Synthesis and properties of 2,4-diallyloxy-6-phenoxy-1,3,5-triazine

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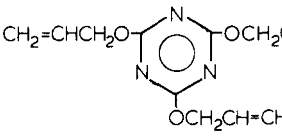
A method of obtaining 2,4-diallyloxy-6-phenoxy-1,3,5-triazine is described. Basic properties of the obtained monomer have been determined. The polymerization capabilities of the monomer have been demonstrated and some properties of the resulting polymer have also been described.

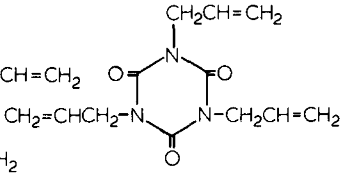
Keywords Cyanuric chloride; allyl alcohol; 1,3,5-triazine; synthesis; polymerization; properties; monomers; polymers

INTRODUCTION

1,3,5-Triazine-(cyanurates and isocyanurates)-allyl derivatives are used as polyfunctional monomers in homo- and copolymerization reactions used in producing special plastics[1-3]. The syntheses of triallyl cyanurate and isocyanurate are well documented[1-5].

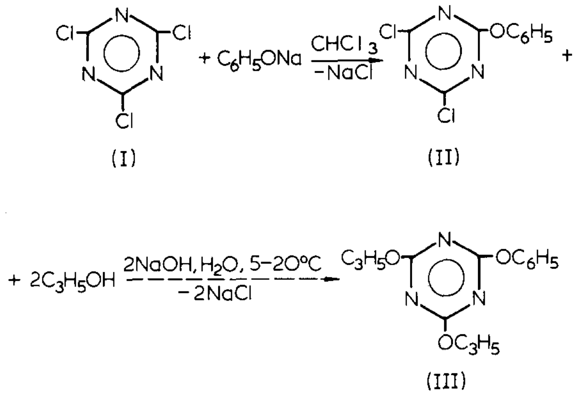


Triallyl cyanurate



Triallyl isocyanurate

However, this is not so in the case of 2,4-diallyloxy-6-phenoxy-1,3,5-triazine synthesis (III). This tetrafunctional monomer can be obtained by reaction of the known compound 2,4-dichloro-6-phenoxy-1,3,5-triazone (II)[6] with allyl alcohol in an aqueous sodium hydroxide solution[7]. The compound (II) is obtained from cyanuric chloride I.



EXPERIMENTAL

2,4-Dichloro-6-phenoxy-1,3,5-triazine (Hirt *et al.*[6]) was recrystallized from chloroform (M.p. 113°–114°C).

In a 2 dm^3 three-necked flask fitted with a mechanical stirrer, a reflux condenser and a thermometer, 2,4-dichloro-6-phenoxy-1,3,5-triazine (242 g (1 mole)) and allyl alcohol (174 g (3 moles)) were placed and mixed for 30 minutes and then cooled down to 5°C in an ice bath. 40% Aqueous sodium hydroxide (560 g) was added to the suspension at such a rate that the reaction temperature was between 5° and 20°C. Having added all the NaOH solution the reaction was allowed to continue for 2 hours at room temperature.

The crude product was extracted from the reaction mixture with carbon tetrachloride (600 cm^3). The organic phase was separated from the remaining solid by filtration and washed several times with water. The solvent was then distilled off under reduced pressure. Other impurities were removed by cooling at −5°C for 24 h. The precipitate was filtrated off and methyl alcohol was added dropwise to the filtrate up to the moment of appearance of a distinct opaque solution. The newly obtained precipitate of impurities was then filtrated off. Methyl alcohol and some other volatile components were distilled out from the filtrate under reduced pressure at a temperature below 140°C in the presence of copper filings. Crude 2,4-diallyloxy-6-phenoxy-1,3,5-triazine was separated from the filings and was subjected to column chromatography on aluminium oxide (Brockmann activity II–III), Merck. Benzene was used as eluent, column packing 400 mm, diameter 30 mm. The fraction of 2,4-diallyloxy-6-phenoxy-1,3,5-triazine in benzene was distilled under reduced pressure to remove the solvent. The final product was obtained in a 70–85% yield[7].

RESULTS AND DISCUSSION

A method of obtaining 2,4-diallyloxy-6-phenoxy-1,3,5-triazine was achieved. The resultant purified product is a dense, light yellow oily liquid whose physical parameters are as given in *Table 1*.

The i.r. spectrum shows the presence of the C–N bond in the triazine ring at 825 cm^{-1} and the C = C bond of the allyl group at 1585 cm^{-1}.

Table 1 Physical parameters at purified 2,4-dialkyloxy-6-phenoxy-1,3,5-triazine

	Found	Calculated
Molecular weight	284 ± 1	285.31
Nitrogen content (%)	14.6	14.73
Boiling point (°C)	237–239 (with polymerization)	
Density in 20°C (kg m^{-3})	1201	
Refraction index n_D^{20}	1.5467	–
Viscosity at 20°C (N s m^{-2})	$692.5 \cdot 10^{-3}$	–
Surface tension at 20°C (N m^{-1})	$27.16 \cdot 10^{-3}$	–

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The pure compound does not polymerize at room temperature and can be preserved without an inhibitor. 2,4-Diallyloxy-6-phenoxy-1,3,5-triazine at room temperature polymerizes very slowly in the presence of 0.1–0.5% dibenzoyl peroxide. An increase in temperature to 60°–80°C in the presence of 0.1% dibenzoyl peroxide causes a rapid polymerization of the compound, the first symptom of which can be observed after 90 min, and the hard polymer is ready after 270 min.

Without an initiator the polymerization starts after 60 min at 150°C and the reaction is rapid at the boiling point.

The polymerized 2,4-diallyloxy-6-phenoxy-1,3,5-triazine is a solid transparent light yellow compound and its physical, mechanical and thermal properties are given in *Table 2*.

Particular kinetic investigations of the homo- and copolymerization reactions, with chosen vinyl monomers, are presently being carried out. Their results will be published in a future paper.

Table 2 Physical, mechanical and thermal properties of poly(2,4-dialkyloxy-6-phenoxy-1,3,5-triazine)

Density (kg m^{-3})	1490
Tensile strength (Nm^{-2})	$391 \cdot 10^5$
Bending strength (Nm^{-2})	$108 \cdot 10^5$
Dynstat impact strength (Nmm^{-2})	$147 \cdot 10^2$
Brinell hardness	17.5
Vicat softening point (°C)	110
Temperature bending point under loading (°C)	91
Temperature half decomposition in air (°C)	318
Temperature half decomposition in nitrogen (°C)	340
Temperature decarbonization (°C)	380

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Activated derivatives of succinic and glutaric half-esters of polypropylene glycols, and their exchange reactions with hydroxy- and amino-compounds

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Succinic and glutaric halfesters of polypropyleneglycols have been prepared, and transformed into the corresponding imidazolides and benzotriazolides. The exchange reactions of the latter with hydroxylated and aminated compounds have been studied.

Keywords Functionalized oligomers; carboxylated polypropylene glycols; imidazolides; benzotriazolides; exchange reactions

INTRODUCTION

In previous papers we have described the ability of several polymeric and oligomeric activated esters and amides to react selectively with hydroxylated or aminated compounds, giving polymeric and oligomeric esters or amides which are not easily obtained by other means[1–4].

Other derivatives of similar activity were also prepared independently by Ringsdorf and his colleagues[5], and by Winston and Mazza[6]. The main purpose of these studies was to develop new synthetic routes to oligomeric or polymeric derivatives of pharmocologically active compounds.

Following this line, we thought it might be interesting to report on the synthesis of succinic and glutaric half-esters of polypropylene glycols, and of the corresponding imidazolides and benzotriazolides. The exchange reactions of the latter with model hydroxylated and aminated compounds were also studied.

Succinic and glutaric half-esters of polypropylene glycols

Polypropylene glycol samples (purchased from Fluka A.G., Buchs S.G., Switzerland) having $\bar{M}_n$ 425 (I) and 725 (II) were chosen as starting materials. Their succinic (III,

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