ACYLATION OF AMINOAROMATIC CARBOXYLIC ACIDS BY METHACRYLYL CHLORIDE

N. M. Ezhova, E. A. Kulina, and N. N. Kuznetsova

The N-methacryloylaminoarylcarboxylic acids are monomers, which are reactive in homo- and copolymerization reactions [1, 2]. The synthesis of methacrylamide derivatives of some aromatic acids has made it possible to ascertain some features of the influence of the structure of aromatic acids on the acylation reaction under various conditions. The original aromatic acids selected were p-aminosalicylic (I), p-aminobenzoic (II), and 5-aminoisophthalic acid (III).

As the basicity of the amine increases, the rate of the acylation of the aromatic amines by acid chlorides, anhydrides, and other acylating agents increases [2]. The basicity of the amine has an effect on the stability of the amide linkage formed and, therefore, on the rate of the reverse alkaline hydrolysis reaction. In the case of unsaturated amides, the charge on the N atom also determines the polarizability of the double bond and, therefore, its reactivity in polymerization reactions, which also influence the yield of the amide when it is synthesized as a result of the secondary polymerization process. The literature offers information on the acylation of aromatic amines in nonaqueous media [2], as well as by the method of interphase condensation [3]. In these cases, the yield of the amide is increased owing to the lowering of the rate of hydrolysis of the acylating agent and the amide in comparison to acylation in an aqueous medium in the presence of alkali.

The basicity of the amino group in the acids indicated apparently decreases along the series I > III > II. For the purpose of studying the influence of the synthesis conditions on the yield and purity of the monomers, the acylation was carried out in an aqueous medium in the presence of alkali (Schotten-Baumann reaction), in a nonpolar organic solvent in the presence of a tertiary amine, and by the method of interphase condensation.

The optimal acylation conditions (the highest yield and the shortest reaction time) in the various media are determined by the basicity of the amine and the structure of the monomer formed (Table 1). Upon acylation in an aqueous alkaline solution over the course of 6 h, I produces a high yield of N-methacryloyl-p-aminosalicylic acid (Ia). Compounds II and III produce low yields of IIa and IIIa, respectively. When the reaction mixture is held for 24 h, the yield of Ia is increased slightly, that of IIIa is decreased, and IIa could not be isolated. In the case of Ia it is possible to recover the monomer in the form of the water-soluble Na salt (Ib), while the production of the very reactive compounds IIb and IIIb does not occur under these conditions. In the case of acylation under the conditions of interphase condensation and in nonaqueous media, the yields of IIa and IIIa are increased significantly.



The high resistance of the amide linkage in Ia to alkaline hydrolysis in comparison to the other monomers is apparently due to the weakening of the acceptor effect of the carboxyl group caused by the ortho effect [4]. The amide linkage least resistant to alkaline hydrolysis is that in IIa, owing to the very strong acceptor influence of the carboxyl group located in the para position (direct polar conjugation). Compound IIIa probably occupies an intermediate position because of the weak transmission of the conjugation effect from the meta position of the benzene ring.

Institute of High-Molecular-Weight Compounds, Academy of Sciences of the USSR, Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 352-354, February, 1980. Original article submitted June 27, 1978.

TABLE 1. Yield of Monomers as a Function of the Acylation Conditions

	Yield of monomer, %					
Monomer	aqueo medio $\tau = 6 h$	bus tr=24 h	interphase condensa - tion at 20°C, $\tau = 3 h$	nonaque - ous med. at 5°C, τ = 6 h		
(Ia) (IIa) (IIIa)	77 28 30	83 0 16	65 75 50	65 75 85		

TABLE 2. Characteristics of the Monomers Obtained

Monomer	mp, ° C	Found/Calculated, %			
		с	H	N	Double bonds,• %
(I a)	220	<u>59,73</u> 59,78	<u>5,01</u> 5,21	<u>6,33</u> 6,27	100
(I p)	257	<u>54,35</u> 54,43	4,14 4,31	<u>5,77</u> 5,75	-
(I! <u>a</u>)	219	<u>64,38</u> 64,33	<u>5,72</u> 5,83	6,82 6,86	100
(IIJa)	297	$\frac{57,83}{57,94}$	4,45 4,34	5,62 5,73	100

*Catalytic hydrogenation in DMFA on PdCO₃.

The identification of the compounds synthesized was carried out with the aid of elemental analysis, IR spectra, and the determination of functional groups. Table 2 presents the characteristics of the monomers synthesized.

EXPERIMENTAL

Acylation of I in the Schotten-Baumann Reaction. A solution of 21.1 g (0.1 mole) of sodium p-aminosalicylate dihydrate in 40 ml of water was given simultaneous dropwise additions over the course of ~1 h of 13 g (0.125 mole) methacrylyl chloride and 60 ml of 2 N NaOH (with maintenance of pH 9-10) at a rate which guarantees a temperature of the mixture in the 0-2°C range. Then the temperature was gradually increased over the course of 2 h to ~20°C. The transparent solution was filtered and left overnight in a refrigerator. The precipitating characteristic needles of Ib were filtered, washed, and recrystallized from 95% aqueous propanol. The yield was 55-60%. Compound Ia was recovered from the filtrate by acidification to pH 1, filtered, washed with water, and recrystallized from 50% aqueous ethanol. The yield was 20-30%. If the reaction mixture is held for 5 h at 0°C, and then the solution is filtered and cautiously acidified with stirring, Ia is isolated with a 77% yield.

Acylation of II under the Conditions of Interphase Condensation. A solution of 13.7 g (0.1 mole) of II in 75 ml of 2 N NaOH was given a dropwise addition over the course of 30 min at 20°C of 13 g (0.125 mole) of methacrylyl chloride in 40 ml of CHCl₃ with vigorous stirring and cooling of the flask by cold water. The mixture was held at 20°C for 2.5 h, filtered, and recrystallized from 30% aqueous ethanol. The yield of the product was 75%.

Acylation of III in a Nonaqueous Medium. A mixture of 18.1 g(0.1 mole) of III, 14 ml of dimethylaniline, and 50 ml of benzene was given a dropwise addition of 13 g(0.125 mole) of methacrylyl chloride over the course of 0.5 h at $3-5^{\circ}$ C and held for 5.5 h. The filtrate was washed free of dimethylaniline hydrochloride with 500-600 ml of 3 N HCl and water, dried, and recrystallized from 30% aqueous ethanol. The yield of the product was 85%.

CONCLUSIONS

1. The applicability of the method of interphase condensation to the acylation of several aminoarylcarboxylic acids has been demonstrated. 2. New methacrylamide derivatives of the acids indicated have been synthesized.

LITERATURE CITED

- 1. N. N. Kuznetsova, K. P. Papukova, N. M. Myagkova-Romanova, and G. V. Samsonov, Inventor's Certificate, No. 384,841 (1971); Byull. Izobr., No. 25 (1973).
- 2. M. M. Koton, T. A. Sokolova, and G. M. Chetyrkina, Zh. Obshch. Khim., 27, 185 (1957).
- 3. A. M. Shur, M. A. Rekhter, and R. I. Ishchenko, Izv. Akad. Nauk MoldSSR, Ser. Biol. Khim. Nauk, <u>6</u>, 56 (1968).
- 4. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry [in Russian], Izd. Rostovsk. Univ. (1966), p. 343.

SYNTHESIS AND PLASMA-CHEMICAL POLYMERIZATION OF $\alpha_{,\beta}$ -DIFLUORO- β -CHLORO DERIVATIVES OF STYRENE AND VINYLPYRIDINE

L. F. Rybakova, R. S. Sorokina,

A. B. Gil'man, G. A. Grigor'eva,

V. M. Kolotyrkin, and K. A. Kocheshkov*

According to the data in [1], α_{β} -difluoro- β -chlorostyrene has a low capacity for the formation of homopolymers in radical polymerization reactions. This is apparently attributable to the absence of coplanarity in the configuration of the CF = CFCl group [2], owing to the existence of steric hindrances caused by the presence of bulky substituents both on the α and on the β C atoms in the vinyl group. In the present communication we report a method for the synthesis of homopolymers of $\alpha_{\beta}\beta$ -difluoro- β -chlorostyrene (DFCS) and 2-[$\alpha_{\mu}\beta$ -difluoro- β -chlorovinylpyridine] (DFCVP) by polymerization in the plasma of a glow discharge [3]. The polymers can be obtained in the form of thin films (with a thickness ranging from several hundred Angstrom units to several microns) on backings made from various metals, glass, etc.

UDC 542.91: 66.095.26: 547.539: 547.822.5

EXPERIMENTAL

The condensation of the organometallic compounds with trifluorochloroethylene was carried out in an atmosphere of dry argon. The analysis of the reaction products was carried out on a Tsvet-4 chromatograph with a thermal-conductivity detector in a $2 \text{ m} \times 3 \text{ mm}$ column with 15% Apiezon L on Chromaton N-AW (0.2 mm). The carrier gas was helium (60 ml/min), and the working temperature was 140°C. The IR spectra of DFCS and DFCVP were recorded on a UR-20 spectrophotometer in the 400-4000-cm⁻¹ region in CCl₄ and CS₂.

 α_{β} -Difluoro- β -chlorostyrene (DFCS) was synthesized according to [4], 70% yield, bp 60-70°C (15-17 mm), n_{D}^{20} 1.5231. 2-[$\alpha_{\beta}\beta$ -Difluoro- β -chlorovinylpyridine] (DFCVP) was synthesized according to the following method. In a solution of 2-pyridyllithium, which was obtained from 31.6 g of 2-bromopyridine and 12.8 g of n-BuLi in 400 ml of ether, 50 g of CF₂=CFCl were condensed at a rate such that the temperature of the mixture should not exceed -70 to -65°C. The mixture was stirred at that temperature to a negative Hillman reaction, then maintained at ~20°C, and decomposed by cooled dilute HCl. The ether layer was separated, and the aqueous layer was extracted with ether. The combined ethereal extracts were washed with water and dried by Na₂SO₄. The ether was distilled off, and the residue was vacuum distilled. This yielded 15 g (35%) of DFCVP, bp 103-105°C (35 mm) n_D²⁰ 1.5210. Found: C, 48.08; H, 2.58; Cl, 20.18; N, 7.97%. Calculated for C₇H₄ClF₂N: C, 47.89; H, 2.29; Cl, 20.19; N, 7.98%.

*Deceased.

L. Ya. Karpov Physicochemical Institute, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 355-358, February, 1980. Original article submitted August 3, 1978.