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The Preparation of a New Series of α, α-Disubstituted Vinyl Monomers

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Summary

A few α,α-disubstituted vinyl monomers were prepared for the first time: They have been polymerized and characterization of these polymers is in progress.

We would like to report the syntheses of methyl α-phenoxymethylacrylate (MPMA), methyl α-para-cresoxymethylacrylate (MCMA) and methyl α-para-nitrophenoxymethylacrylate (MNMA), hitherto not reported in the literature. The method, consisting of four steps, involves well-studied organic reactions.

Step 1 (WELCH, 1930)

$$CH_2(CO_2C_2H_5)_2 + 2HCHO \xrightarrow[\text{pH } 8.5, 15\,°C]{K_2CO_3} \underset{I}{(CH_2OH)_2C(CO_2C_2H_5)_2}$$

Step 2 (FERRIS, 1955)

$$I + 4HBr \longrightarrow \underset{II}{(CH_2Br)_2CHCO_2H} + 2C_2H_5Br + 2H_2O + CO_2$$

Step 3

$$II + CH_3OH \xrightarrow{\text{conc. } H_2SO_4} \underset{III}{(CH_2Br)_2CHCO_2CH_3} + H_2O$$

In this reaction, one mole of II was combined with 250 ml of methanol and 3 ml of conc. sulphuric acid and refluxed for 12 hours. The reaction mixture was extracted with 100 ml of water, the nonaqueous layer was dried over anhydrous sodium sulfate and distilled to remove the methanol. The remaining liquid distilled under 5 mm Hg, resulted in 70 % yield of the ester III. It is a colorless liquid of b.p. 70-72 °C/5 mm.

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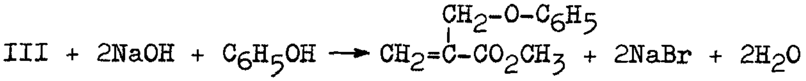
Step 4



$$\text{III} + 2\text{NaOH} + C_6H_5OH \longrightarrow CH_2{=}\overset{\overset{\displaystyle CH_2\text{-}O\text{-}C_6H_5}{|}}{C}\text{-}CO_2CH_3 + 2\text{NaBr} + 2H_2O$$

For this reaction, 0.5 mole of III was slowly added to a well-dissolved mixture of one mole each of sodium hydroxide and phenol in 200 ml of methanol. After the addition of the ester, the contents were stirred for 6 hours and the methanol was distilled off. The residual liquid was extracted with ether, washed with 10 % sodium hydroxide and 50 ml of water, and then dried over anhydrous magnesium sulfate. Removal of ether, followed by vacuum distillation, gave a colorless liquid of b.p. 85°C/2 mm. MPMA is immiscible with water, but it is freely miscible with benzene, toluene, n-hexane, n-heptane, petroleum ether, diethyl ether, diisopropyl ether, methanol, ethanol, dimethyl formamide, chloroform, carbon tetrachloride and trifluoroacetic acid.

The preparations of MCMA and MNMA were similar; instead of phenol, para-cresol, and para-nitrophenol, respectively, were used in step 4. MCMA is a colorless liquid of b.p. 80°C/2 mm but MNMA is a crystalline solid of m.p. 103°C (uncorrected). In their solubility they resemble MPMA.

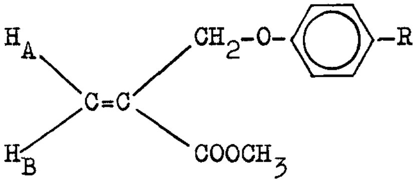
The IR spectra of these compounds contain strong absorption bands at 1605 cm^{-1} and 1650 cm^{-1} pertaining to $>C{=}C<$ function and α,β-unsaturated carbonyl function, respectively.

The nmr spectra of the compounds were taken at room temperature, 1 % w/v solution in trifluoroacetic acid, in a Varian 60 MHz spectrometer. The nmr spectrum of MPMA: ^{1}H-nmr 6.6δ multiplet for the five phenyl protons, 6.1δ and 5.7δ for the two unsymmetrical protons (H_A and H_B) at the β-carbon atom, 4.4 δ for the $>CH_2$ and 3,45 δ for the methoxy methyl protons. Integration heights are in the expected ratios for the number of protons. The nmr spectrum of MCMA (^{1}H-nmr 6.6δ , 6.1δ and 5.7δ , 4.4δ , 3.5δ and 3.45δ) resembles that of MPMA with the additional signal at 3.5δ for the methyl group in para-cresol. The nmr spectrum of MNMA yields a AB quadret for the phenyl protons, one pair at 6.65δ and 6.8 δ and the other at 7.8δ and 8.0 δ (^{1}H - nmr, 8.0δ and 7.8 δ and 6.8 δ and 6.65 δ , 4.4 δ , 3.45 δ).

Elemental analyses:

Compound	Theoretical			Experimental		
	C	H	N	C	H	N
MPMA	68.73	6.30	-	67.69	6.54	-
MCMA	69.91	6.79	-	70.02	6.60	-
MNMA	55.70	4.67	5.91	55.90	4.68	5.74

With these facts, the structures assigned are



R = H (MPMA), CH_3 (MCMA) and NO_2 (MNMA).

All the monomers have been polymerized thermally and photochemically. The thermal polymerization of the monomers was carried out at 80°C in dimethylformamide, using AIBN catalyst. The monomers underwent photopolymerization at 3000 Å and 3600 Å and at room temperature (27°C), in n-hexane; benzoin was used as a sensitizer. In both methods the ratio between catalyst and monomer was maintained at 1:50, throughout. The yields in photopolymerization were quantitative, but varied between 10-20 % for thermal polymerization.

Characterization of these polymers is in progress.

Acknowledgements

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