PS-100 spectrometer at 25 MHz under pulse conditions, with accumulation of the signal. The experiments with (Ia-d) and (IIa-d) were run in a dry argon atmosphere in anhydrous solvents.

Preparation of (IIa). To 0.39 g of (Ia) in 2 ml of CH_2Cl_2 was added 0.19 g of C_5H_5N (or 0.4 g of C_5H_5N) at 20°. Complex (IId) was obtained in a similar manner.

Preparation of (IIb). To a stirred solution of 2.8 g of (Ib) in 4 ml of CH_2Cl_2 at −40° was added 1.35 ml of C_5H_5N. Complex (IIc) was obtained in a similar manner. The amount of the starting (Ic) was determined by the PMR method, using toluene as the internal standard.

CONCLUSIONS

When the diethylboric esters of alkanenitronic acids of general formula RR'C = $NOOBEt_2$ (R = H or alkyl, and R' = alkyl or $COOCH_3$) are treated with pyridine the intramolecular coordination bond is cleaved to give the complexes of diethylboric esters of alkanenitronic acids with pyridine.

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CONDENSATION OF N-METHYL-4-IODOPYRAZOLECARBOXYLIC ACIDS WITH COPPER ACETYLIDES

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The condensation of o-halobenzoic acids with substituted copper acetylides in pyridine or DMF leads to phthalides; only the n-propylacetylide gives, along with 3-n-butylidenephthalide, 3-n-propylisocoumarin [1, 2]. In contrast, 3-iodothiophene-4-carboxylic acid reacts with the phenyl- and alkylacetylides to give thiophenopyrones [3].

While studying methods for inserting the acetylene group into the pyrazole nucleus we established that N-methyl-4-iodopyrazolecarboxylic acids when condensed with copper acetylides form exclusively the δ-lactones or pyranopyrazoles.

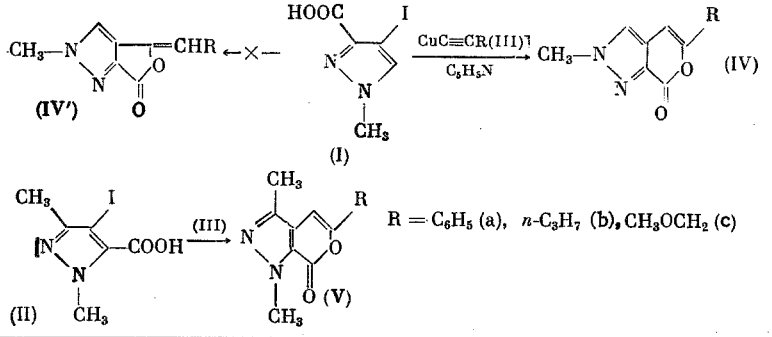

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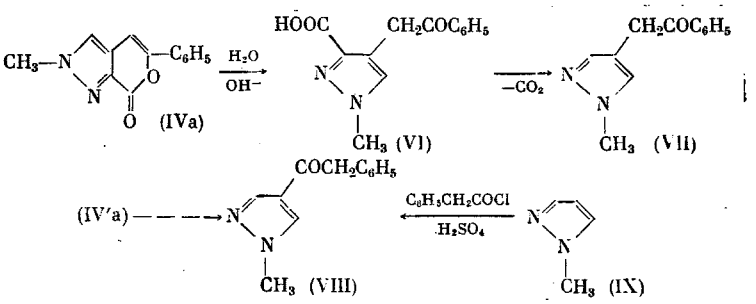
TABLE 1. Synthesis of 3-Substituted 1-Oxo-6-methylpyrano[3,4-c]-pyrazoles (IV) and 1-Oxo-5,7-dimethylpyrano [3,4-d]pyrazoles (V)

Compound	Yield, %	T mp, °C	Empirical formula	Found / Calculated % C	Found / Calculated % H	Found / Calculated % N	PMR spectrum (δ, ppm)	$\nu_{C=O}$, cm^{-1}
(IVa)	61,5	174–175 (ethanol)	$C_{13}H_{10}N_2O_2$	69,17 / 69,02	4,65 / 4,46	12,23 / 12,38	$CDCl_3$:4,03 (NCH_3); 6,76 (4–H); 7,2–7,6 m (C_6H_5, 5–H)	1760
(IVb)	53,3	64–65 (hexane -C_6H_6)	$C_{10}H_{12}N_2O_2$	62,23 / 62,48	6,03 / 6,29	14,57 / 14,58	$CHCl_3$:4,03 (NCH_3); 6,11 (4–H) 7,25 (5–H); 2,40 t (α-CH_2); 1,30 sextet (β-CH_2); 0,90 t (CH_3)	1748
(IVc)	58,6	115,5–116,5 (C_6H_6)	$C_9H_{10}N_2O_3$	55,69 / 55,66	5,18 / 5,19	14,07 / 14,43	$CHCl_3$:4,05 (NCH_3); 6,40 (4–H); 7,60 (5–H); 4,13 (CH_2); 3,33 (OCH_3)	1755
(Va)	58,3	149,5–150,5 (C_6H_6–petroleum ether	$C_{14}H_{12}N_2O_2$	69,88 / 69,98	4,92 / 5,03	11,62 / 11,66	CCl_4:4,20 (NCH_3); 6,77 (4–H); 2,42 (5–CH_3); 7,4–7,8 m (C_6H_5)	1749
(Vb)	61,5	75–76 petroleum ether	$C_{11}H_{14}N_2O_2$	64,41 / 64,06	6,93 / 6,84	13,63 / 13,58	CCl_4:4,05 (NCH_3); 5,97 (4–H), 2,23 (5–CH_3); 2,40 t (α-CH_2); 1,65 sextet (β-CH_2); 0,93 t (CH_3)	1750
(Vc)	60,0	119,5–120 (C_6H_6)	$C_{10}H_{12}N_2O_3$	57,65 / 57,68	5,97 / 5,81	13,43 / 13,45	CCl_4:4,22 (NCH_3); 6,52 (4–H); 2,33 (5–CH_3); 4,27 (CH_2); 3,47 (OCH_3)	1755

The condensation of acids (I) and (II) with copper acetylides (III) was run by heating in pyridine; the yields of (IV) and (V) were ~60%. The structure of (IVb, c) and (Vb, c) is confirmed by the data of the PMR spectra, which have a singlet in the 5.97-6.77 ppm region. In order to ascertain if the direction of the cyclization remains unchanged when condensation is with phenylacetylide (IIIa), compound (IVa) was saponified with aqueous alkali quantitatively to keto acid (VI), which then was decarboxylated to 4-phenacyl-1-methylpyrazole (VII) in 74% yield.



The position of the carbonyl group in the side chain of (VII) followed from the nonidentity of (VII) and 4-phenylacetyl-1-methylpyrazole (VIII), which was obtained by the acylation of 1-methylpyrazole (IX) with $C_6H_5CH_2COCl$ as described in [4].

EXPERIMENTAL

4-Iodo-1-methylpyrazole-3-carboxylic Acid (I). To 6.6 g of 4-iodo-1,3-dimethylpyrazole [5] in 180 ml of water at 60°C was added 9.5 g of $KMnO_4$ in portions, and after decolorization of the mixture the precipitate was separated, while the filtrate was evaporated to a small volume and acidified with HCl to pH 3-4. The obtained precipitate was recrystallized from water to give 2.4 g (31.8%) of (I), mp 180.5-181.5° (decompn.). Found, %: C 23.94; H 1.92; I 50.87; $C_5H_5IN_2O_2$. Calculated, %: C 23.83; H 2.00; I 50.30. 4-Iodo-1,3-dimethylpyrazole-5-carboxylic acid (II) was obtained in 35% yield by the oxidation of 4-iodo-1,3,5-trimethylpyrazole as described in [6], mp 234-235° (decompn.) (from alcohol).

In [6] compound (I) was erroneously assigned the structure of 4-iodo-1-methylpyrazole-5-carboxylic acid, while (II) was characterized as being 4-iodo-1,5-dimethylpyrazole-3-carboxylic acid [5].

Condensation of (I) and (II) with Copper Acetylides (III). A mixture of 0.01 mole of (I) or (II) and 0.012 mole of (III) in 50 ml of abs. pyridine was refluxed in a nitrogen atmosphere for 1-3 h, cooled, diluted with 200 ml of ether, filtered, the ether and pyridine were vacuum-distilled, and the residue was dissolved in $CHCl_3$, washed in succession with aqueous ammonia and water, and dried over K_2CO_3. The product was purified by filtration through a silica gel bed and recrystallization. The yields and constants of (IV) and (V) are given in Table 1.

4-Phenacyl-1-methylpyrazole-3-carboxylic Acid (VI). A solution of 0.80 g of (IVa) in 65 ml of 0.1 N aqueous KOH solution was heated at 100° for 30 min, cooled, acidified with HCl, and the crystals were filtered and washed with water to give 0.85 g (99.8%) of (VI), mp 170-171° (from dichloroethane). Found: 63.96; H 4.98; N 11.45%, $C_{13}H_{12}N_2O_3$. Calculated: C 63.93; H 4.95; H 11.47%.

4-Phenacyl-1-methylpyrazole (VII). Compound (VI) (0.20 g) was heated in a vacuum-sublimation apparatus until molten and then sublimed at 2 mm. The operation was repeated twice to give 0.12 g (73.2%) of (VII), mp 92-93° (from C_6H_6–petroleum ether). Found: C 72.03; H 6.04; N 13.94%, $C_{12}H_{12}N_2O$. Calculated: C 71.98; H 6.04; N 13.99%. PMR spectra ($CDCl_3$, δ, ppm): 3.78 (N–CH_3); 4.08 (CH_2); 7.3-7.6 (C_6H_5, 3- and 5-H). Infrared spectrum ($CHCl_3$, ν, cm^{-1}): 1690 (C=O).

4-Phenylacetyl-1-methylpyrazole (VIII). To 14.7 g of $C_6H_5CH_2COCl$ were added 1 ml of conc. H_2SO_4 and 5.1 g of (IX), and the mixture was heated for 5.5 h at 170-175°, cooled, stirred with 60 ml of 20% NaOH solution, and reflexed for 30 min. The product was extracted with $CHCl_3$, and the extract was dried over $MgSO_4$ and distilled. The fraction with bp 160-170° (2 mm) was recrystallized from a C_6H_6–petroleum ether mixture to give 3.3 g (26.7%) of (VIII), mp 78-79°. Found: C 72.01; H 6.28; N 13.93%, $C_{12}H_{12}N_2O$. Calculated: C 71.98; H 6.04; N 13.99%. PMR spectrum ($CDCl_3$, δ, ppm): 3.76 (N–CH_3); 3.95 (CH_2); 7.81 and 7.88 (3- and 5-H); 7.0-7.4 (C_6H_5). Infrared spectrum ($CHCl_3$, ν, cm^{-1}): 1672 (C=O).

CONCLUSIONS

The condensation of N-methyl-4-iodopyrazolecarboxylic acids with substituted copper acetylides gave derivatives of two new heterocyclic systems, and specifically of 1-oxo-6-methylpyrano[3,4,-c]- and 1-oxo-5,7-dimethylpyrano[3,4-d]pyrazole.

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