and heated at 80° for 2 h. The excess mercaptan was removed by distillation, and the residue was dissolved in chloroform and purified with a column filled with Al_2O_3 (elution with $CHCl_3$) to give 0.9 g (75%) of X. Compound XI was similarly obtained.

Compounds VIII-X were obtained as white crystalline substances that were stable in air (Table 1).

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RESEARCH ON UNSATURATED AZOLE DERIVATIVES

V.* TRANSFORMATIONS OF 3-FORMYLINDAZOLES IN THE WITTIG REACTION

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3-Formylindazoles are converted to 1-methyl- and 2-methyl-substituted β -(3-indazolyl)acrylic and α -bromoacrylic acids by the Wittig reaction. Dehydrohalogenation of the β -(3-indazolyl)- α bromoacrylic acid esters gave β -(3-indazolyl)propiolic acids, the decarboxylation of which gives isomeric 1-methyl- and 2-methyl-substituted 3-ethynylindazoles.

Continuing our research on the synthesis of vinyl and ethynyl derivatives of azoles we subjected 1-methyland 2-methyl-3-formylindazoles (I, II) to reaction with carbomethoxy- and carbethoxymethylenetriphenylphosphoranes IIIa, b. The β - (1-methyl- and 2-methyl-3-indazolyl)acrylic acid esters (IVa, b and Va, b) obtained in this way were subsequently hydrolyzed to the corresponding β - (3-indazolyl)acrylic acids (VI, VII). β - (1-Methyl-3-indazolyl)- and β - (2-methyl-3-indazolyl)- α -bromoacrylic acid esters IVc and Vc were obtained in good yields by reaction of aldehydes I and II with the more reactive carbethoxybromomethylenetriphenylphosphorane (IIIc) at 17-20°C, the best yields of reaction products can be obtained when ethanol is used as the solvent. The action of alcoholic alkali on ethyl β - (1-methyl-3-indazolyl)- α -bromoacrylate (IVc) at 15-20° leads only to hy-



drolysis of the ester group to give β -(1-methyl-3-indazolyl)- α bromoacrylic acid (VIII), whereas β -(2-benzimidazolyl)- α -bromoacrylic acid esters are converted under these conditions to 2-benzimidazolylpropiolic acids [2]. A difficult-to-separate mixture of products was obtained in the hydrolysis of ethyl β -(2methyl-3-indazolyl)- α -bromoacrylate (Vc) under these conditions.

A mixture of products, the IR spectrum of which contains absorption bands of the $-C \equiv C-$ bond of the corresponding β -(3indazolyl)propiolic acids (IX and X), is formed by the action of alcoholic alkali on esters IVc and Vc at 50-60°. Treatment of the mixture of esters IVc and Vc with aqueous alkali at 55-60° gave

*See [1] for communication IV.

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii. No. 12, pp. 1678-1681, December, 1975. Original article submitted December 20, 1974.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50. 1-methyl- and 2-methyl- β -(3-indazolyl)propiolic acids (IX and X, respectively) in good yields. The intensity of the absorption of the $-C \equiv C$ - bond in the IR spectra of these acids (see Fig. 1) constitutes evidence for the high asymmetry of the molecules of these compounds.



III, IV a $R = CH_3$, X = H; b $R = C_2H_5$, X = H; c $R = C_2H_5$, X = Br; VI, VII X = H; VIII X = Br

соединения IV, VI, VIII, IX, XI — 1-methyl-substituted indazole derivatives нения V, VII, X, XII — 2-methyl-substituted indazole derivatives

Acids IX and X undergo decarboxylation (along with pronounced resinification) on fusion to give the corresponding 1-methyl- and 2-methyl-3-ethynylindazoles (XI and XII) in low yields. Considerably better results were obtained by thermal decomposition of acids IX and X in vacuo at $150-160^\circ$ with simultaneous sublimation of the resulting 3-ethynylindazoles.

EXPERIMENTAL

The IR spectra of chloroform solutions of the compounds were recorded with a UR-20 spectrometer.

<u>1-Methyl-3-formylindazole (I).</u>* A solution of 1.62 g (10 mmole) of 1-methyl-3-hydroxymethylindazole [3] in 10 ml of chloroform was stirred with 8.7 g (0.1 mole) of active manganese dioxide and allowed to stand overnight. The manganese dioxide was removed by filtration and washed thoroughly with chloroform. The filtrate was evaporated, and the residue was chromatographed on aluminum oxide in chloroform to give 1.1 g (70%) of a product with mp 47° (mp 47-48° [3]).

<u>2-Methyl-3-hydroxymethylindazole.</u> A 10-g sample of methyl 1-methylindazole-3-carboxylate was reduced with 2 g of lithium aluminum hydride by the method in [5] to give 6 g (70%) of a product with mp 152-157° (6 mm). Found %: C 66.5; H 6.0; N 17.5. $C_9H_{10}N_2O$. Calculated %: C 66.6; H 6.2; N 17.3.

<u>2-Methyl-3-formylindazole (II).</u>* This compound was obtained by oxidation of 2-methyl-3-hydroxymethylindazole with active manganese dioxide as in the preparation of I; the yield was 68%. The yield obtained by oxidation with potassium dichromate solution in dilute sulfuric acid by the method in [3] was 28%. The product had mp 79-80° (from petroleum ether).

Reaction of 3-Formylindazoles I and II with Carbomethoxy- and Carbethoxymethylenetriphenylphosphoranes IIIa and IIIb. A 4-mmole sample of the appropriate phosphorane and 4 mmole of the appropriate aldehyde were dissolved in 20 ml of benzene, and the solution was refluxed for 12 h, during which the course of the reaction was followed by thin-layer chromatography (TLC). The solvent was removed by distillation, and the residue was chromatographed on activity V aluminum oxide in ether; esters IVa, b and Va, b were collected in the first portions of the eluate (Table 1).

<u>Hydrolysis of Esters IVa.</u> b and Va. b. A 4-mmole sample of the appropriate ester was dissolved in 5 ml of a 15% alcohol solution of potassium hydroxide, and the solution was refluxed for 4 h. The solvent was removed by distillation, and the residue was treated with water. The aqueous mixture was filtered, and the filtrate was neutralized with dilute hydrochloric acid. The precipitated VI or VII was removed by filtration (Table 1).

^{*} This compound was previously obtained in 25% yield by oxidation of 1-methyl-3-hydroxymethylindazole with chromic acid [3], whereas II was obtained in 60% yield by formylation of 2-methyl-3-lithioindazole with dimethylformamide [4].

Com- pound	mp, °C -	Solvent	Empirical formula	Found, %			Calc., % ,			1, %
				с	н	N	с	н	N	Yield
IVa	184 ^a	Ethanol	$C_{12}H_{12}N_2O_2 \cdot C_2H_2N_2O_2$	48,3	3,8	16,0	48,5	3,4	15,7	51
IVb	159ª	Ethanol	$C_{13}H_{14}N_2O_2 \cdot C_6H_3N_3O_7$	49,3	4,0	14,8	49,6	3,7	15,2	54
Va Vb	87 99	Hexane Ether-benzene	$\begin{array}{c} C_{12}H_{12}N_2O_2\\ C_{13}H_{14}N_2O_2\end{array}$	66,7 68,2	5,3 6,4	13,3 12,0	66,7 67,8	5,5 6,1	12, 9 12,2	62 60
VI	218 ^b	Dilute acetic	$C_{11}H_{10}N_2O_2$	64,9	5,1	14,2	65,3	4,9	13,9	80
VII IVc ^c Vc ^c	198 95—96 143	Alcohol—water Ethanol Ethanol	$\begin{array}{c} C_{11}H_{10}N_2O_2\\ C_{13}H_{13}BrN_2O_2\\ C_{13}H_{13}BrN_2O_2 \end{array}$	65,0 50,6 50,4	4,9 4,3 4,6	14,2 9,4 9,5	65,3 50,5 50,5	4,9 4,2 4,2	13,9 9,1 9,1	75 60 65

TABLE 1. β -(3-Indazolyl)acrylic Acids and Their Derivatives

^aThis is the melting point of the picrate. ^bAccording to [3], this compound has mp 219-220°. ^cCompound IVc. Found %: Br 26.0. Calculated %: Br 25.9. Compound Vc. Found %: Br 25.6. Calculated %: Br 25.9.

Reaction of 3-Formylindazoles I and II with Carbethoxybromomethylenetriphenylphosphorane (IIIc). A 0.02-mole sample of the appropriate aldehyde and 0.02 mole of IIIc were dissolved in 22 ml of ethanol, and the solution was allowed to stand at room temperature for 24 h. The precipitated IVc or Vc was removed by filtration and washed with ethanol (Table 1).

 $\frac{\beta - (1-\text{Methyl}-3-\text{indazolyl}) - \alpha - \text{bromoacrylic Acid (VIII).}}{5 \text{ ml of } 15\% \text{ alcoholic potassium hydroxide solution, and the solution was allowed to stand at 17-20° for 2 days.}}$ The solvent was evaporated, and the residue was treated with water. The aqueous mixture was filtered, and the filtrate was neutralized with dilute hydrochloric acid. The resulting precipitate was removed by filtration to give 0.8 g (70\%) of a product with mp 205° (from methanol). Found %: C 46.6; H 3.2; Br 28.9; N 10.2. C₁₁H₉-BrN₂O₂. Calculated %: C 46.9; H 3.2; Br 28.5; N 9.9.

<u>1-Methyl-3-indazolylpropiolic Acid (IX).</u> A mixture of 0.6 g (2 mmole) of IVc and 5 ml of 15% aqueous alkali was stirred at 60° for 2 h, after which it was neutralized to pH ~ 4 with dilute hydrochloric acid, and the resulting precipitate was removed by filtration to give 0.3 g (75%) of light-yellow prisms (from aqueous ethanol) with mp 135-136° (dec.). IR spectrum, cm⁻¹: 1700, 1680 ($\tilde{\nu}_{C=O}$): 2225 ($\tilde{\nu}_{C\equiv C}$). Found %: C 66.3; H 4.1; N 14.0. C₁₁H₈N₂O₂. Calculated %: C 66.0; H 4.0; N 14.0.

 $\frac{2-\text{Methyl-3-indazolylpropiolic Acid (X).}}{\text{pound as needles (from water-ethanol) with mp 132° (dec.) in 78% yield. Found %: C 66.3; H 4.2; N 14.1. C_{11}H_8N_2O_2. Calculated %: C 66.0; H 4.0; N 14.0.$

<u>1-Methyl-3-ethynylindazole (XI)</u>. This compound was obtained in 65% yield by thermal decomposition of 1-methyl-3-indazolylpropiolic acid at 150-160° in a vacuum sublimation apparatus. The colorless prisms had mp 45-46° (after two sublimations). IR spectrum: 2120 ($\tilde{\nu}_{C} \equiv C$) and 3305 ($\tilde{\nu}_{\Xi} = C-H$) cm⁻¹. Found %: C 76.6: H 5.0; N 18.1. C₁₀H₈N₂. Calculated %: C 76.9; H 5.2; N 17.9.

 $\frac{2-\text{Methyl-3-ethynylindazole (XII).}}{\text{needles (after two sublimations) with mp 122-124° (dec.). IR spectrum: 2120 (<math>\tilde{\nu}_{C \equiv C}$) and 3305 ($\tilde{\nu}_{\equiv C-H}$) cm⁻¹. Found %: C 76.6; H 4.9; N 18.1. C₁₀H₈N₂. Calculated %: C 76.9; H 5.2; N 17.9.

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