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Bifunctional initiators: synthesis of phenylazo-formamidoethyl 4-t-butylazo-4-cyanovalerate

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SUMMARY

The paper deals with the synthesis of the phenylazo-formamidoethyl 4-t-butylazo-4-cyanovalerate, a product which - by its two azo groups having different thermal stabilities - may be used in initiating processes of stepwise radicalic polymerization. The preparation is based on the condensation of the 4-t-butylazo-4-cyanovaleric acid chloride with N-hydroxy ethyl-phenylazoformamide (HEPF) in anhydrous chloroform, in the presence of pyridine. The initiator purification involves its passing over an alumina column, on using methylene chloride as eluent. HEPF is a new intermediate obtained by the reaction of the ethyl phenylazocarboxylate with ethanolamine. Both the HEPF structure and that of the bis-azo initiator is confirmed by elemental analysis and spectroscopic measurements (IR and ^{1}H-NMR spectra), as well.

INTRODUCTION

Aliphatic di- and polyazo compounds are accesible (MacLeay and Sheppard, 1976; Sheppard and MacLeay, 1976; MacLeay and Sheppard, 1978) by coupling - through a chemical reaction - between two or several monoazo derivatives, which are linked through certain reactive groups, esters, thioesters, amides, urethanes, carbamates etc. being formed. An important structural characteristic - besides the number of the constituting azo groups - derives from the nature of the groups adjacent to the nitrogen atoms, which can be alkyl, aryl or formyl rests. The last ones induce stability to the thermal cleavage to the -CO-N= bond, due to electron delocalization from nitrogen to oxygen-atom.

It is known that, when azo groups present in the structure of a certain compound show different thermal or photochemical stability, it may act as a stepwise generator of free radicals, playing the role of a sequential initiator in the successive polymerization of two vinyl monomers; thus "active" polymers with labile groups and finally, block copolymers are obtained (Sheppard and MacLeay, 1970; MacLeay and Sheppard, 1976; MacLeay and Sheppard, 1977; MacLeay and Sheppard, 1980).

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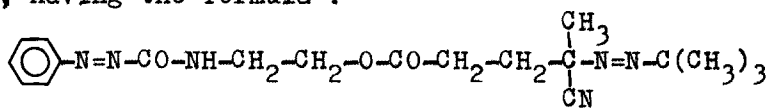
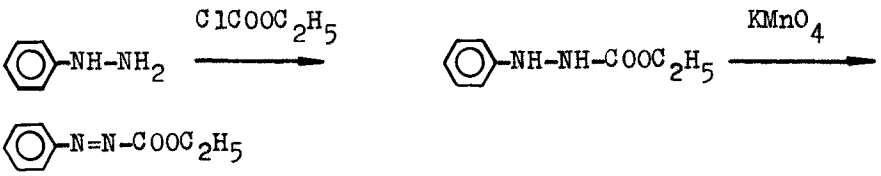
RESULTS AND DISCUSSION

The paper relates on the synthesis of a new bis-azo initiator, the phenylazo-formamidoethyl 4-t-butylazo-4-cyanovalerate, having the formula :

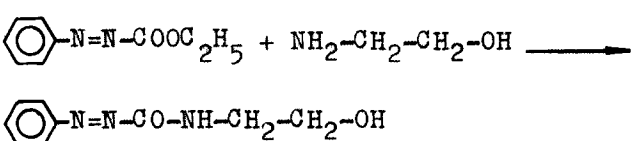


The arylcarbonylazo group, due to its extended conjugation, shows and increased thermostability, as compared to the dialkylazo one.

The synthesis involves two monoazo intermediates: N-hydroxyethyl-phenylazoformamide (HEPF), an azo-hydroxylic compound, and the 4-t-butylazo-4-cyanovaleric acid chloride (BACV chloride). The former one, the HEPF, is obtained through several consecutive reactions, in which the starting substance is the phenylhydrazine; on treatment with ethyl chloroformate, it is transformed into ethyl phenylhydrazo carboxylate, this being finally oxidized with $KMnO_4$ at ethyl phenylazocarboxylate (EPAC) (Heller, 1891; Widman, 1895).



The azoester, a red liquid, is quite stable on heating, so that it can be purified by distillation at reduced pressure. For the obtainment of HEPF, the EPAC is submitted to condensation with ethabolamine, in ethanol, under cooling.



After removing the solvent, the azo-alcohol crystallizes quite slowly, through repeated washings with non-polar solvent (carbontetrachloride, petroleum ether) or by extraction with benzene.

The structure of the new intermediate, HEPF, is confirmed by elemental analysis and spectroscopic measurements, as well. The IR spectrum contains the following bands: ν_{CO} amide I (1715 cm^{-1}), ν_{NH}(3310 cm^{-1}), ν_{OH}(3460 cm^{-1}), $\nu_{C=C}$(1595 cm^{-1}), $\nu_{N=N}$(990 cm^{-1}), ν_{CH}(2885, 2940 and 2960 cm^{-1}), $\nu_{=CH}$(3080 cm^{-1}) etc.

The ^{1}H-NMR spectrum, recorded in $CDCl_3$, evidences resonance signals of the phenyl, CH_2-N, OH, NH protons of relative intensities, corresponding to the number and type of pro-

tons (Fig. 1).

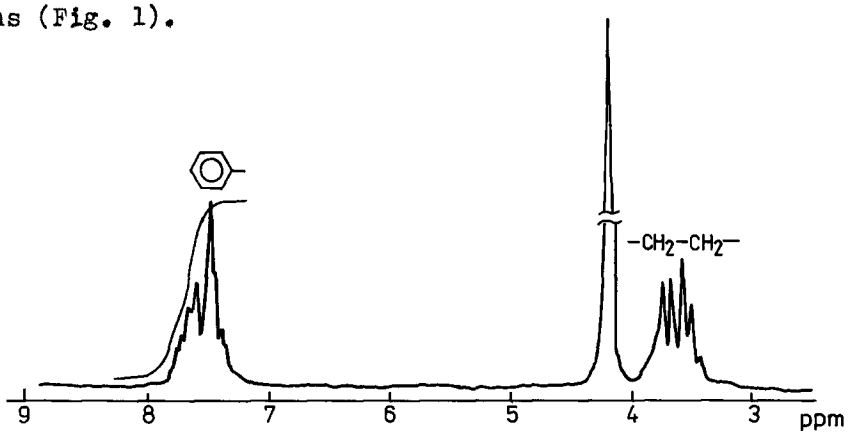
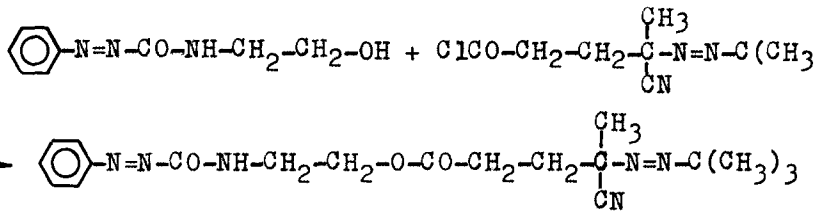


Fig. 1 The ^{1}H-NMR spectrum ($CDCl_3$) of N-hydroxyethyl-phenylazoformamide

For the synthesis of the second intermediate, the BACV chloride, the BACV acid has been first prepared from t-butylhydrazine chlorhydrate, natrium cyanide and levulinic acid, through an intermediate stage of t-butylhydrazovaleric acid, which has been oxidized with bromine at the azoacid (Sheppard, Bafford and MacLeay, 1969; Sheppard and MacLeay, 1977). The transformation into acid chloride has been carried out with phosphorus pentachloride, in anhydrous benzene. The synthesis of the bis-azo initiator involves the condensation of the HEPF with the BACV chloride, an ester link being thus formed.



The reaction takes place in anhydrous chloroform, in the presence of pyridine, on cooling at 0°C. After successive washings with water, diluted solutions of H_2SO_4 and Na_2CO_3 and again water, the chloroformic solution of the initiator is concentrated by partial distillation of the solvent, then chromatographically purified on an alumina column, on using methylene chloride as eluent.
The azo ester is an orange, viscous liquid, insoluble in petroleum ether, hexane, etc. yet soluble in chloroform, methylene chloride, methanol, acetone, etc.
Its structure has been confirmed by elemental analysis as well as by spectroscopic investigations. The IR spectrum contains the ν_{CO} ester band and ν_{CO} amide I one, at 1740 and 1715 cm^{-1}, respectively. Absorptions at high fre-

quencies of 3310-3360, 3080 cm^{-1} are due to NH stretching vibrations. Peaks corresponding to C-H bonds (2985, 2945, 2885 cm^{-1}), δ_{CH_3}(1372 cm^{-1}), ν_{CN}(2245 cm^{-1}), $\nu_{N=N}$(980 cm^{-1}) etc. are also identified in the spectrum.
The ^{1}H-NMR spectrum shows resonance signals centered on the following (ppm) values: 1.25 (singlet, 9 protons $C(CH_3)_3$; 1.6 (singlet, 3 protons $CH_3-\overset{|}{C}-CN$); 2.38 (4 protons $-CO-CH_2-CH_2-C-CN$); 3.7 (triplet, 2 protons $CH_2-NH-CO$); 4.3 (triplet, 2 protons $-CO-O-CH_2$); 7.06 (1 proton NH); 7.25; 7.4; 7.75 (5 protons phenyl). The $-CO-CH_2-CH_2-\overset{|}{C}-$ protons are not coupled as in the spectrum of the BACV acid, due to chemical equivalency (Fig. 2).

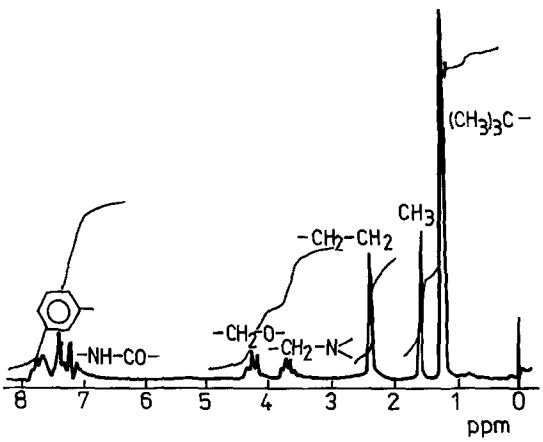


Fig. 2 The ^{1}H-NMR spectrum ($CDCl_3$) of Phenylazo-formamidoethyl 4-t-butylazo-4-cyanovalerate

EXPERIMENTAL

N-Hydroxyethyl-azoformamide (HEAF)

4g (0.0022 mole) of EPC are dissolved into 2o mL ethanol, 1.5 mL (0.025 mole) of ethanolamine, solved in 5 mL ethanol, being dropwise added for 1/2 hour, to the solution cooled with ice and salt. The mixture is further stirred, on cooling for 2 hours and then for 1 hour at room temperature and left still overnight. On removing the solvent under reduced pressure, a viscous, reddish-orange liquid is obtained, which crystallizes by rod-rubbing and washing with petroleum ether and CCl_4 (m.p. 59-60°C from benzene).

Phenylazo-formamidoethyl 4-t-butylazo-4-cyanovalerate

5.8 g (0.03 mole) of HEAF are dissolved into 25 mL chloroform and cooled with ice and salt at -5°C. Over the solution, 2.83 mL (0.035 mole) of pyridine are dropped, the BACV acid chloride (prepared from 7.4 g (0.025 mole) BACV acid and

solved into 20 mL chloroform) being then added - for 1 hour. The mixture is stirred for other 5 hours, while maintaining the temperature between 0-5 °C; then it is left overnight at room temperature. The chloroformic solution of the inititor is washed with water, 5 % solutions of H_2SO_4 and Na_2CO_3 and again with water, then it is dried over natrium sulphate. After concentration by distillation under reduced pressure, the solution is passed over an alumina column and elluted with methylene chloride (the operation being repeated). On removing the solvent under reduced pressure, a dense, orange liquid is obtained, which is soluble in methylene chloride, chloroform, acetone, methanol, benzene, yet insoluble in carbontetrachloride, hexane, petroleum ether.

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