis of some dipropargyl acetals and the preparation of polyethers from these. The dipropargyl acetals were prepared from propargyl alcohol and aldehydes in the presence of acid catalysts. In an attempt to prepare a dipropargyl acetal from paraldehyde and propargyl alcohol two products were isolated—monopropargyl acetal and the dipropargyl acetal of the dimer of acetaldehyde of linear structure. The structures of these compounds were shown by elementary analysis, molecular refraction, molecular weight and infrared analysis (see diagram).

The polymers from the dipropargyl acetals, prepared by oxidative polydehydrocondensation are dark coloured, insoluble products, containing complexed copper.

EXPERIMENTAL

Dipropargyl formal. A mixture of 100 ml of 30% formalin, 110 ml of propargyl alcohol and 15 ml of conc. HCl was heated, with stirring, for 1½ hours. After cooling the mixture was washed with 10–15% aqueous potassium hydroxide and extracted twice with ether (100 ml portions). The solution was dried over anhydrous potassium carbonate and after distillation a substance of b.p. 44°/7 mm was obtained. According to the literature [4] b.p. 174°/760 mm. Yield 55% of theory, n_D^{20} 1.4350; d_4^{20} 0.9622; $MR_{\text{calc.}}$ 33.25; MR_{found} 33.62

Found, %: C 66.97; H 6.41
 $C_7H_8O_2$. Calculated, %: C 67.77; H 6.45

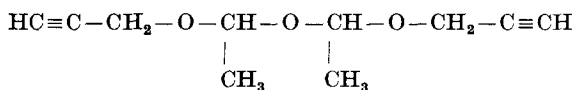
Dipropargyl acetal of acetaldehyde. A solution of 50 g of anhydrous calcium chloride in 320 g of propargyl alcohol was cooled to 0°, then 150 g of acetaldehyde was added. The mixture was shaken vigorously for 15 minutes and was then allowed to stand for 20 hours with occasional shaking. The product was washed with water and dried over anhydrous potassium carbonate. Distillation yielded dipropargyl acetal of b.p. 70–71°/6.5–7 mm, n_D^{20} 1.4459. Yield 60% of theory.

Found, %: C 69.51; 69.50; H 7.57; 7.41
 $C_8H_{10}O_2$. Calculated, %: C 69.56; H 7.24

Reaction of paraldehyde with propargyl alcohol. One hundred and five millilitres of paraldehyde, 100 ml of propargyl alcohol and 1.5 ml of conc. HCl were heated, with stirring, for 3½ hours at 110–120°. The mixture was neutralized with 10% aqueous sodium hydroxide and after the usual treatment was distilled under reduced pressure. This yielded fractions of b.p. 68–69°/1 mm and 62–63°/6–7 mm. Fraction 1: n_D^{20} 1.4479; d_4^{20} 1.1232; MR_{found} 43.27; $MR_{\text{calc.}}$ 44.00. Molecular weight (cryoscopic) 187, calculated 182.

Found, %: C 66.33; H 7.55
 $C_{10}H_{14}O_3$. Calculated, %: C 65.93; H 7.69

These results and the infrared spectrum are in agreement with the structure



Fraction 2 is the hemiacetal of propargyl alcohol

Found, %: C 60.37; H 8.31
 $C_5H_8O_2$. Calculated, %: C 60.00; H 8.00.

Dipropargyl benzal. Concentrated HCl (1.5–2 ml) was added to 101.5 ml of freshly distilled benzaldehyde then 115.6 ml of anhydrous propargyl alcohol was added dropwise over a period of an hour. The mixture was treated as for the other acetals and distilled. Dipropargyl benzal was obtained in 35% yield; b.p. 132°/2 mm; n_D^{20} 1.5200; d_4^{20} 1.0539; $MR_{\text{calc.}}$ 56.29; MR_{found} 57.25.

Found, %: C 77.42; H 6.00
 $C_{13}H_{12}O_2$. Calculated, %: C 78.00; H 6.00

Monopropargyl furfural was obtained from furfuraldehyde under similar conditions; b.p. 48–51°/3 mm.

Found, %: C 62.70; H 5.30
 $C_8H_6O_3$. Calculated, %: C 63.10; H 5.26

Polymers of the dipropargyl acetals were obtained by oxidative polydehydrocondensation, by the method described previously [1–3]. Dipropargyl benzal yielded a polymer, part of which is soluble in tetrahydrofuran (mol. wt. 585).

Found, %: C 71.47; H 6.10; ash 0.34
 $[C_{13}H_{12}O_2]_n$. Calculated, %: C 78.7; H 5.05

The insoluble polymer from dipropargyl benzal has the following composition:

Found, %: C 68.25; H 5.25; ash 4.84

The ash formed by combustion of the polymers is evidently the result of decomposition of complex copper compounds. The low carbon content can be explained by hydrolysis of the end groups of the polymers.

CONCLUSIONS

The dipropargyl acetals of acetaldehyde and benzaldehyde, which have not previously been described in the literature, have been prepared.

Polymers of a new type have been prepared by oxidative polydehydrocondensation of dipropargyl acetals and formals.

Translated by E. O. PHILLIPS

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