PREPARATION AND PROPERTIES OF cis- AND trans-β-(BENZOTHIAZOL-2-YLTHIO)ACRYLIC ACIDS

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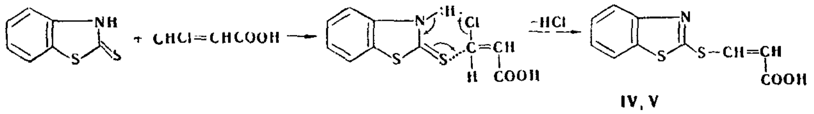
The reaction of benzothiazoline-2-thione with cis- and trans-β-chloroacrylic acids has yielded cis- and trans-β-(benzothiazol-2-ylthio)acrylic acids. The conversion of trans-β-(benzothiazol-2-ylthio)acrylic acid into the cis isomer in the presence of hydrogen halides and on irradiation with UV light has been observed.

In connection with the search for new defoliants and in view of the known defoliant activity of some derivatives of benzothiazoline-2-thione (I) and of cis-β-chloroacrylic acid (II) [1, 2], we have synthesized cis- and trans-β-(benzothiazol-2-ylthio)acrylic acids (IV) and (V). The reaction of (I) with (II) or its trans isomer (III) took place in organic solvents (acetone, toluene) at 50-60°C with the retention of the configuration of the initial acid (II or III). Heating at 100-110°C led to the formation of the trans acid (V) alone, which is explained by the thermal isomerization of the initial (II) into (III).

The carboxy group is shown in the IR spectrum in the 1680-cm^{-1} region for (IV) and 1700 cm^{-1} for (V). The molecular weight of the methyl esters (251) corresponded to the calculated figure. In the PMR spectrum there is a doublet (6.25 ppm) of a $-CH=$ group, the signal of the second $-Ch=$ group being masked by the signals of the aromatic nucleus. The assignment of the acids (IV) and (V), respectively, to the cis and trans configurations was performed on the basis of the spin–spin coupling constants [$J = 15$ Hz for (IV) and 9.8 Hz for (V)] [3] and also on the basis of the conversion of (V) into (IV) on irradiation with UV light. The hydrogenation of (V) led to the known β-(benzothiazol-2-ylthio)propionic acid (VI), which confirms, in addition to everything else, substitution of the sulfur atom in the molecule of (I). In the UV spectra of (IV) and (V) there is a bathochromic shift to 310 nm as compared with the 285 nm for (VI) [4] [log ε 3.94 for (IV) and 4.11 for (V)]. The higher intensity of the absorption band in (V) as compared with (IV) also confirms the correctness of their assignments to the trans and cis configurations, respectively.

By the reaction of (I) with propiolic acid, Grinblat and Postovskii obtained β-(benzothiazol-2-ylthio)-acrylic acid to which, on the basis of its IR spectrum, they ascribed the trans configuration. We have repeated this synthesis and have convinced ourselves that this acid is identical with the cis acid (IV) that we have obtained.

Two mechanisms may be considered for nucleophilic substitution at a double bond as applied to the present reaction: addition–elimination and elimination–addition [6]. The presence of the weak nucleophile (I), the absence of bases, which favor elimination, and the stereospecificity of the reaction all permit the assumption of an addition–elimination mechanism. It is possible that both stages take place almost simultaneously in the following way:



IV, V

Hydrogenation with nascent hydrogen took place only for the trans isomer, the cis isomer being recovered unchanged, and under the action of HCl and HBr an anomalous conversion of (V) into (IV) was observed, al-

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though it is known that in the presence of hydrogen halides the cis isomer generally isomerizes into the more stable trans isomer. It is possible that this behavior of the double bond and the anomalous isomerization are connected with the greater stability of the cis acid (IV). This stability can be explained by the formation of an intramolecular hydrogen bond between the proton of the hydroxy group and the nitrogen of the nucleus [7]. In favor of this assumption is the shift in the carbonyl frequency of the cis isomer (IV) by 20 cm^{-1} in the long-wave direction as compared with the carbonyl frequency of the trans isomer (V), which is characteristic for unsaturated acids with an intramolecular hydrogen bond [8].

EXPERIMENTAL

The IR spectra were taken in KBr tablets on a UR-10 spectrophotometer, the UV spectra on an EPS-3T spectrometer in ethanol, and the PMR spectra on a JNM-4H-100 instrument in trifluoroacetic acid solution.

The initial β-chloroacrylic acids were obtained by the addition of HCl to propioloc acid [9], which was obtained by the oxidation of propargyl alcohol [10].

cis-β-(Benzothiazol-2-ylthio)acrylic Acid (IV). To a solution of 0.83 g (5 mmoles) of benzothiazoline-2-thione in 30 ml of acetone was added 0.5 g (5 mmoles) of cis-β-chloroacrylic acid, and the mixture was boiled for 10 h. Then the solvent was driven off, the resulting crystals were treated with concentrated HCl, and the unchanged benzothiazoline-2-thione was separated off. The hydrochloric acid solution was diluted with a fourfold amount of water, and the crystals that deposited were separated off. This gave 86.9% of lustrous faintly yellowish needles with mp 182-183°C (from methanol). Found, %: C 50.8; H 3.1; N 5.8. $C_{10}H_7NO_2S_2$. Calculated, %: C 50.6; H 3.0; N 5.9.

trans-β-(Benzothiazol-2-ylthio)acrylic Acid (V). Similarly, 0.83 g (5 mmoles) of benzothiazoline-2-thione and 0.5 g (5 mmoles) of trans-β-chloroacrylic acid gave 76.9% of (V) with mp 158-159°C (from methanol). Found, %: N 5.8. $C_{10}H_7NO_2S_2$. Calculated, %: N 5.9. The same compound was isolated by boiling benzothiazoline-2-thione with cis- or trans-β-chloroacrylic acid in toluene for 10 h. The respective yields were 63.6 and 84.6%.

Hydrogenation of trans-β-(Benzothiazol-2-ylthio)acrylic Acid (V). With vigorous stirring at room temperature, 0.1 g of metallic sodium was added over 20 min to a solution of 0.2 g (0.8 mmole) of (V) in 20 ml of absolute ethanol. After all the sodium had reacted, stirring was continued for another 1 h. Then the ethanol was driven off, the crystals obtained were dissolved in water, and the solution was made faintly acid. This yielded 0.08 g (40%) of colorless crystals with mp 148-149°C (from benzene). A mixture with β-(benzothiazol-2-ylthio)propionic acid gave no depression of the melting point.

Isomerization of the β-(Benzothiazol-2-ylthio)acrylic Acids. 1. A solution of 0.2 g (0.8 mmole) of (IV) or (V) in 5 ml of concentrated HCl was heated at 70-75°C for 3 h. The reaction mixture was diluted with a fivefold amount of water, whereupon 0.18-0.17 g of crystals separated out with mp 182-183°C (from methanol). A mixed melting point with (IV) gave no depression of the melting point.

2. A rapid current of HBr was passed into a solution of 0.2 g (0.8 mmole) of (IV) or (V) in 20 ml of glacial acetic acid at 23-25°C for 2 h. The reaction mixture was kept at room temperature for 12 h and was then diluted with water, giving 0.18 g of crystals with mp 182-183°C (from methanol). A mixture with (IV) gave no depression of the melting point.

3. In quartz test-tubes, 0.1 g of dry crystals or a methanolic solution of (IV) was irradiated for 12 h. In both cases the unchanged acid with mp 182-183°C was isolated. When a methanolic solution of (V) was irradiated for 12 h, compound (IV) with mp 182-183°C was again isolated.

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