

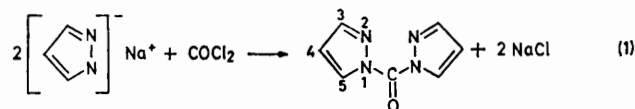
Novel Metal-catalysed Reactions of Dipyrazol-1-yl Ketone with Ketonic Solvents

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Summary Dipyrazol-1-yl ketone reacts with ketonic solvents in the presence of certain metal ions, producing carbon dioxide and new dipyrazolyl-hydrocarbon compounds.

REACTION of sodium pyrazolide with phosgene (2:1 molar ratio Et_2O) gave dipyrazol-1-yl ketone (cdp) (85–90%), m.p. 61.5–62.5°, according to equation (1).



The ligand cdp was purified by zone fractionation; correct analyses were obtained, and the structure was confirmed by n.m.r., mass spectral, and i.r. data.

Reaction of CoCl_2 with cdp in acetone gave CO_2 and a blue complex A, which, surprisingly, showed no CO stretching vibration, while new i.r. bands (2900–3000 cm^{-1}) indicated the presence of methyl groups. The same complex was obtained with acetone which had been dried over CaSO_4 , showing that the drying agent, 2,2-dimethoxypropane, was not the source of methyl groups; with $(\text{CD}_3)_2\text{CO}$ as solvent, CoCl_2 and cdp yielded CO_2 and complex B, containing CD_3 i.r. bands and again with $\nu(\text{C}=\text{O})$ absent. Complexes A and B were hydrolysed, and the ligand

fragments were extracted with Et_2O . The ligands were purified by vacuum fractionation, and were identified as 2,2-dipyrazolylpropane (dpp), m.p. 83.5–84.0°, derived from complex A, and as 2,2-dipyrazolylhexadeuteriopropane (dpdp), m.p. 85.0–85.5°, from complex B, on the basis of analytical, mass spectral, and n.m.r. data. For both dpp and dpdp, major mass spectral fragments were observed at m/e 109 and at 115 respectively, representing cleavage of one of the exocyclic C–N bonds to give $\text{pyR}(\text{CX}_3)_2^+$ (R = H or D; py = pyrazolyl). Compound dpp and CO_2 were also formed quantitatively from cdp and acetone, in the presence of catalytic amounts of CoCl_2 or $\text{Co}(\text{NO}_3)_2$. CoCl_2 and dpp gave a product with the same i.r. spectrum and analytical data as complex A. Complexes A and B gave analytical data consistent with the formulations $\text{Co}(\text{dpp})\text{Cl}_2$ and $\text{Co}(\text{dpdp})\text{Cl}_2$, respectively.

Further preliminary studies indicate that metal-catalysed reactions of dipyrazol-1-yl ketone occur with various ketonic solvents, including ethyl methyl ketone, cyclopentanone, and cyclohexanone, and that nickel(II), but not mercury(II), is effective as a catalytic ion. A test run showed that no reaction occurred between acetone and cdp in the absence of cobalt(II) or nickel(II).

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