Synthesis and Characterization of Dipyrazolylalkanes, and Some of Their Complexes With $CoCl_2$

K. I. THÉ AND L. K. PETERSON

Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia

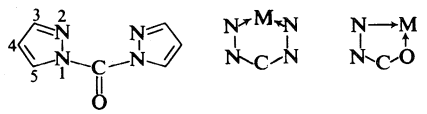
Received August 24, 1972

The reaction of dipyrazol-1-yl ketone with appropriate ketonic compounds is catalyzed by the presence of $CoCl_2$, to yield dipyrazolylalkanes $(C_3H_3N_2)_2CRR'$, (*a*) where R = R′ = CH_3, CD_3, C_2H_5; (*b*) where R = H, R′ = CH_3, C_6H_5; (*c*) where R = CH_3, R′ = C_2H_5; and 1,1-dipyrazolylcycloalkanes derived from cyclobutanone, pentanone, hexanone, 3-methyl and 4-methylhexanone. Cobalt(II) chloride reacts with dipyrazol-1-yl ketone, in tetrahydrofuran, to yield the complex $CoCl_2(C_3H_3N_2)_2CO$, and in acetone or acetone-d_6 to yield $CoCl_2(C_3H_3N_2)_2C(CH_3)_2$ or $CoCl_2(C_3H_3N_2)_2C(CD_3)_2$.

La réaction de la dipyrazol yl-1 cétone avec des composés cétoniques appropriés, est catalysée par la présence de $CoCl_2$ et conduit aux dipyrazolylalcanes $(C_3H_3N_2)_2CRR'$; (*a*) où R = R′ = CH_3, CD_3, C_2H_5; (*b*) où R = H, R′ = CH_3, C_6H_5; (*c*) où R = CH_3, R′ = C_2H_5; et aux dipyrazolylcycloalcanes-1,1 dérivés de la cyclobutanone, pentanone, hexanone, méthyl-3 et méthyl-4 hexanone. Le chlorure de cobalt(II) réagit avec la dipyrazol yl-1 cétone dans le tétrahydrofurane pour donner le complexe $CoCl_2(C_3H_3N_2)_2CO$ et dans l'acétone ou l'acétone-d_6 pour conduire au $CoCl_2(C_3H_3N_2)_2C(CH_3)_2$ ou au $CoCl_2(C_3H_3N_2)_2C(CD_3)_2$. [Traduit par le journal]

Can. J. Chem., **51**, 422 (1973)

Polydentate ligands may be designed with various electronic and steric characteristics, which, in conjunction with the nature of metal ion or other acceptor species, will determine the properties of complexes that may form. Because the pyrazole ring is planar (1), due to a delocalization of π-electron density, the coupling of two pyrazole rings to the sp^2 hybridized carbon atom of a carbonyl group, as in dipyrazol-1-yl ketone (**1**) (2) (structure **I**) should lead to a polydentate ligand with the four nitrogen atoms of the rings essentially coplanar with the carbonyl group. Complexation with metal ions may then lead to six-atom coplanar chelate systems, via two nitrogen atoms, or to five-atom systems, via N and O atoms (structures **II** and **III**) or ligand bridging may lead to polymeric structures.



I **II** **III**

Our studies of the complexing properties of dipyrazolyl-1-ketone lead to unexpected reactions which represent the discovery of a new synthetic route to dipyrazolyl compounds (3), and to other novel organic molecules. Our synthetic work is reported in this paper.

Experimental

The manipulation of compounds was performed under anhydrous conditions, using a nitrogen-filled dry box or high vacuum system. Solvents were rigorously dried before use (4). Most of the preparative reactions were quantitative, although quoted yields of pure products are low, due to losses during work-up.

Melting points (uncorrected) were measured using Gallenkamp or Fisher–Johns m.p. apparatus. N.m.r. spectra were determined with a Varian A56/60 or Varian XL100 spectrometer, using $CDCl_3$ as solvent and with TMS as internal standard, i.r. spectra with a Perkin–Elmer 457 spectrophotometer, and mass spectra with a double focusing RMU-6E Hitachi Perkin–Elmer instrument.

Analyses, for C, N, and H, were performed by the departmental analyst.

Preparation of Dipyrazol-1-yl Ketone (1)

Sodium amide (0.26 mol) and pyrazole (0.26 mol) were placed under nitrogen into a 200 ml reaction vessel which was joined to a 2 l ballast bulb. The vessel was evacuated, dry ether (150 ml) was introduced, and after sealing, the flask was agitated for 16 h at room temperature, and for 3 h at 70 °C. Following the removal of volatile materials under vacuum, dry ether (150 ml) and phosgene (0.125 mol) were added to the residue of sodium pyrazolide, and the mixture was stirred for 3 h at room temperature, and for 14 h at 70 °C. Sodium chloride (0.252 mol) was filtered off, and the ethereal filtrate was distilled under nitrogen to yield a yellow solid, which was purified by zone fractionation under vacuum (sublimation temperatures, 85–90°) to give compound **1**, 0.112 mol, 87% yield; m.p. 61.5–62.5°.

Anal. Calcd. for $C_7N_4H_6O$: C, 51.9; N, 34.7; H, 3.7. Found: C, 52.0; N, 34.7; H, 3.7.

Mass spectrum: P_{obs} 162; P_{calcd} 162; n.m.r.: τ 2.10

(H_3) (q, $J_{3,4}$ = 2.2, $J_{3,5}$ = 0.6 Hz); 3.40 (H_4) (q, $J_{3,4}$ = 2.2, $J_{4,5}$ = 3.0 Hz); 1.27 (H_5) (q, $J_{3,5}$ = 0.6, $J_{4,5}$ = 3.0 Hz).

The $CoCl_2$-catalyzed Reaction of Dipyrazol-1-yl Ketone with Acetone

An exploratory experiment indicated that no reaction occurs in a two-component mixture of **1** and acetone. When a mixture of **1** (1.50 mmol), acetone (~5 ml), and a catalytic amount of dry $CoCl_2$ (0.005 g) was allowed to stand at room temperature, an initially purple solution, turning to dark blue, was observed. The slow evolution of a gas was noted. After 16 h, the products were separated into CO_2 (1.45 mmol), identified by its i.r. spectrum and vapor phase molecular weight (M_{obs} 44.1, M_{calcd} 44.0), and a residue of solids; extraction of the latter with ether yielded a white solid, 2,2-dipyrazolylpropane (**2**), m.p. 83.5–84.0°.

Anal. Calcd. for $C_9N_4H_{12}$: C, 61.4; N, 31.8; H, 6.8. Found: C, 61.3; N, 32.0; H, 6.9.

Mass spectrum: P_{obs} 176; P_{calcd} 176; n.m.r.: τ 7.20 (CH_3) (singlet); 2.40 (H_3) (q, $J_{3,4}$ = 1.8, $J_{3,5}$ = 0.7 Hz); 3.70 (H_4) (q, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.5 Hz); 2.57 (H_5) (q, $J_{4,5}$ = 2.5, $J_{3,5}$ = 0.7 Hz).

Other Products of the $CoCl_2$-catalyzed Reaction of Dipyrazol-1-yl Ketone with Ketonic Solvents

Reactions between **1** and various ketonic solvents, in the presence of catalytic amounts of $CoCl_2$, were carried out in essentially the same way as the reaction of **1** with acetone, as summarized below:

(*a*) Acetaldehyde yielded 1,1-dipyrazolylethane (**3**), m.p. 53.5–54.0 °C; yield 75%.

Anal. Calcd. for $C_8N_4H_{10}$: C, 59.2; N, 34.5; H, 6.2. Found: C, 59.3; N, 34.8; H, 6.1.

Mass spectrum: P_{obs} 162, P_{calcd} 162; n.m.r.: τ 7.83 (CH_3) (doublet, J = 6.8 Hz); 3.39 (CH) (q, J = 6.8 Hz); 2.46 (H_3) (q, $J_{3,4}$ = 2.0, $J_{3,5}$ = 0.6 Hz); 3.75 (H_4) (q, $J_{3,4}$ = 2.0, $J_{4,5}$ = 2.4 Hz); 2.43 (H_5) (q, $J_{3,5}$ = 0.6, $J_{4,5}$ = 2.4 Hz).

(*b*) Hexadeuteroacetone yielded 2,2-dipyrazolylhexadeuteropropane (**4**), m.p. 85.0–85.5 °C.

Anal. Calcd. for $C_9N_4H_6D_6$: C, 59.3; N, 30.8; H(D), 6.6. Found: C, 59.6; N, 31.0; H(D), 6.9.

Mass spectrum: P_{obs} 182, P_{calcd} 182; n.m.r.: τ 2.62 (H_3) (q, $J_{3,4}$ = 1.7, $J_{3,5}$ = 0.6 Hz); 3.77 (H_4) (q, $J_{3,4}$ = 1.7, $J_{4,5}$ = 2.5 Hz); 2.62 (H_5) (q, $J_{3,5}$ = 0.6, $J_{4,5}$ = 2.5 Hz).

(*c*) Methylethyl ketone yielded 2,2-dipyrazolylbutane (**5**), m.p. 54.5–55.0 °C; yield, 84%.

Anal. Calcd. for $C_{10}N_4H_{14}$: C, 63.2; N, 29.5; H, 7.4. Found: C, 63.1; N, 29.7; H, 7.3.

Mass spectrum: P_{obs} 19.0, P_{calcd} 190; n.m.r.: τ 9.12 (CH_3) (triplet, J = 7.5 Hz); 7.80 (CCH_3) (singlet); 7.27 (CH_2) (q, J = 7.5 Hz); 2.43 (H_3) (q, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.5 Hz); 2.60 (H_5) (q, $J_{3,5}$ = 0.6, $J_{4,5}$ = 2.5 Hz).

(*d*) Diethylketone yielded 3,3-dipyrazolylpentane (**6**), m.p. 55.3–56.0 °C; yield 80%.

Anal. Calcd. for $C_{11}N_4H_{16}$: C, 64.7; N, 27.4; H, 7.8. Found: C, 64.6; N, 27.8; H, 7.7.

Mass spectrum: P_{obs} 204, P_{calcd} 204; n.m.r.: τ 9.22 (CH_3) (triplet, J = 7.3 Hz); 7.25 (CH_2) (q, J = 7.3 Hz); 2.48 (H_3) (q, $J_{3,4}$ = 1.8 Hz); 3.75 (H_4) (q, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.5 Hz); 2.53 (H_5) (q, $J_{3,5}$ = 0.7, $J_{4,5}$ = 2.5 Hz).

(*e*) Benzaldehyde yielded 1,1-dipyrazolylphenylmethane (**7**), m.p. 61.6–62.0 °C; yield, 48%.

Anal. Calcd. for $C_{12}N_4H_{12}$: C, 69.6; N, 25.0; H, 5.4. Found: C, 69.8; N, 25.4; H, 5.4.

Mass spectrum: P_{obs} 224, P_{calcd} 224; n.m.r : τ 2.37 (H_3) (q, $J_{3,4}$ = 1.8, $J_{3,5}$ = 0.6 Hz); 3.60 (H_4) (q, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.4 Hz); 2.49 (H_5) (q, $J_{3,5}$ = 0.6, $J_{4,5}$ = 2.4 Hz); 2.25 (CH) (singlet). The phenyl resonances consisted of two sets of complex multiplets, centered at 2.67 τ.

(*f*) Cyclobutanone yielded 1,1-dipyrazolylcyclobutane (**8**), m.p. 79.5–80.2 °C; yield, 82%.

Anal. Calcd. for $C_{10}N_4H_{12}$: C, 63.8; N, 29.8; H, 6.4. Found: C, 63.4; N, 30.1; H, 6.3.

Mass spectrum: P_{obs} 188, P_{calcd} 188; n.m.r.: τ 2.45 (H_3) (q, $J_{3,4}$ = 1.7, $J_{3,5}$ = 0.7 H_2); 3.75 (H_4) (q, $J_{3,4}$ = 1.7, $J_{4,5}$ = 2.4 Hz); 2.62 (H_5) (q, $J_{3,5}$ = 0.7, $J_{4,5}$ = 2.4 Hz). The CH_2 protons of the cyclobutyl ring gave complex resonances centered at 6.77 and 8.93 τ.

(*g*) Cyclopentanone yielded 1,1-dipyrazolylpentane (**9**), m.p. 133.0–133.5 °C; yield, 60%.

Anal. Calcd. for $C_{11}N_4H_{14}$: C, 65.3; N, 27.7; H, 6.9. Found: C, 65.3; N; 28.0; H, 6.9.

Mass spectrum: P_{obs} 202, P_{calcd} 202; n.m.r.: τ 2.50 (H_3) (q, $J_{3,4}$ = 1.8, $J_{3,5}$ = 0.6 Hz); 3.80 (H_4) (q, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.5 Hz); 2.53 (H_5) (q, $J_{3,5}$ = 0.6, $J_{4,5}$ = 2.5 Hz). The CH_2 protons of the cyclopentyl ring gave complex resonances at 7.07 and 8.17 τ.

(*h*) Cyclohexanone yielded 1,1-dipyrazolyl cyclohexane (**10**), m.p. 76.0–76.5 °C; yield, 62%.

Anal. Calcd. for $C_{12}N_4H_{16}$: C, 66.7; N, 25.9; H, 7.4. Found: C, 66.7; N, 26.1; H, 7.5.

Mass spectrum: P_{obs} 216, P_{calcd} 216; n.m.r.: τ 2.45 (H_3) (q, $J_{3,4}$ = 1.8, $J_{3,5}$ = 0.6 Hz); 3.77 (H_4) (q, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.5 Hz); 2.58 (H_5) (q, $J_{3,5}$ = 0.6, $J_{4,5}$ = 2.5 Hz). The CH_2 protons of the cyclohexyl ring gave complex resonances at 7.17 and 8.40 τ.

(*i*) 4-Methylcyclohexanone yielded 1,1-dipyrazolyl-4-methylcyclohexane (**11**), m.p. 89.0–89.3 °C; yield, 50%.

Anal. Calcd. for $C_{13}N_4H_{18}$: C, 68.1; N, 24.5; H, 7.4. Found: C, 68.3; N, 24.4; H, 7.6.

Mass spectrum: P_{obs} 230, P_{calcd} 230; n.m.r.: τ 2.53, 2.39 (H_3 and H_3') (two quartets with identical coupling constants, $J_{3,4}$ = 1.8, $J_{3,5}$ = 0.7 Hz); 3.85, 3.67 (H_4, H_4') (two quartets, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.4 Hz); 2.29, 2.88 (H_5, H_5') (two quartets, $J_{3,5}$ = 0.7, $J_{4,5}$ = 2.4 Hz).

(*j*) 3-Methylcyclohexanone yielded 1,1-dipyrazolyl-3-methylcyclohexane (**12**), m.p. 61.2–61.5 °C; yield 30%.

Anal. Calcd. for $C_{13}N_4H_{18}$: C, 67.9; N, 24.3; H, 7.8. Found: C, 67.9; N, 24.6; H, 7.9.

Mass spectrum: P_{obs} 230, P_{calcd} 230; n.m.r.: τ 8.97 (CH_3) (doublet, J = 5.5 Hz); 6.65–8.97 (CH_2) (complex pattern); 2.52, 2.38 (H_3, H_3') (two quartets, $J_{3,4}$ = 1.8, $J_{3,5}$ = 0.6 Hz); 3.87, 3.65 (H_4, H_4') (two quartets, $J_{3,4}$ = 1.8, $J_{4,5}$ = 2.6 Hz); 2.95, 2.25 (H_5, H_5') (two quartets, $J_{3,5}$ = 0.6, $J_{4,5}$ = 2.6 Hz).

(*k*) Unsuccessful reactions: The following compounds, containing the C=O group, did not react with dipyrazol-1-yl ketone when $CoCl_2$ was used as a catalyst: 2-methylcyclohexanone, acetophenone, benzophenone, ethyl acetate, dimethylacetamide, and δ- and γ-valerolactone.

*Preparation of 2,2-Dipyrazolylpropanecobalt Dichloride (**13**)*

Cobalt(II) chloride (0.82 mmol), dried by refluxing with thionyl chloride, **1** (0.82 mmol), and dry acetone

(~5 ml) were sealed together in a reaction flask. After 16 h at room temperature, the products were CO_2 (0.80 mmol) and a non-volatile blue solid; the latter was recrystallized from acetone to yield pure 2,2-dipyrazolylpropanecobalt dichloride, $CoCl_2[(C_3H_3N_2)_2C(CH_3)_2]$ (**13**).

Anal. Calcd. for $CoCl_2[(C_3H_3N_2)_2C(CH_3)_2]$: C, 35.3; N, 18.3; H, 3.9. Found: C, 35.0; N, 18.2; H, 3.9.

A solution of **2** (0.5 mmol) in acetone (10 ml) was added with stirring to a solution of $CoCl_2$ (0.5 mmol) in acetone (25 ml), to give a dark blue solution. Upon concentrating the solution, a blue product, with the same composition and i.r. spectrum as compound **13** prepared by the above method, was obtained.

*Hydrolysis of **13***

Compound **13** (2.0 mmol) was dissolved in water (20 ml) to give a pink solution which was extracted with diethyl ether (5 × 15 ml). The work-up of the organic layer yielded a solid residue, which was purified by zone fractionation; this product (1.2 mmol, 60% yield) was identical with a sample of **2** prepared by the $CoCl_2$-catalyzed reaction of acetone with dipyrazol-1-yl ketone.

*Preparation of 2,2-Dipyrazolylhexadeuteropropanecobalt Dichloride (**14**)*

This complex was prepared in the same way as **13**, using $CoCl_2$ (4.95 mmol), and **1** (4.95 mmol) in hexadeuteroacetone as solvent. Carbon dioxide (4.70 mmol) was formed quantitatively; the blue complex (**14**) was recrystallized from hot acetone.

Anal. Calcd. for $[(C_3H_3N_2)_2C(CD_3)_2]CoCl_2$: C, 34.0; N, 18.0; H (D), 4.0. Found: C, 34.5; N, 17.9; H (D), 3.9.

*Hydrolysis of **14***

Compound **14** (3.2 mmol) was dissolved in D_2O (10 ml) and the resulting solution was extracted with diethyl ether. The work-up of the organic layer produced the free ligand (1.95 mmol 61% yield), with the same physical properties and composition as **4** prepared above.

*Preparation of Dipyrazol-1-yl Ketonecobalt Dichloride (**15**)*

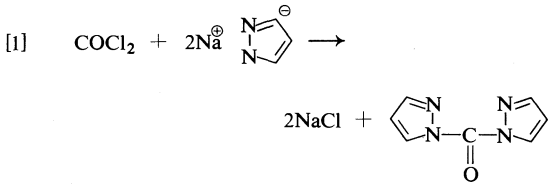
A mixture of $CoCl_2$ (1.07 mmol) **1** (1.07 mmol) and dry tetrahydrofuran (10 ml) was agitated at room temperature for 16 h. The absence of CO_2 was noted, and the solution was concentrated to yield a violet solid, which was filtered off under a dry nitrogen atmosphere. The product, **15**, was extremely sensitive to moisture.

Anal. Calcd. for $[C_3H_3N_2)_2CO]CoCl_2$: C, 28.8; N, 19.2; H, 2.1. Found: C, 29.0; N, 19.3; H, 2.0.

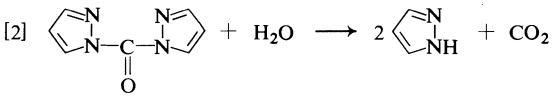
A sample of **15** (1.05 mmol) was dissolved in dry acetone (5 ml); after 16 h, the products were CO_2 (1.00 mmol) and a blue solid, which, after recrystallization, was identified as **13** on the basis of its i.r. spectrum; this complex was hydrolyzed by the methods described above to yield the free ligand, identified by its i.r. and n.m.r. spectra as **2**.

Discussion

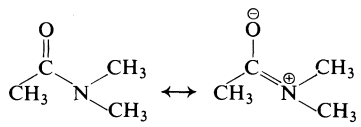
The new compound dipyrazol-1-yl ketone is formed quantitatively in the reaction of phosgene with sodium pyrazolide according to eq. 1:



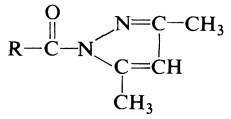
The use of lithium pyrazolide is precluded, since carbon atom lithiation occurs during the reaction of pyrazole with butyl lithium (5). The product, **1**, is very sensitive to water, yielding pyrazole and CO_2 (eq. 2). Whereas the ν(C=O)



stretching vibration for amides usually occurs in the 1650 cm^{-1} region, this band appears at 1740 cm^{-1} for compound **1**, suggesting an absence of the resonance interaction postulated for amides (6):



The absence of resonance may be due to aromaticity in the pyrazole ring system, requiring the lone pair of the amide nitrogen atom to be associated with the π-electron density of the ring, rather than with the carbonyl group. The monopyrazole systems, **IV**, show a trend in ν(C=O) values which may be accounted for on the basis of increasing resonance interactions with the R group, in the series R = CH_3CH_2, phenyl, and styryl, where the ν(C=O) values are 1722, 1700, and 1694 cm^{-1}, respectively (7).



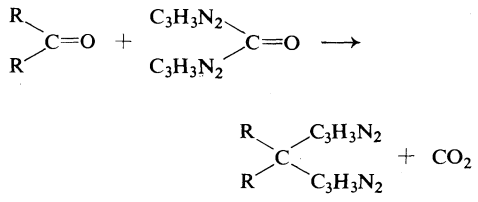
IV

The position of the ν(C=O) band for **1** indicates a similarity to the carbonyl bond in acetone (ν(C=O) = 1715 cm^{-1}), while the greater electronegativity of chloro and fluoro groups is reflected in the ν(C=O) values for $COCl_2$ (1827 cm^{-1}) and for COF_2 (1928 cm^{-1}) (8).

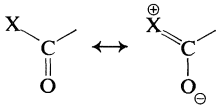
Compound **1** forms a violet complex with $CoCl_2$ in tetrahydrofuran solution. The car-

bonyl frequency is essentially unchanged (1735 cm^{-1}), hence coordination must involve N rather than O atoms. The complex is hydrolytically unstable, being readily converted into a cobalt–pyrazole complex, with elimination of CO_2.

Compound **1** is soluble in acetone, and in other ketonic or carbonyl solvents, without reaction; the presence of Co(II) species, even in catalytic amounts, does promote a reaction in which the carbonyl group of the solvent is exchanged for the dipyrazolylmethylene group, with evolution of carbon dioxide (2) (eq. 3).

[3] 

The reaction has wide applicability, to aliphatic ketones and aldehydes, to aromatic substances such as benzaldehyde, but not to benzophenone and acetophenone, and to cyclic ketones, but not to lactones. Other carbonyl systems which do not react include hexafluoro and hexachloroacetone, esters of carboxylic acids, and dimethylacetamide. It is likely that steric factors are important for benzophenone, acetophenone, and 2-methylcyclohexanone; in other cases, resonance interactions,



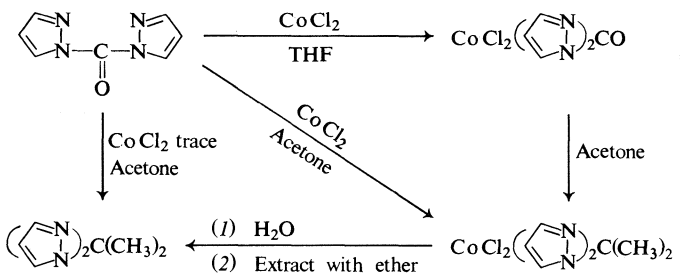
may diminish the reactivity of the carbonyl group. Further studies of the steric, electronic, and catalytic factors influencing this type of reaction are in progress. When stoichiometric proportions of compound **1** and $CoCl_2$ are dissolved in ketonic solvents, the new ligand L derived from **1** and the solvent remains complexed to the cobalt ion in a 1:1 molar ratio, giving $CoCl_2L$.

Such complexes are less susceptible to hydrolysis than those of **1**, and may be handled in the atmosphere. In aqueous solution, however, the complexes are hydrolyzed, producing free ligand which may be extracted into organic solvents. The hydrolytic stability of the dipyrazolyl alkanes is in marked contrast to the observed instability of dipyrazol-1-yl ketone, and, unlike *N*-alkylpyrazoles (9), our compounds are not hygroscopic.

Evidence for reaction between dipyrazol-1-yl ketone and acetone was first observed in the i.r. spectrum of the product, 2,2-dipyrazolylpropane, by the appearance of ν(C—H) bands at ~3000 cm^{-1}, due to CH_3 groups, and by the disappearance of ν(C=O). The ν(CH) vibrations of the "aromatic" pyrazole ring occur at 3120 and 3140 cm^{-1} (10), and hence are distinguishable from the ν(CH) stretching vibration of alkyl groups (2900–3000 cm^{-1}) for compounds **2**, **3**, **5**–**12**, and from the vibrations of the phenyl ring system (3040–3060 cm^{-1} (10)) in **7**. Comparison of the n.m.r. spectra of **1** and **2** corroborated the presence of the methyl groups in the latter molecule (at 7.2 τ); the hexadeutero analog **4** did not exhibit this resonance, showing acetone to be the source of methyl groups; the observed n.m.r. spectra of compounds **1**–**11** were in agreement with the given formulations.

The resonance positions of H_3 (2.37–2.50 τ), H_4 (3.60–3.80 τ), and H_5 (2.4–2.6 τ) were assigned on the basis of expected shielding effects associated with the carbonyl group and the nitrogen atoms; the bands were observed as quartets, due to long-range coupling with different C—H protons, ($J_{3,4}$ = 1.7–2.0, $J_{3,5}$ = 0.6–0.7, $J_{4,5}$ = 2.4–2.5 Hz) and not as doublets or triplets, as reported by Trofimenko (3). The H_x and H_x' protons of the two pyrazole rings were equivalent in all cases, except in the 1,1-dipyrazole-methylcyclohexane derivatives, where the resonances due to H_x and H_x' were observed as separate pairs of quartets, of equal intensity. The different bands presumably reflect the different positions of the pyrazole substituents, *viz.*, axial or equatorial, in the methylhexane ring. The H_3 resonance was significantly broader than that of H_5; a similar effect is reported for the two protons of substituted pyridines (11). Bands due to the R groups of compounds **2**–**12** were clearly identified, with appropriate intensities.

Mass spectra further confirmed the formulations of products; parent peaks were observed in all cases, and the larger fragments of compounds **2**–**7** were clearly identifiable as $(C_3H_3N_2)CRR'$, $C_3H_3N_2)_2CR$, and $C_3H_3N_2$. Compound **1** gave recombination products, such as *N*,*N'*-dipyrazole, as well as $(C_3H_3N_2)CO$ and $C_3H_3N_2$. The derivatives of the cycloalkanes **8**–**12**



SCHEME 1

gave $(C_3H_3N_2)$C-cycloparaffin, $(C_3H_3N_2)$-$C(CH_2)_{1,3,2,}$ and the free cycloparaffin fragment.

Interrelationships among various dipyrazolyl compounds are shown in Scheme 1.

Financial support from the National Research Council of Canada is gratefully acknowledged.

1. H. W. W. EHRLICH. Acta Cryst. **13**, 946 (1960).
2. L. K. PETERSON and K. I. THÉ. Chem. Commun. 841 (1972).
3. S. TROFIMENKO. J. Am. Chem. Soc. **92**, 5118 (1970).
4. A. WEISSBERGER. Technique of organic chemistry. Vol. VII. Organic Solvents. Interscience Publishers, Inc., N.Y. 1955.
5. R. HÜTTEL and M. E. SCHON. Ann. **625**, 55 (1959).
6. R. S. DRAGO. Physical methods in inorganic chemistry. Reinhold Publishing Corp. New York. 1965. p. 230.
7. W. REID and F-J. KÖNIGSTEIN. Ann. **625**, 53 (1959).
8. K. NAKAMOTO. Infrared spectra of inorganic and coordination compounds. J. Wiley and Sons, Inc., New York. 1963. p. 95.
9. G. ZERBI and C. ALBERTI. Spectrochim. Acta, **18**, 407 (1962).
10. H. A. SZYMANSKI. Theory and practice of infrared spectroscopy. Plenum Press, New York. 1964.
11. V. J. KOWALEWSKI and D. G. DE KOWALEWSKI. J. Chem. Phys. **36**, 266 (1962).