under reduced pressure and the residual solid triturated with 2-propanol. Filtration gave 0.27 g (52%) of a yellow solid which was recrystallized from 2-propanol, mp 266–267 °C dec.

Anal. Calcd for $C_{11}H_{14}N_6O_2$: C, 50.38; H, 5.38; N, 32.04. Found: C, 50.37; H, 5.44; N, 31.91.

2,4-Diamino-6-phthalimidomethylpteridine (22). A mixture of 2.5 g (9 mmol) of **10**, 1.13 g (9.5 mmol) of guanidine acetate, and 50 ml of DMF was heated at 120 °C for 48 h. The reaction mixture was cooled, diluted with an equal volume of methanol, and filtered. The collected solid was washed copiously with methanol and recrystallized from 1:1 DMF/methanol to give 1.5 g of **22** as yellow needles, mp 338 °C dec.

Anal. Calcd for $C_{15}H_{11}N_7O_2$: C, 56.07; H, 3.45; N, 30.52. Found: C, 55.70; H, 3.56; N, 29.55.

2-(*N,N*-Dimethylformamidylamino)-3-cyano-5-methylpyrazine (23). A mixture of 2.68 g (20 mmol) of **2**, 20 ml of dimethylformamide dimethyl acetal, and 30 ml of dry DMF was stirred at room temperature for 12 h. Evaporation in vacuo then gave a residual oil which solidified on trituration with cyclohexane. Recrystallization from cyclohexane then gave 3.48 g (92%) of **23** as white, fluffy needles, mp 102.5–103.5 °C.

Anal. Calcd for $C_9H_{11}N_5$: C, 57.13; H, 5.86; N, 37.01. Found: C, 57.22; H, 5.68; N, 37.01.

2-(*N,N*-Dimethylformamidylamino)-3-cyano-6-methylpyrazine (24) was prepared in 82% yield from 2-amino-3-cyano-6-methylpyrazine[11] as described above for the conversion of **2** to **23**, yellow needles (from benzene), mp 182.5–183 °C.

Anal. Calcd for $C_9H_{11}N_5$: C, 57.13; H, 5.86; N, 37.01. Found: C, 57.24; H, 5.85; N, 36.92.

2-Amino-3-cyano-6-*n*-propylpyrazine (25). A 5.3-mmol solution of lithium diisopropylamide was prepared in a 100-ml round-bottomed flask fitted with a septum, addition funnel, and gas inlet tube, by syringe addition of 2.2 ml of a 2.4 M solution of *n*-butyllithium to 0.54 g (5.3 mmol) of diisopropylamine in 10 ml of dry THF under nitrogen. This was stirred at −78 °C for 30 min and then to it was added a solution of 0.95 g (5 mmol) of **24** in 40 ml of warm THF. After addition was complete, the reaction mixture was stirred for 1 h at −78 °C and a solution of 0.94 g (6 ml) of ethyl iodide in 10 ml of dry THF was added. Stirring was continued as the reaction mixture was allowed to warm to room temperature. After 20 h the solution was quenched with 25 ml of 10% HCl, heated on a steam bath for 15 min, and then extracted with chloroform. The combined chloroform extracts were dried (Na_2SO_4), filtered, and evaporated to give 0.51 g of a crude solid. Sublimation at 100 °C (0.1 Torr) gave 0.42 g (52%) of **25** as a white, crystalline solid, mp 115–116 °C.

Anal. Calcd for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.54. Found: C, 59.13; H, 6.21; N, 34.25.

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Registry No.—**1**, 61267-55-8; **2**, 17890-82-3; **3**, 61267-56-9; **4**, 61267-57-0; **6**, 61267-58-1; **7**, 61303-84-2; **8**, 61267-59-2; **9**, 61267-60-5; **10**, 61267-61-6; **11**, 61288-80-0; **13**, 61267-62-7; **14**, 61267-63-8; **15**, 61267-64-9; **16**, 61267-65-0; **17**, 61267-66-1; **18**, 61267-67-2; **19**, 61267-68-3; **20**, 61267-69-4; **21**, 61267-70-7; **22**, 61267-71-8; **23**, 61303-85-3; **24**, 61267-72-9; **25**, 61267-73-0; diethyl malonate Na salt, 996-82-7; sodium cyanide, 143-33-9; ethyl acetoacetate Na salt, 19232-39-4; potassium phthalimide, 1074-82-4; ethyl γ-ethoxyacetoacetate Na salt, 61267-74-1; methyl cyanoacetate Na salt, 24163-38-0; ethylene glycol, 107-21-1; guanidine HCl, 14317-32-9; guanidine acetate, 34771-62-5; dimethylformamide diethyl acetal, 1188-33-6; 2-amino-3-cyano-6-methylpyrazine, 58091-66-0; lithium diisopropylamide, 4111-54-0.

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Highly Stereospecific Dimerization of 5-Formyl-5-methyl-1-pyrazolines. Preparation and Characterization of Stable Carbinolamines (Amino Hemiacetals)

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The unstable 5-methyl-5-formyl-2-pyrazolines **3**, generated in situ by a 1,3-dipolar additon of α-methylpropenal (methacrolein) to α-diazo esters, dimerize in a highly specific way to *meso*-**4**, which are stable carbinolamines. Surprisingly, the latter show no equilibrium with the monomers (pyrazolines) in solution, even at 90 °C in Me_2SO, but they are cleanly transformed into the aminals **5** by a variety of nucleophiles. The conversion of **4** to **5** occurs with retention of configuration at the reacting center, as established by x-ray diffractometry.

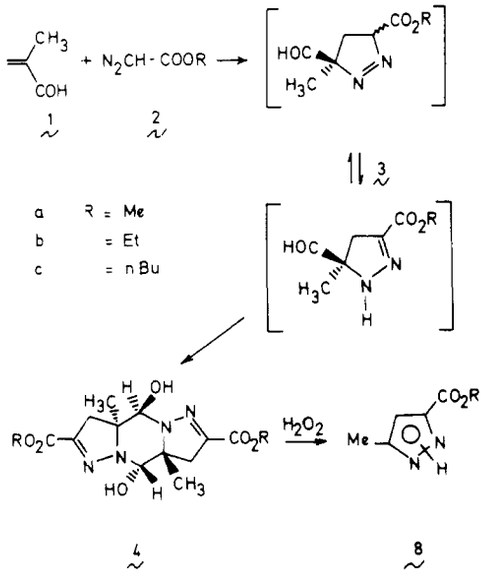
It has been clearly recognized for a long time that the formation of hydrazones, imines, oximes, etc., is a two-step reaction, a carbinolamine being an obligatory intermediate.[1] However, the carbinolamine function itself (also called hemiaminal or amino hemiacetal) has attracted much less attention, although several natural compounds have recently been recognized to possess a stable amino hemiacetal function.[2] From a synthetic point of view, with the exceptions of halogen stabilized molecules,[3] or derivatives of strained cyclopropanones,[4] the dimerization of five-membered heterocycles with a formyl group α to an endocyclic NH constitutes to our best knowledge the only systematic attempts to the synthesis of heterocyclic amino hemiacetals;[5] however, in this case, never was the function clearly and fully characterized, because of nonresolved mixtures and of a dimer–monomer equilibrium in solution. We now report the facile synthesis and characterization of stable carbinolamines from the stereospecific dimerization of substituted 5-formyl-2-pyrazolines.

Results and Discussion

When equimolecular amounts of 2-methylpropenal 1 (methacrolein) and of a diazo ester 2 are mixed in an aprotic solvent at room temperature, a white precipitate begins to appear after about 12 h; its yield, about 45%, is maximum after 2 weeks of standing. Some evolution of nitrogen is also observed; the total amount of gas is proportional to the dilution of the solution, and is quantitative for molar ratios of solvent (CCl_4) to reactants above 50.

The elemental analysis of the precipitates corresponds to equimolecular addition of the starting materials without loss of nitrogen and fits formula 4 (Scheme I) which is further

Scheme I



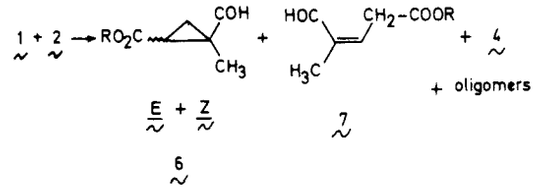
supported by the following spectroscopic characterizations. The main features in the spectra of 4 are, in the infrared, the absence of any peaks due to free hydroxyl group; rather, the sharp and intense absorptions which are seen at about 3500 cm^{-1} indicate hydrogen bonding. Moreover, conjugated azomethine and ester absorptions are seen at respectively 1545 and 1668 cm^{-1}. Although azomethine conjugated esters are quoted to absorb as low as 1680 cm^{-1} in some pyrazolines,[7] such an unusually low frequency is indicative of intermolecular interactions. Indeed, it is shifted up to 1690 cm^{-1} when the -OH function is replaced by $-OCH_3$ (vide infra) or in Me_2SO, while the position of the hydroxyl vibration remains unaffected in the same solvent. On the other hand, the ^1H NMR spectrum shows, beside the AB pattern of the pyrazoline methylene, an uncoupled methyl on a saturated carbon, and an AX system. The latter results from the coupling of the hydroxylic proton with the methine.

Remarkable is the fact that even at 90 °C, no aldehyde (i.e., no equilibrium with 3) is observed. The AX pattern is still present and indicates a slow exchange in the NMR time scale.

Dipolar additions of diazo compounds to activated double bonds such as 1 are well known and need no further comments, but the stereospecific dimerization of 3 to 4 (Scheme I) which follows the tautomeric equilibrium 1-pyrazoline ⇄ 2-pyrazoline seems to be unique. The mixture complexity made any NMR or IR monitoring of the reaction very difficult. Some points stand out, however. It appeared that the pyrazoline (3) concentration is low throughout the reaction (less than an estimated 3–5%, as indicated by integration of the aldehydic region) and, consequently, the dimerization should be fast relative to the pyrazoline formation. The important point in the structure of 4 is the presence of an inversion center, as revealed by the simplicity of both ^1H and ^{13}C NMR spectra. Examination of molecular models did not formally rule out other isomers of 4 on purely steric grounds. However, none of them was observed and that implies a highly stereospecific dimerization of 3.

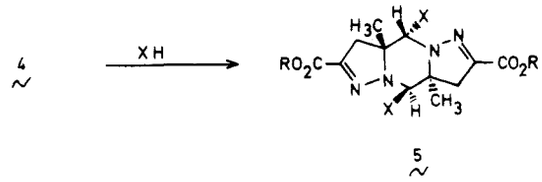
On the other hand, the reaction solution, after filtration of 4 and precipitation by a nonsolvent (hexane), gives a noncrystalline yellow solid, the analysis and spectra of which are indicative of oligomers with a probable polyacetal structure, as described for the reaction of acrolein with ethyl diazoacetate,[7] whereas three additional products are still present in the solution. Their yield increases with dilution and is proportional to the amount of nitrogen evolved. After isolation by VPC, two of them are identified as the *E* and *Z* isomers of cyclopropanes 6, and the third one is the previously unknown ethyl (*Z*)-4-formyl-3-pentenoate 7 (Scheme II), resulting from

Scheme II



a formal insertion of a carbomethoxycarbene into the CH group of methacrolein. Oxidation of 4 by activated manganese dioxide or hydrogen peroxide allowed the isolation of pyrazoles 8 in moderate yields[8] (Scheme I). Substituting the hydroxyl group of the carbinolamine function appears to have broad synthetic potentialities, that are illustrated in Scheme III by some chosen derivatives resulting from the reaction of

Scheme III



5 a X = -O CH_3
b = -O CH_2-CF_3
c = -O C_6H_5
d = -NH-C_6H_4F (p)
e = -N

4 with quite various nucleophiles (e.g., alcohols, phenol, aniline, and pyrazole). A complete retention of configuration obtains in these reactions: crystals of **5a** (R = Me) and of **4b** have been analyzed by x-ray diffractometry and the structure fully confirmed.[9] The central piperazine ring is in a chair conformation with a methoxy group trans to the vicinal methyl, and the ester carbonyl (1695 cm^{-1}) lies in the plane of the conjugated azomethine double bond.

On the other hand, crystals of **4b** have the same overall stereochemistry as **5**, the hydroxyl is also trans to the α-methyl,[10] and the conversion of 4 into 5 occurs with retention of configuration. The above observation ought to reflect some kind of intramolecular participation since purely steric effects should not be large enough to promote a total retention at the reacting center.

Experimental Section

Boiling points and melting points are uncorrected. ^1H NMR spectra were recorded on Varian T60 or HA-100 spectrometers; ^{13}C spectra

on a Brucker HFX 90 instrument at 22.63 MHz. All chemical shifts are measured in parts per million (δ) downfield from Me_4Si or HMDS. The ^{13}C resonance frequencies have been assigned by comparison with a nondecoupled spectrum of **5a** (Alk = CH_3) in $CDCl_3$.

Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer and frequencies are given in cm^{-1}.

Preparative VPC was carried out on a Varian 2800 instrument; the columns used were 16 × 0.75 in., 20% SE-30 on Chromosorb W 30–60.

The following descriptions are typical for the preparation of **4** and **5**.

I. Preparation of 2,7-Diethoxycarbonyl-3a,8a-dimethyl-4,9-dihydroxy-3*H*,8*H*-dipyrazolino[1,5-*a*:5',1'-*d*]-4*H*,9*H*-pyrazine (4b). In 5 mL of benzene are added 1.14 g (1 mmol) of ethyl diazoacetate and 0.77 g (1.1 mmol) of 2-methylpropenal. The solution is let without stirring at room temperature for several days and **4** slowly precipitates. After 10 days, the yield is about 40% but some precipitation still occurs during the following weeks. The solid is filtered, washed with benzene, and crystallized in acetone.

4b (R = C_2H_5): mp 219–224 °C dec; IR (OH, COOEt, C=N, respectively) (KBr) 3497, 1668, 1547 cm^{-1}; (Nujol) 3500, 1665, 1547 cm^{-1}; (Me_2SO) 3500, 1690, 1537 cm^{-1}; other absorptions (KBr) 1340 (s), 1292 (m), 1266 (s), 1250 (m), 761 (s), 752 (s), 732 cm^{-1} (m); NMR (Me_2SO-d_6, HMDS, 100 MHz) δ 6.47 (d, 1, J = 3.75 Hz, OH), 5.08 (d, 1, J = 3.75 Hz, CH), 4.10 (q, 2, CH_2CH_3), 3.28 and 2.50 [m, 2, J = 16.75 Hz, CH_2 (AB)], 1.24 (s, 3, CH_3), 1.16 (t, 3, CH_2CH_3); ^{13}C NMR (Me_2SO-d_6, Me_4Si-C_6D_6 with proton noise decoupling) 159.6 (COO), 132.0 (C=N), 82.6 (COH), 65.6 (CCH_3), 39.8 [CH_2 (AB)], 24.9 (CCH_3); ethyl ester 59.0 (CH_2), 13.9 ppm (CH_3). Anal. Calcd for $C_{16}H_{24}N_4O_6$: C, 52.17; H, 6.52; N, 15.22. Found: C, 52.2; H, 6.6; N, 15.2.

4a (R = CH_3), mp 208.5–210 °C dec. Anal. Calcd for $C_{14}H_{20}N_4O_6$: C, 49.41; H, 5.88; N, 16.47. Found: C, 49.5; H, 6.0; N, 16.5.

4c (R = *n*-Bu), mp 181–183 °C dec. Anal. Calcd for $C_{20}H_{32}N_4O_6$: C, 56.60; H, 7.55; N, 13.20. Found: C, 56.7; H, 7.7; N, 13.4.

A. Preparation of Aminoacetal 5a from 4a. **4a** is refluxed in methanol with stirring. After dissolution heating is continued for about 0.5 h. Upon slow cooling, **5a** precipitates: mp 218–224 °C; IR (KBr) 3018 (w), 2850 (w), 1695 (s, $COOCH_3$), 1545 (s, C=N), 1333 (s), 763 (s), 756 (s), 727 cm^{-1} (m); NMR ($CDCl_3$, Me_4Si, 100 MHz) δ 4.91 (s, 1, CH), 3.84 (s, 3, CO_2CH_3), 3.34 (s, 3, $-OCH_3$), 3.62–2.69 [m, 2, J = 17.2 Hz, CH_2 (AB)], 1.41 (s, 3, CH_3). Anal. Calcd for $C_{16}H_{24}N_4O_6$: C, 52.17; H, 6.52; N, 15.22. Found: C, 52.3; H, 6.6; N, 15.3.

B. Preparation of 5b (R = Et). **4b** (2 g) in 15 mL of 2,2,2-trifluoroethanol is heated at 60 °C for 3 h. After cooling, **5b** is precipitated by addition of ether and crystallized from carbon tetrachloride: yield 86%; mp 233–236 °C; IR (KBr) 1720 (s, ester), 1552 (s, C=N), 757 (s), 747, 668 cm^{-1} (m); NMR ($CDCl_3$, HMDS, 60 MHz, only quoted are the absorptions of the substituted part of the molecule) 3.7 (q, 2, J = 8 Hz, $-CH_2CF_3$), 5.03 (s, 1 H, CH methine). Anal. Calcd for $C_{20}H_{26}N_4O_6F_6$: C, 45.11; H, 4.89; N, 10.53. Found: C, 45.0; H, 4.9; N, 10.5.

C. Preparation of 5c (R = Et). **4b** (0.5 g) and 3 g of phenol are heated at 40 °C overnight. The excess of phenol is sublimed under vacuum and the residue crystallized from toluene: yield 61%; mp 231 °C; IR (KBr) no OH, 1693 (s, ester), 1556 (s, C=N), 756 (s), 734 cm^{-1} (m); NMR ($CDCl_3$, HMDS, 60 MHz) δ 7.10 (m, 5, C_6H_5), 5.73 (s, 1, CH). Anal. Calcd for $C_{28}H_{32}N_4O_6$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.5; H, 6.6; N, 10.6.

D. Preparation of 5d. **4b** (2 g) is heated in 5 mL of *p*-fluoroaniline for 3 h at 100 °C, 30 mL of benzene is then added, and the solution is refluxed for 1 h. After evaporation of the solvent, the residue is crystallized from acetonitrile: yield 79%; mp 242 °C; IR (KBr) 3450 (s, NH), 1680 (s, ester), 1540 (m), 1510 (s), 823 cm^{-1} (s). Anal. Calcd for $C_{28}H_{32}N_6O_4F_2$: C, 60.65; H, 5.78; N, 15.16. Found: C, 61.0; H, 5.8; N, 15.2.

E. Preparation of 5e. **4b** (1.5 g) and 2 g of pyrazole are refluxed overnight in 830 mL of acetone. After filtration, the solvent is evaporated under vacuum, the solid kept under vacuum for a few hours, and the residue crystallized from a mixture of benzene–cyclohexane: yield 42%; mp 228–232 °C; IR (KBr) no OH, 1714 (s, ester), 1545 (s, C=N), 1212 (s), 772 (m), 763 (s), 753 cm^{-1} (s); NMR ($CDCl_3$, HMDS, 60 MHz) δ 7.60 (d, 1, J = 2 Hz, pyrazole), 7.45 (large d, 1, H pyrazole), 6.20 (t, 1, H_4 pyrazole), 6.08 (s, CH).

II. Preparation of 3(5)-Carboethoxy-5(3)-methylpyrazole (8). The product **4b** (R = Et) is dissolved with stirring in an excess of hot H_2O_2 (15%) for 5 min. After cooling, the solution is extracted several times with chloroform, the organic solution dried ($CaSO_4$), and the solvent evaporated under vacuum. The oily residue is crystallized twice from hexane (38%): mp 82–83 °C, identical with the literature data;[11] (KBr) 3300–2900 (s, NH), 1725 cm^{-1} (s, COOEt); NMR ($CDCl_3$, HMDS, 60 MHz) δ 11.73 (s, 1, NH), 6.47 (s, 1, H aromatic), 4.25 (q, 2, CH_2CH_3), 2.26 (s, 3, CH_3), 1.22 (t, 3, CH_2CH_3).

III. Reactions in Diluted Medium. Preparation of 6 and 7. To a solution of 1.7 mL (20 mmol) of α-methylacrolein in 25 mL of benzene is added 2.1 mL (20 mmol) of ethyl diazoacetate. The mixture is stirred at 40 °C until the evolution of nitrogen is over (80% in volume). The solid **4** is filtered off, the solvent eliminated, and the crude mixture distilled under vacuum before preparative VPC. The crude yield of **6** and **7** is about 80%.

IV. (*Z*)-1-Formyl-1-methyl-2-carboethoxycyclopropane (6, R = Et): bp 43–46 °C (1 mm); IR (neat) 3060 (w, cycle), 1735 (s, COOEt), 1720 (s, CHO), 1029, 878 cm^{-1}; NMR ($CDCl_3$, Me_4Si, 60 MHz) δ 9.09 (s, 1, CHO), 4.05 (q, 2, OCH_2CH_3), 2.2–1.5 (m, 3, ring), 1.17 (t, 3, OCH_2CH_3), 1.15 (s, 3, CH_3).

V. (*E*)-1-Formyl-1-methyl-2-carboethoxycyclopropane (6, R = Et): NMR ($CDCl_3$, Me_4Si, 60 MHz) δ 8.66 (s, 1, CHO), 2.3–1.8 and 1.6–1.1 (m, 3, ring), 1.25 (s, 3, CH_3).

Anal. (mixture of both isomers of **6**) Calcd for $C_8H_{12}O_3$: C, 61.55; H, 7.69. Found: C, 61.6; H, 7.8.

VI. Ethyl (*Z*)-4-Formyl-3-pentenoate (7): 10%; bp 52–54 °C (1 mm); IR (neat) 1749 (s, COOEt), 1700 (s, CHO), 1030 (s), 812 cm^{-1} (w); NMR ($CDCl_3$, Me_4Si, 60 MHz) δ 9.24 (s, 1, CHO), 6.53 (d of t, 1, ^3J = 7.0, ^4J = 1.4 Hz, H vinyl), 4.11 (q, 2, OCH_2CH_3), 3.23 (d of d, 2, ^3J = 7.0, ^5J = 1.0 Hz, CH_2), 1.66 (m, 3, CH_3).

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Registry No.—**1**, 78-85-3; **2a**, 6832-16-2; **2b**, 623-73-4; **2c**, 24761-88-4; **4a**, 61597-89-5; **4b**, 60323-59-3; **4c**, 61597-90-8; **5a** (R = Me), 55199-74-1; **5b** (R = Et), 61597-91-9; **5c** (R = Et), 61597-92-0; **5d** (R = Et), 61597-93-1; **5e** (R = Et), 61597-94-2; *E*-**6** (R = Et), 13949-97-8; *Z*-**6** (R = Et), 13950-14-6; *Z*-**7** (R = Et), 61597-95-3; **8**, 4027-57-0; methanol, 67-56-1; 2,2,2-trifluoroethanol, 75-89-8; phenol, 108-95-2; *p*-fluoroaniline, 371-40-4; pyrazole, 288-13-1.

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