ditions. The 6-alkoxybenzo[a]phenothiazin-5-ones were crystallized from acetone. The characteristics of the compounds are presented in Table 1. Compound IV was also obtained from 2,3-dichloronaphthoquinone and o-aminothiophenol by the method in [10] (method B).

Benzo[a][1,4]benzothiazino[3,2-c]phenothiazine (IV) (Method C). A solution of 0.25 g (1 mmole) of I in 25 ml of DMF was heated to 100°C, and 0.13 g (1 mmole) of o-aminothiophenol was added to it with stirring. After stirring for 1 h, the reaction mixture was diluted with 50 ml of water, and the resulting precipitate was removed by filtration, dried, dissolved in 25 ml of chloroform, and chromatographed with a column packed with silica gel (100-250 μ) by elution with chloroform. The first (violet) fraction was collected, and the eluent was removed to give 0.14 g (40%) of IV in the form of violet crystals with mp 290°C (mp 291°C [10]) and R_f 0.95 (chloroform). Found: C 71.7; H 3.7; N 117.4%. $C_{22}H_{12}N_2S_2$. Calculated %: C 71.7; H 3.7; N 117.6%. No melting-point depression was observed for mixtures of IV obtained by the methods described above.

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SYNTHESIS OF 1,3,4-TRIPHENYL-1H-PYRAZOLO[3,4-e][1,4]THIAZEPIN-7-ONE

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UDC 547.778'779.1'892.07:543.422

The reaction of 5-amino-1,3-diphenylpyrazole with benzaldehyde gives 5-benzylideneamino-1,3-diphenylpyrazole, which then undergoes cyclization with mercaptoacetic acid to give 1,3,4-triphenyl-1H-pyrazolo[3,4-e][1,4]thiazepin-7-one.

The available data relative to the synthesis of pyrazolothiazepines by the reaction of 5-aminopyrazoles with benzaldehyde and mercaptoacetic acid are contradictory. Reactions involving the formation of 5-benzylideneaminopyrazoles II and their subsequent cyclization to pyrazolo[3,4-d][1,3]thiazepines IV [1], as well as reactions with the isolation of intermediate 4-benzylidene-5-iminopyrazoles III, which subsequently react with mercaptoacetic acid to give pyrazolo[3,4-e][1,4]thiazepines V [2-5], have been described.

However, repetition of the syntheses in the case of 5-amino-1,3-diphenylpyrazole (I) in order to obtain isomeric pyrazolothiazepines IV and V led us to the conclusion that only 5-benzylideneamino-1,3-diphenylpyrazole (II) is an intermediate [which was proved by hydrogenation of the latter with sodium borohydride to 5-benzylamino-1,3-diphenylpyrazole (VI)], and only one pyrazolothiazepine is also formed. Pyrazolothiazepine V was subjected

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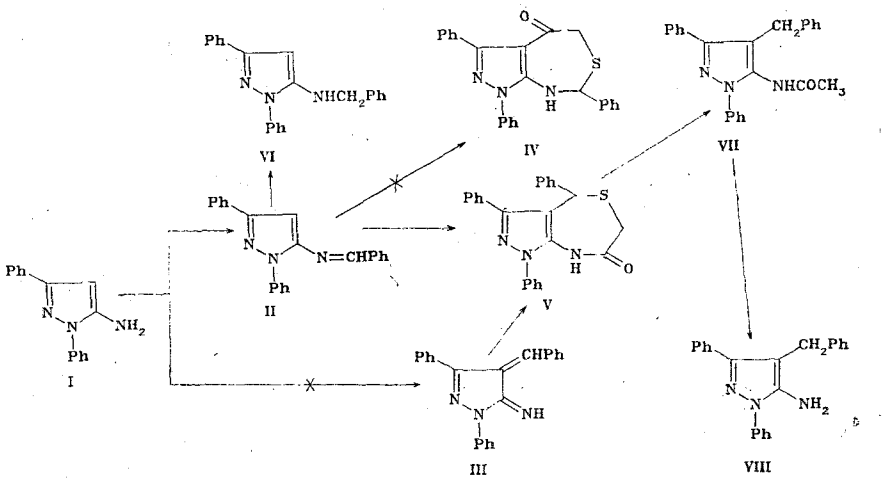
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 464-465, April, 1984. Original article submitted July 11, 1983.

0009-3122/84/2004-0370$08.50



to desulfuration by means of Raney nickel [3], and desulfuration product VII was then hydrolyzed with hydrochloric acid to give 5-amino-4-benzyl-1,3-diphenylpyrazole (VIII), whereas the product of desulfuration of pyrazolothiazepine IV should not undergo any changes under hydrolysis conditions.

Thus it was shown that the product of cyclization of 5-benzylideneamino-1,3-diphenylpyrazole (II) with mercaptoacetic acid is 1,3,4-triphenyl-1H-pyrazolo[3,4-e][1,4]thiazepin-7-one (V); this can be explained either by the II → III rearrangement under the reaction conditions or by the addition of mercaptoacetic acid to the C=N bond with subsequent rearrangement.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were obtained with a Varian T-60 spectrometer (60 MHz) with tetramethylsilane as the internal standard. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates in an ether–petroleum ether system (2:1).

5-Benzylideneamino-1,3-diphenylpyrazole (II). A) A mixture of 11.7 g (0.05 mole) of pyrazole I and 5.3 g (0.05 mole) of benzaldehyde in 50 ml of anhydrous ethanol was refluxed for 3 h, after which the solvent was removed by vacuum distillation, and the residue was recrystallized from ethanol to give 12.3 g (76%) of pyrazole II with mp 116-117°C and R_f 0.74. IR spectrum: 1630 cm^{-1} (C=N). PMR spectrum ($CDCl_3$): 8.58 (1H, s, CH=N), 7.0-8.0 (15H, m, aromatic protons), and 6.5 ppm (1H, s, pyrazole ring 4-H). Found: C 81.8; H 5.3; N 13.1%; M 323. $C_{22}H_{17}N_3$. Calculated: C 81.7; H 5.2; N 13.0%; M 323.

B) A mixture of 11.7 g (0.05 mole) of pyrazole I and 5.3 g (0.05 mole) of benzaldehyde in 50 ml of anhydrous toluene was refluxed with a Dean–Stark adapter until water separation ceased. The toluene was removed by vacuum distillation, and the residue was recrystallized from ethanol to give 11 g (69%) of pyrazole II.

5-Benzylamino-1,3-diphenylpyrazole (VI). A 0.2-g (5 mmole) sample of sodium borohydride was added in small portions with stirring to a solution of 1.6 g (5 mmole) of pyrazole II in 20 ml of methanol, and the mixture was stirred for 2 h. The methanol was removed by vacuum distillation, 20 ml of water was added to the residue, and the liberated oily substance was extracted with chloroform (three 20-ml portions). The solvent was removed by vacuum distillation, and the residue was recrystallized from ether to give 1.9 g (88%) of pyrazole VI with mp 108-109°C and R_f 0.77. IR spectrum: 3410 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 7.0-8.0 (15H, m, aromatic protons), 5.8 (1H, s, pyrazole ring 4-H), and 4.15 ppm (2H, s, NCH_2). Found: C 81.3; H 5.9; N 12.7%; M 325. $C_{22}H_{19}N_3$. Calculated: C 81.2; H 5.8; N 12.9%; M 325.

1,3,4-Triphenyl-1H-pyrazolo[3,4-e][1,4]thiazepin-7-one (V). A mixture of 3.2 g (0.01 mole) of pyrazole II, 0.9 g (0.01 mole) of mercaptoacetic acid, and 50 ml of anhydrous toluene was refluxed with a Dean–Stark adapter until water separation ceased. The toluene was removed by vacuum distillation, and the residue was recrystallized from ethanol to give 2.9 g (75%) of pyrazolothiazepine V with mp 211-212°C and R_f 0.6. IR spectrum: 1690 (C=O) and 3200 cm^{-1} (NH). PMR spectrum (d_6-DMSO): 9.83 (1H, s, N–H), 7.2-7.8 (15H, m, aro-

matic protons), 5.7 (1H, s, CH—C_6H_5), and 3.77 and 3.01 ppm (each 1H, d, J = 13.5 Hz, CH_2). Found: C 72.3; H 4.6; N 10.7; S 8.1%; M 397. $C_{24}H_{19}N_3OS$. Calculated: C 72.5; H 4.7; N 10.5; S 8.0%; M 397.

5-Acetamido-4-benzyl-1,3-diphenylpyrazole (VII). A mixture of 7.8 g (0.02 mole) of pyrazolothiazepine V and 20 of Raney nickel in 50 ml of ethanol was refluxed for 4 h, after which the hot mixture was filtered, and the catalyst was washed with 10 ml of hot ethanol. The filtrate was evaporated in vacuo, and the residue was recrystallized from ethanol to give 4.8 g (65%) of pyrazole VII with mp 214-215°C and R_f 0.27. IR spectrum: 1690 (C=O) and 3245 cm^{-1} (NH). PMR spectrum (d_6-DMSO): 7.1-7.8 (15H, m, aromatic protons), 3.9 (2H, s, CH_2—C_6H_5), and 1.93 ppm (3H, s, CH_3—C=O). Found: C 78.3; H 5.5; N 11.3%; M 367. $C_{24}H_{21}N_3O$. Calculated: C 78.4; H 5.7; N 11.4%; M 367.

5-Amino-4-benzyl-1,3-diphenylpyrazole (VIII). A 3.6-g (0.01 mole) sample of pyrazole VII was heated in 10 ml of concentrated HCl on a boiling-water bath for 1 h, after which the mixture was cooled to room temperature, neutralized with dilute sodium carbonate solution, and extracted three times with ether. The extract was dried with magnesium sulfate, the solvent was removed by distillation, and the residue was recrystallized from ether—petroleum ether (1:1) to give 2.5 g (78%) of pyrazole VIII with mp 104-105°C and R_f 0.7. IR spectrum: 3290 and 3425 cm^{-1} (NH_2). PMR spectrum ($CDCl_3$): 7.2-7.8 (15H, m, aromatic protons), 3.87 (2H, s, CH_2—C_6H_5), and 3.5 ppm (2H, s, NH_2). Found: C 81.3; H 5.9; N 12.7%; M 325. $C_{22}H_{19}N_3$. Calculated: C 81.2; H 5.8; N 12.9%; M 325.

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INDOLE DERIVATIVES.

124.* 5-(2-PHENYLETHENYL)INDOLINES AND 5-(2-PHENYLETHENYL)INDOLES

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UDC 547.753'754'212'313.2'53.024.07:543.422'51

5-(2-Phenylethenyl)indolines, the dehydrogenation of which leads to the formation of the corresponding compounds of the indole series, were obtained from 5-formyl-1-methyl(or benzyl)indolines via the Grignard reaction with benzylmagnesium chloride and subsequent dehydration. The hormonal activity of the synthesized compounds was studied.

Indole and indoline derivatives that contain a 2-phenylethenyl substituent in the benzene part of the molecule are unkown in the literature. These compounds are heterocyclic analogs of diarylethylenes, which display biological activity (estrogenic activity, for example [2, 3]).

*See [1] for communication 123.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 466-469, April, 1984. Original article submitted July 27, 1983.

0009-3122/84/2004-0372$08.50