Die Spaltungsuntersuchungen wurden unter „Standardbedingungen"[1] mit Piperidin, Benzylamin und Benzylmercaptan vorgenommen. Die Ausbeuten beziehen sich auf die nach Abzug des nicht gespaltenen Anteils maximal mögliche Umsetzung als 100 %-Wert.

Anmerkung zu den Tabellen:

IR = angegeben sind NH und Amid Banden; Et = absol. Ester; Pe = absol. Petrolether; Ee = Essigsäureethylester; Di = Dichlormethan; Cyclo = Cyclohexan; t-But = tert. Butyl-Rest; i-Prop = Isopropyliden-Rest.

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Studies with Heterocyclic Hydrazidic Halides: New Pyrazolo[5,1-*c*]-1,2,4-triazoles and Pyrazolo[5,1-*c*][1,2,4]triazines

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Syntheses of the title compounds using the hydrazone **3** as starting material are reported.

Untersuchungen mit Heterocyclischen Hydrazidhalogeniden: Neue Pyrazolo[5,1-*c*]-1,2,4-triazole und Pyrazolo[5,1-*c*][1,2,4]triazine

Synthesen der Titelverbindungen aus dem Hydrazon **3** werden beschrieben.

Interest in condensed pyrazoles has been recently revived[1]. The considerable biological activities of these compounds are most likely beyond this interest[2]. In previous work we have reported several new approaches for the synthesis of fused pyrazoles utilizing readily obtainable functionally substituted pyrazo-

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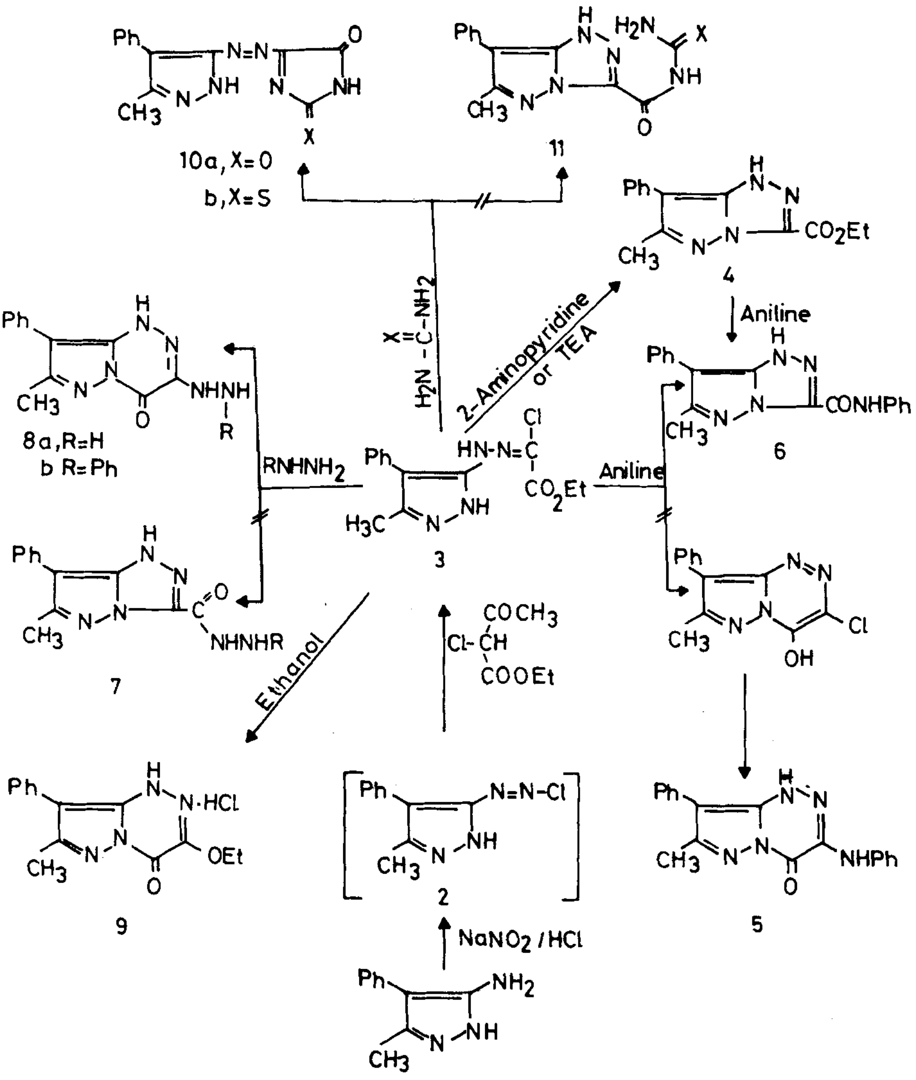
les as starting materials[1, 3]. Although the ethoxycarbonylmethano-(3-methyl-4-phenylpyrazol-5-yl)hydrazonyl chloride (**3**) is an interesting starting material for the synthesis of fused pyrazoles[4, 5], the chemistry of these new pyrazoles has received little attention compared to the broad synthetic utilities of its aryl counter analogues.

Here we report on the synthesis of ethoxycarbonylmethano-(3-methyl-4-phenylpyrazol-5-yl)hydrazonyl chloride (**3**) and its utility in synthesis of fused pyrazoles. Thus, diazotized 5-amino-3-methyl-4-phenylpyrazole (**1**) couples with ethyl α-chloroacetoacetate to yield **3**, formed via coupling and *Japp-Klingemann* acyl group cleavage.

The pyrazolo[5,1-*c*]-1,2,4-triazole **4** was obtained by cyclization of **3** under basic conditions.



When **3** was heated with aniline, a product which may be formulated as **5** or its isomer **6** was isolated. Structure **6** was established for this product based on its identity with a specimen prepared from **4** with aniline.

3 reacted with hydrazine hydrate and phenylhydrazine to yield products that can be formulated as **7** or its isomer **8**. Structure **8** is assumed for the reaction product as it could not be obtained from the ester **4**. A similar reaction of hydrazines with pyrazol-5-ylhydrazonyl derivatives leading to pyrazolo[5,1-*c*][1,2,4]triazines has been reported[4].

3 was converted into a product $C_{14}H_{15}N_4O_2 \cdot Cl$ on long reflux in EtOH. The ^{1}H-NMR spectrum revealed a pattern very similar to that of the starting hydrazonyl chloride. So, structure **9** was suggested.

3 reacted with urea and thiourea to yield a product that can be formulated as **10** or **11**. Structure **11** was eliminated as urea failed to react with **4** under similar conditions. The proposed structures are in agreement with analytical and spectra data.

Experimental Part

Melting points: uncorrected. – IR spectra (KBr): Pye-Unicam SP 1000. –^{1}H-NMR spectra: EM-390 90 MHz spectrometer, Me_4Si as internal standard, chemical shifts as δ (ppm). Analytical data: Analytical Data Unit at Cairo University.

Ethoxycarbonylmethano-(3-methyl-4-phenylpyrazol-5-yl)hydrazonyl chloride (**3**)

Ethyl α-chloroacetoacetate (0.01 mole) in EtOH (100 ml) was treated with anhydrous sodium acetate (0.02 mole) and then cooled to 0°. To this solution a solution of diazotized **1** (prepared at 0° from 0.01 mole of **1**, 25 ml of HCl and the appropriate quantity of $NaNO_2$) was added. The mixture was stirred at 0° for 1 h. The solid yellow product, so formed, was collected and crystallized from water; yield 80 %, m.p. 100°. – $C_{14}H_{15}ClN_4O_2$ (306.5) Calc. C 54.7 H 4.93 N 18.2 Cl 11.5 Found C 54.2 H 4.91 N 18.0 Cl 11.3. – IR: 3560, 3180 (NH), 1700 (CO), 1635 cm^{-1} (C=N). – ^{1}H-NMR: δ (ppm) = 1.2 (t, 3H, CH_3); 3.3 (s, 3H, CH_3), 4.2 (q, 2H, CH_2), 7.4 (m, 7H, C_6H_5 and 2NH).

6-Ethoxycarbonyl-2-methyl-3-phenylpyrazolo[5,1-c]-1,2,4-triazole (**4**)

3 (0.01 mole) in EtOH (50 ml) and either 2-aminopyridine (0.01 mole) or triethylamine (1 ml) were refluxed for 2 h, evaporated in vacuo and then triturated with water. The resulting solid yellow product was crystallized from EtOH; yield 70 %, m.p. 154°. – $C_{14}H_{13}N_4O_2$ (269.1) Calc. C 62.4 H 4.86 N 20.8 Found C 62.0 H 4.93 N 20.5. – IR: 3460, 3340 (NH), 1710 (CO), 1640 cm^{-1} (C=N). – ^{1}H-NMR: δ (ppm) = 1.4 (t, 3H, CH_3), 3.3 (s, 3H, CH_3), 4.5 (q, 2H, CH_2), 7.2–7.5 (m, 6H, C_6H_5 and NH).

Reaction of **3** *with aniline:*
6-Benzamido-2-methyl-3-phenylpyrazolo[5,1-c]-1,2,4-triazole (**6**)

3 (0.01 mole) and aniline (0.01 mole) were heated at 100° (bath temp.) for 3 h, then triturated with EtOH. The solid yellow product was crystallized from EtOH/DMF; yield 70 %, m.p. > 300°. – $C_{18}H_{15}N_5O$ (317.2) Calc. C 68.1 H 4.76 N 22.0 Found C 67.8 H 5.02 N 21.9. – IR: 3335, 3140 (NH), 1680 (CO), 1620 cm^{-1} (C=N).

The same product **6** (m.p. and mixed m.p.) was isolated by refluxing **4** (0.01 mole) with aniline (0.01 mole) in EtOH (50 ml) for 5 h.

Reaction of **3** *with hydrazines, urea and thiourea*

3 reacted with hydrazine hydrate, phenylhydrazine, urea and thiourea following the procedure described above for the reaction of **3** with aniline.

6-Hydrazino-2-methyl-3-phenylpyrazolo[5,1-c][1,2,4]triazin-7-one (**8a**)

Brown crystals from EtOH/H_2O; yield 65 %, m.p. 215°. – $C_{12}H_{12}N_6O$ (256.1) Calc. C 56.2 H 4.72 N 32.8 Found C 56.8 H 4.46 N 32.5. – IR: br (3300–3160) (NH), 1710 (CO), 1620 cm^{-1} (C=N).

6-Phenylhydrazino-2-methyl-3-phenylpyrazolo[5,1-c][1,2,4]triazin-7-one (**8b**)

Yellow crystals from DMF/H_2O; yield 80 %, m.p. > 300°. – $C_{18}H_{16}N_6O$ (332.2) Calc. 65.0 H 4.85 N 25.3 Found C 65.6 H 4.51 N 25.0. – IR: 3300, 3120 (NH), 1670 (CO), 1620 cm^{-1} (C=N).

5-(2,5-Dioxo-imidazol-4-yl)azo-2-methyl-3-phenylpyrazole (**19a**)

Yellow crystals from EtOH; yield 60 %, m.p. > 300°. – $C_{13}H_{10}N_6O_2$ (282.1) Calc. C 55.3 H 3.57 N 29.7 Found C 56.1 H 3.28 N 29.5. – IR: 1620 (C=N), 1700 (CO), 3020, 3200, 3175 cm^{-1} (NH).

5-(5-Oxo-imidazol-2-thion-4-yl)azo-2-methyl-3-phenylpyrazole (**10b**)

Brown crystals from EtOH; yield 65 %, m.p. 205°. – $C_{13}H_{10}N_6OS$ (298.2) Calc. C 52.3 H 3.38 S 10.7 Found C 52.0 H 3.07 S 10.5. – IR: 3200 (NH), 1700 (CO), 1600 cm^{-1} (C=N).

6-Ethoxy-2-methyl-3-phenylpyrazolo[5,1-c][1,2,4]triazin-4-one hydrochloride (**9**)

3 (1 g) in 50 ml EtOH was refluxed for 2 h and the mixture was evaporated in vacuo. The solid colourless product, so formed, was crystdallized from EtOH; yield 70 %, m.p. 140°. – $C_{14}H_{15}N_4O_2 \cdot Cl$ (306.6) Calc. C 54.7 H 4.93 Cl 11.5 Found C 54.3 H 5.22 Cl 11.6. – IR: 3200, 3080 (NH), 1720 (CO), 1650 cm^{-1} (C=N). – ^{1}H-NMR: δ (ppm) = 1.2 (t, 3H, CH_3), 3.3 (s, 3H, CH_3), 4.2 (q, 2H, CH_2), 7.3 (m, 6H, C_6H_5 and NH).

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