SYNTHESIS AND PESTICIDAL ACTIVITY OF N,N'-DIACYL DERIVATIVES OF 4-CHLORO-1,2-PHENYLENEDIAMINE

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

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The acylation of 2-aminoacyl-4-chloroanilines with acid anhydrides has given N,N'-diacyl derivatives of 4-chloro-1,2-phenylenediamine. Their fungicidal activities have been investigated. It has been shown that in cotton plants they are converted into 2-alkyl-5-chlorobenzimidazoles.

N,N'-Disubstituted derivatives of o-phenylenediamine, just like N,N'-dialkyl allophanate derivatives of 1,2-phenylenediamine, have come into wide use as systemic fungicides [1].

It is considered that the fungicidal action of such compounds is connected with their conversion into benzimidazole derivatives [2].

The aim of the present work was to obtain N,N'-diacyl derivatives of 1,2-phenylenediamine which may also be converted into benzimidazoles in plants.

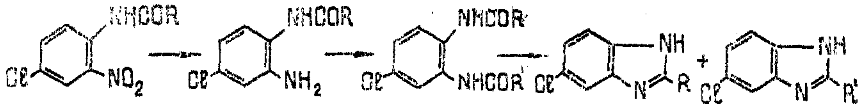
The direct acylation of o-phenylenediamines leads to the closure of a ring [3], and we therefore used an indirect route. The N,N'-diacyl derivatives of 4-chloro-1,2-phenylenediamine were synthesized by heating carboxylic acid 2-amino-4-chloroanilides in an excess of the corresponding acid anhydrides. The aniline derivatives were obtained by the reduction of the 4-chloro-2-nitroanilides with hydrazine hydrate in the presence of Raney nickel in an open vessel [4]. The initial carboxylic acid 4-chloro-2-nitroanilides were obtained by a method which we have proposed previously [5].

Below we give the physical constants of the 2-amino-4-chloroanilides:

2-Amino-4-chloroanilides of the following carboxylic acids	Yield, %	mp, °C (solvent)	Cyclization product
Acetic	75	143 (water)	5-Chloro-2-methylbenzimidazole
Propionic	80	121-122 (water)	5-Chloro-2-ethylbenzimidazole
Butyric	60	133-134 (water)	5-Chloro-2-propylbenzimidazole
Isobutyric	75	174-175 (water)	5-Chloro-2-isopropylbenzimidazole
Valeric	62	171-172 (aq. ethanol)	5-Chloro-2-butylbenzimidazole

The structures of the compounds obtained were shown by independent synthesis, i.e., the 2-amino-4-chloroanilides were converted by the action of 4 N hydrochloric acid into the 2-substituted 5-chlorobenzimidazoles, the physicochemical properties of which coincide with those of the 2-substituted 5-chlorobenzimidazoles obtained by a different method [6].

The desired N,N'-diacyl derivatives of 4-chloro-1,2-phenylenediamine were obtained by the following scheme:



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The physical constants of the N,N'-diacyl-substituted 4-chlorophenylenediamines were as follows:

	N,N'-Disubstituted 4-chloro-1,2-phenylenediamines	R	R'	Yield, %	mp, °C
I.	N,N'-Diacetyl	CH_3	CH_3	60	194—196
II.	N-Acetyl-N'-propionyl	CH_3	C_2H_5	82	195—196
III.	N-Acetyl-N'-butyryl	CH_3	C_3H_7	90	166—167
IV.	N-Propionyl-N'-acetyl	C_2H_5	CH_3	88	185—186
V.	N,N'-Dipropionyl	C_2H_5	C_2H_5	84	155—156
VI.	N-Propionyl-N'-butyryl	C_2H_5	C_3H_7	89	171—173
VII.	N-Butyryl-N'-acetyl	C_3H_7	CH_3	86	170—171
VIII.	N-Butyryl-N'-propionyl	C_3H_7	C_2H_5	82	150—152
IX.	N-Valeryl-N'-acetyl	C_4H_9	CH_3	80	160—162
X.	N-Valeryl-N'-propionyl	C_4H_9	C_2H_5	75	145—147
XI.	N-Isobutyryl-N-acetyl	C_3H_7-iso	CH_3	65	158—159

The structures of the compounds synthesized were confirmed by their IR and mass spectra. The IR spectra of the initial 2-amino-4-chloroanilides contained bands at 3480 and 3445 cm^{-1} corresponding to the absorption of a primary amino group (NH_2). The presence of a band at 1460 cm^{-1} can be ascribed to the deformation vibrations of the amino group. In the spectra of compounds (I-XI) these bands were absent, while two new bands were observed in the regions of 1665 cm^{-1} (amide I) and 1525 cm^{-1} (amide II). The mass spectra of the N,N'-disubstituted 4-chloro-1,2-phenylenediamines showed the peaks of the molecular ions, the subsequent fragmentation pathways of which were characterized by the initial ejection of the acyl groups $(R{-}CO)^+$ and $(R'{-}CO)^+$.

The results of a study of the pesticidal activities of the N,N'-diacyl-4-chloro-1,2-phenylenediamines synthesized for the first time showed that they exhibited a weak fungicidal activity. A study of their biochemical transformations in cotton plants using N-acetyl-N'-propionyl-4-chloro-1,2-phenylenediamine (II) as an example confirmed our assumption that they would be converted into benzimidazole derivatives — 2-alkyl-5-chlorobenzimidazoles.

EXPERIMENTAL

Mass spectra were taken on a MKh-1310 instrument and IR spectra on a UR-20 spectrometer (KBr). The results of elementary analyses corresponded to the calculated figures.

The 2-amino-4-chloroanilides were obtained by the reduction of the corresponding 4-chloro-2-nitroanilides [4].

Cyclization of the 2-Amino-4-chloroanilides. A mixture of 0.001 mole of a 2-amino-4-chloroanilide and 5 ml of 4 N hydrochloric acid was boiled for 30 min. The cooled hydrochloric acid solution was neutralized with ammonia. The white crystals of the corresponding 2-alkyl-5-chlorobenzimidazole the deposited were filtered off. The yields were quantitative; the melting points agreed with those given in the literature [6].

General Method for the Synthesis of N,N'-Diacyl-4-chloro-1,2-phenylenediamines. A mixture of 0.01 mole of a 2-amino-4-chloroanilide and 5 ml of the corresponding acid anhydride was heated on the water bath until the initial substance had dissolved. After cooling, 10 ml of water was added to the mixture and the white crystals that deposited were filtered off and washed on the filter with 50 ml of hot water. The desired products were crystallized from aqueous ethanol.

Transformation of N-Acetyl-N'-propionyl-4-chloro-1,2-phenylenediamine (II) in Cotton Plants. The investigations were performed on a cotton plant of the variety Tashkent 1. To introduce the compound (II) into the plants, 20-day cotton-plant shoots were placed with their roots in a 0.1% aqueous solution of (II) for 24 h, and the shoots, washed free from (II), were immersed with their roots in a vessel containing water and were kept at 26°C with continuous illumination for 48 h. Then the shoots were fixed with liquid nitrogen. The plant mass (10 g) was ground and extracted with mechanical shaking for 24 h with two 50-ml portions of benzene. The combined extracts were filtered and evaporated to dryness in vacuum. The residue was dissolved in benzene (0.4 ml) and deposited on a chromatographic plate (silufol UV-254). The spots of the extracts on the plate were washed free from pigments with toluene. The initial compound – N-acetyl-N'-propionyl-4-chloro-1,2-phenylenediamine (II) – and its possible transformation products 5-chloro-2-methylbenzimidazole (A) and 5-chloro-2-ethylbenzimidazole (B) were deposited on the plate in parallel. The acetone–benzene (3:2) system was used. Visualization with UV light showed a single spot of the extract with R_f 0.2 (R_{fII} 0.6; R_{fA} 0.2; R_{fB} 0.4). It follows from this that in cotton plants (II) is converted into 5-chloro-2-methylbenzimidazole, while compounds (II), and B were not detected visually on the chromatogram.

A comparison of the UV spectra of compound (II) (λ_1 max 222 nm; λ_2 max 245 nm) and its possible transformation products A (λ_1 max 250 nm, λ_2 max 285 nm; λ_3 max 292 nm) and B (λ_1 max 250 nm; λ_2 max 284 nm; λ_3 max 291 nm) with the UV spectrum of the extract, in which absorption curved were shown with λ_1 max 250 nm; λ_2 max 285 nm; λ_3 max 292 nm likewise confirmed what has been said above. Compound (II) is converted into 5-chloro-2-methylbenzimidazole containing traces of 5-chloro-2-ethylbenzimidazole under the action of 4 N hydrochloric acid.

SUMMARY

The synthesis of N,N'-diacyl derivatives of 4-chloro-o-phenylenediamine, not described in the literature, has been performed. Using N-acetyl-N'-propionyl-4-chloro-o-phenylenediamine as an example, it has been shown that compounds (I)-(XI) are converted in cotton plants into 2-alkyl-5-chlorobenzimidazoles.

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