SYNTHESIS AND HERBICIDAL ACTIVITY OF 4-CHLORO-2-NITROANILIDES OF α,β-UNSATURATED ACIDS

L. V. Molchanov, Ch. Sh. Kadyrov,
and A. T. Ayupova

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The acylation of 4-chloro-2-nitroaniline by α,β-unsaturated acids in the presence of a threefold excess of phosphorus pentoxide has been studied. The 4-chloro-2-nitroanilides of acrylic, methacrylic, crotonic, cinnamic, β,β-dimethylacrylic, and α,β,β-trichloroacrylic acids have been obtained for the first time.

Many carboxylic acid anilides possess pesticidal activity [1]. They are typical inhibitors of photosynthesis [2]. Particular interest is presented by anilides containing chlorine atoms in the benzene ring [3], the majority of which exhibit a herbicidal action.

With the aim of synthesizing 4-chloro-2-nitroanilides of carboxylic acids, we have studied the acylation of 4-chloro-2-nitroaniline by α,β-unsaturated acids (acrylic, methacrylic, cortonic, β,β-dimethacrylic, α,β,β-trichloroacrylic, and cinnamic).

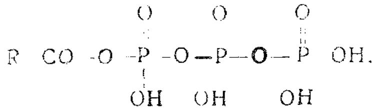
In order to obtain acylation products of 4-chloro-2-nitroaniline, which is weakly basic and is spatially hindered by the nitro group, we attempted to direct the reaction by the A_{AC_1} mechanism, i.e., to perform it in the presence of acids. For such reactions the influence of spatial factors is less characteristic. Furthermore, in this case an activation of the carbonyl group is possible [4]. In actual fact, good yields of the products of the acylation of 4-chloro-2-nitroaniline were obtained by using phosphorus pentoxide taken in threefold excess:

I $R=R'=R''=H$ III. $R=CH_3$; $R'=R''=H$ V. $R=R'=R''=Cl$

II. $R=R'=H$; $R''=CH_3$ IV. $R=R'=CH_3$; $R''=H$ VI. $R=C_6H_5$; $R'=R''=H$

A decrease in the amount of phosphorus pentoxide led to a fall in the yields of acylation products (below 25%).

We assume that the acylating agent in these reactions is a compound of the type of phosphates and triphosphoates of organic acids:



$$R\,CO{-}O{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}\,OH.$$

In favor of this assumption are the results of an investigation on the carbamoylation of amino acids by carbamoyl phosphate in the presence of enzymes [5]. Triphosphates are reagents with a large store of energy. Their formation explains the possibility of the acylation of even weak bases by acids.

The structures of the compounds synthesized were confirmed by the results of an elementary analysis and of IR and PMR spectroscopy.

A study of the pesticidal activity of the new 4-chloro-2-nitroanilides of α,β-unsaturated acids obtained has shown that they possess a moderate herbicidal activity.

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TABLE 1. Physical Constants of the Anilides

4-Chloro-2-nitroanilides of α,β-unsaturated acids	mp, °C; solvent	Yield, %	Chemical shifts of the protons in the PMR spectra, (δ, ppm; relative to HMDS)		
			olefinic	methyl	aromatic
Acrylic (I)	120–121, (hexane)	52	5,98–6,20 (multiplet) 5,5–5,9 (multiplet)		(H_3, H_5, H_6) 7,70–7,9; 7,12 7,4; 8,01–8,25
Methacrylic (II)	117 119, (hexane)	60	5,3–5,8 (multiplet)	1,5–1,82 (split doublet)	7.7–7,9; 7 12–7,42; 8,03–8,33
Crotonic (III)	155–156, (ethanol)	50	6,5–7,00 (multiplet) 5,6–6,1 (multiplet)	1,4–1,7 (split doublet)	7 7–8,00; 7 1–7,4; 8,02–8,4
β, β-Dimethylacrylic (IV)	137–138, (ethanol)	64	5,4 5,6 (multiplet)	1,4–1,7 (split doublet)	7,69–7,80; 7,03–7,4; 7,90 8,12
α,β,β-Trichloroacrylic (V)	118 118,5, (ethanol)	58			7,7–7,9; 1 7,5: 8 00–8,33
Cinnamic (VI)	158–159, (benzene)	65	6,1–6,5 (multiplet) 7,48–7.73 (multiplet)		7,73–7,83; 7,1–7 4; 8,02–8,3 6,7 7,22 (multiplet, second aromatic ring)

EXPERIMENTAL

The results of elementary analysis corresponded to the calculated figures, and the IR spectra of all the compounds obtained contained the absorption bands in the 1700-1690 cm^{-1} region that are characteristic for an amide carbonyl and at 3400-3300 cm^{-1} for an NH group. PMR spectra were taken on a JNM-4H-100/100 MHz instrument in trifluoroacetic acid.

Preparation of the 4-Chloro-2-nitroanilides of α,β-Unsaturated Acids. A. A mixture of 1.72 g (0.01 mole) of 4-chloro-2-nitroaniline, 1.44 g (0.02 mole) of purified acrylic acid, and 4.62 g (0.03 mole) of phosphorus pentoxide in 20 ml of absolute xylene was boiled for 30 min. The xylene layer was run off and the solvent was distilled off in the hot state. The crystals of product that deposited on cooling were filtered off and recrystallized from hexane. This gave 1.18 g (52%) of the 4-chloro-2-nitroanilide of acrylic acid (I) mp 121-122°C. Compounds (II), (III), (IV), and (VI) were obtained similarly (Table 1).

B. A mixture of 1.72 g (0.01 mole) of 4-chloro-2-nitroaniline, 2.63 g (0.015 mole) of α,β,β-trichloroacrylic acid, and 4.62 g (0.03 mole) of phosphorus pentoxide was heated at 150°C for 2 h. The reaction mixture, which had crystallized on cooling was treated with water, the water was poured off, the solid matter was filtered off, and it was recrystallized from 75 ml of ethanol. After recrystallization, 1.9 g (52%) of the 4-chloro-2-nitroanilide of α,β,β-trichloroacrylic acid (V) was obtained with mp 118-120°C.

CONCLUSION

The synthesis of 4-chloro-2-nitroanilides of acrylic acids, not previously described in the literature, had been performed by using a threefold excess of phosphorus pentoxide. Their herbicidal activity has been studied.

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