8.25 ppm (10H, m, Ar—H). Mass spectrum, m/e (I_{rel}, %): 289 (28.8), 274 (56.6), 246 (9.5), 212 (5.7), 184 (14.9), 105 (100). Yield 0.45 g (61%).

4-Acylaminopyrylium Perchlorates (Xa-e). To 7.0 g (68 mmoles) acetic anhydride cooled to 0°C was added sequentially 1 ml (10 mmoles) 70% $HClO_4$, 10 mmoles 1,3-diketone, and 40 mmoles nitrile. The reaction mixture was heated to the onset of boiling (5 min), and cooled. The resulting precipitate was separated by filtration and recrystallized from ethanol.

4-Benzoylaminopyrylium Hexachloroantimonates (XIa-c). A mixture of 5 mmoles salt IIIb-e, 15 ml acetic acid, and 3 ml nitromethane was boiled for 3 min, cooled, and after 1 h 200 ml ether was added. The resulting precipitate was separated by filtration and recrystallized from acetic acid.

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REACTIONS OF BENZOTHIAZOLE-2-THIONE AND BENZOTHIAZOLE-2-ONE WITH ACETYLENE

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UDC 547.314.2'569.1'789.6.04:
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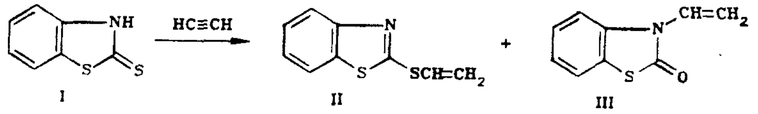
Reaction of benzothiazole-2-thione and benzothiazole-2-one with acetylene in the presence of potassium hydroxide or cadmium acetate gives 2-vinylthiobenzothiazole and 3-vinylbenzothiazol-2-one, respectively. Benzothiazole-2-thione is partially converted to benzothiazol-2-one by the action of Cd(OAc)₂. Under vinylation conditions the latter also forms 2-vinylthioaniline.

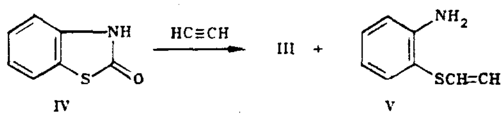
The reaction of benzothiazole-2-thione (I) with acetylene under alkaline catalytic conditions has been reported to give only 2-vinylthiobenzothiazole (II) [1]. In this work we have studied the reaction of thione I with acetylene in the presence of $Cd(OAc)_2$, which is effective in catalyzing the vinylation of azolethiones [2] and azolones [3]. Standard conditions for this reaction [20% $Cd(OAc)_2$, 180°C, 3 h] gives the basic product II together with a small amount (≈10%) of 3-vinylbenzothiazol-2-one (III). The yield of III was not affected by raising the reaction temperature or increasing the amount of catalyst.



The appearance of III may be due either to substitution of the exocyclic sulfur atom for oxygen in thione I or scission of the 2-thiovinyl group from II to give benzothiazol-2-one (IV) with subsequent vinylation. At first sight, the second of these is the more likely since side chain splitting is a characteristic reaction of azolylvinylsulfides [4]. We have found that azolone IV is formed by heating thione I with $Cd(OAc)_2$. Compound II is stable toward cadmium acetate.

Interesting results were obtained for the reaction of azolone IV with acetylene. In the presence of KOH, vinylation occurs at the nitrogen atom to give the vinylketone III.

Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 270-271, February, 1991. Original article submitted July 6, 1989.



At 180°C the latter is formed in small amounts, the optimal temperature of the process being 220°C. In this case, however, 2-vinylthioaniline (V) was produced in quantities up to 38% in the reaction mixture. Formation is a consequence of the destruction of the thiazole ring in azolone IV at raised temperature with vinylation of the 2-aminothiophenol [5] produced. In this reaction, use of $Cd(OAc)_2$ as catalyst leads principally to compound V. Despite variation of the reaction conditions, the vinyl ether of benzothiazol-2-one was not observed.

EXPERIMENTAL

PMR spectra were recorded on a Tesla BS-487B spectrometer (80 MHz) at ≈20°C with $CDCl_3$ solvent, HMDS internal standard, and sample concentration of 5%. IR spectra were recorded on a Specord 75-IR spectrometer as a thin layer.

Elemental analytical data for C, H, N, and S for III agreed with those calculated.

The starting benzothiazol-2-one (IV) was obtained by fusing 2-aminothiophenol with urea [6].

Reaction of Benzothiazol-2-one (I) with Acetylene in the Presence of $Cd(OAc)_2$. A rotating steel autoclave was charged with thione I (10 g, 0.06 mole), $Cd(OAc)_2$ (2 g, 20% of the weight of thione I), and dioxane (100 ml). Acetylene was passed from a cylinder with a starting pressure of 17 atm. The mixture was heated for 3 h at 180°C, the precipitate filtered off, and dioxane removed by distillation. Vacuum distillation gave 2-vinylthiobenzothiazole (II, 8.1 g, 70%) and 3-vinylbenzothiazol-2-one (III, 0.9 g, 8.5%).

Compound II: bp 135-136°C (2 mm Hg), n_D^{20} 1.6860 [1]. PMR spectrum: 5.52 (β-H, d), 5.56 (β-H, d), 6.94 (α-H, q); 7.20, 7.60, 7.80 ppm (Ar); $^3J_{AX}$ = 9.6, $^3J_{BX}$ = 16.7 Hz. Compound III, C_9H_7NOS: light yellow oily liquid, bp 146-148°C (2 mm Hg), n_D^{20} 1.6365. PMR spectrum: 5.31 (β-H, dd), 5.80 (β-H, dd); 6.71 (α-H, q); 7.02-7.39 ppm (Ar, m); $^2J_{AB}$ = 0.7, $^3J_{AX}$ = 9.2, $^3J_{BX}$ = 15.8 Hz. IR spectrum: 1680 (C=O); 1635 cm^{-1} (NC=C).

Action of Cadmium Acetate on Thione I. The autoclave was charged with thione I (3 g, 0.02 mole), $Cd(OAc)_2 \cdot 2H_2O$ (5.33 g, 0.02 mole), and dioxane (50 ml). The mixture was heated for 3 h at 180°C. After cooling, the precipitate was filtered off and dioxane removed by distillation. From the solid residue, column chromatography (Al_2O_3, eluent chloroform—benzene—ethanol, 20:4:1) gave azolone IV (0.33 g, 12%) with mp 137-138°C [6].

Vinylation of Benzothiazol-2-one (IV) in the Presence of KOH. The autoclave was charged with azolone IV (5 g, 0.03 mole), KOH (0.75 g, 15% of the weight of azolone IV), and dioxane (100 ml). Acetylene was passed from a cylinder at an initial pressure of 17 atm. The reaction mixture was heated for 2 h at 220°C, cooled, the precipitate filtered off, and the dioxane distilled off. Vacuum distillation gave III (2.2 g, 38%) and the vinylthioaniline V (1.9 g, 38%, bp 105-110°C at 3 mm Hg) [5]. PMR spectrum for V: 4.20 (NH_2, br.s); 5.15 (β-H, d); 4.91 (β-H, d); 6.27 (α-H, q); 6.70, 7.10, 7.35 ppm (Ar); $^3J_{AX}$ = 9.7, $^3J_{BX}$ = 16.6 Hz.

Vinylation of Azolone IV in the Presence of $Cd(OAc)_2$. A similar reaction of IV with $Cd(OAc)_2$ (1 g, 20% of the weight of azolone IV) gave V (3.25 g, 65%) and III (0.6 g, 10%).

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