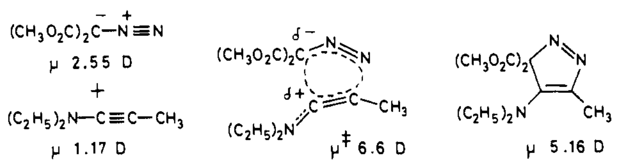
reaction via a zwitterionic intermediate? We measured the dependence of the rate constant on solvent polarity, based on the IR diazo absorption at 2129 cm^{-1}, for diethylaminopropyne + dimethyldiazomalonate and observed a small positive effect (10^5k_2 (L mol^{-1} s^{-1}) at 80.3 °C): decalin, 42; toluene, 45; dioxane, 41; chlorobenzene, 69; HMPTA, 132; DMF, 158; Me_2SO, 265. When log k_2 was plotted vs. the empirical polarity parameter E_T,[15] a linear function (r = 0.95) resulted.



Whereas the data rule out a zwitterionic intermediate, the question of transition-state polarity still deserves attention. We determined the dipole moments of reactants and adduct (benzene, 25 °C). The log k_2 values above fit fairly well a linear relation with $(\epsilon - 1)/(2\epsilon + 1)$ with ϵ being the dielectric constant of the solvent. Based on the Kirkwood-Laidler-Eyring equation,[16] we calculated from the slope of the line and from the dipole moments and molecular volumes of the reactants the dipole moment of the transition state, μ = 6.6 D.[17] Unequal bond formation in the transition state of the concerted cycloaddition induces, in accordance with the PMO treatment, a partial charge separation which exceeds that of the cycloadduct slightly.

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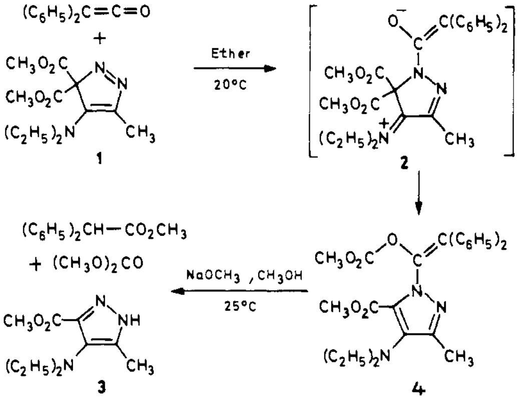
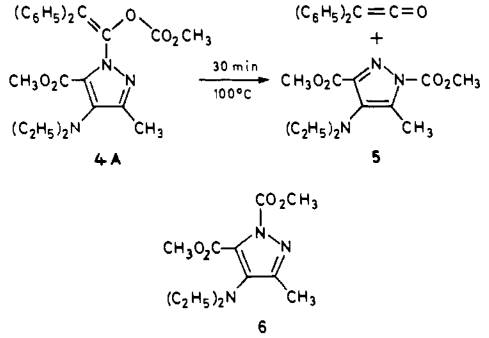
Conducted Tour Mechanism of Ester Group Migration in a 3*H*-Pyrazole

Sir:

Dimethyl 4-dimethylamino-5-methyl-3*H*-pyrazole-3,3-dicarboxylate (**1**)[1] and diphenylketene in ether at 25 °C produced quantitatively the colorless crystals of a 1:1 adduct, mp 72–73 °C.[2] The ^{13}C chemical shifts indicate that all five skeletal carbon atoms are sp^2 hybridized which is incompatible with a cycloadduct. The ketene *O,N*-acetal structure **4** was suggested by the base-catalyzed methanolysis which provided 97% pyrazole **3**[1] besides methyl diphenylacetate and dimethyl carbonate. The similarity of the NMR spectra of **3** and **4** allude to an aromatic pyrazole ring in **4**. The IR absorption at 1777 cm^{-1} is assigned to the enol ester carbonyl and the weak band at 1659 cm^{-1} to the CC double bond.

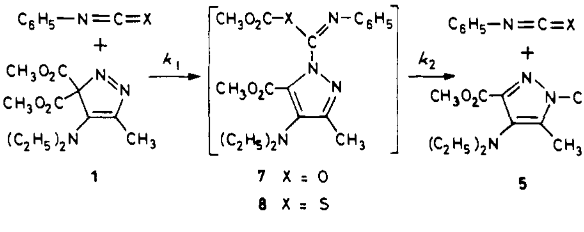


The diethylamino group confers nucleophilicity on the heterodiene system of **1**. In a likely mechanism, diphenylketene attacks at N-1 and affords the iminium enolate zwitterion **2**. Now the anionic oxygen takes over an ester group from the quaternary carbon atom, a process which is facilitated by the aromatization of the heterocycle.



At 100–110 °C **4** was smoothly cleaved, whereby diphenylketene was distilled under high vacuum and furnished 98% methyl diphenylacetate with methanol. The residue turned out to be pure 1,3-dicarboxylic ester **5** which is formed irreversibly; **5** is inert to diphenylketene. The thermal aromatization of the 3*H*-pyrazole **1** by a twofold 1,5-sigmatropic shift, **1** → **6** ⇌ **5**, was described in the preceding communication; the second step requires ~180 °C and results in a 1:3 equilibrium of **6** and **5**.[1] Thus, **1** cannot be an intermediate in the conversion of **4** to **5** + diphenylketene.

The ketene acylal group in **4** is an acylating reagent. In the return of the ester group to C-5, i.e., the regeneration of **1**, the pyrazole aromaticity would be sacrificed. However, the transfer of the ester group to N-2, starting from the rotamer **4A**, offers an attractive pathway. Had we carried out the reaction of **1** with diphenylketene at 100 °C, a mere isomerization, **1** → **4**, would have been observed.



Phenyl *isocyanate* effected an analogous acylation of **1** (45 min, 20 °C, ether) resulting in a 96% yield of **7**: mp 66–67°C; NMR δ 2.18 (s, 3-CH_3), 1.00 and 3.05 (t and q, J = 7.0 Hz, 2 NCH_2CH_3), 3.73 and 3.87 (2 s, 2 OCH_3). Base-catalyzed methanolysis produced **3** + methyl *N*-phenylcarbamate. The pyrocarbonic acid system in **7** transfers its ester group to the adjacent nitrogen at 120 °C; phenyl isocyanate was removed by distillation in vacuo and the residue consisted of 98% **5** in analogy to the behavior of **4**. The high yield of the isolated adduct **7** leaves no doubt about $k_1 \gg k_2$.

On treating **1** with phenyl *isothiocyanate*, one noticed no adduct formation in the NMR spectrum. Slowly—within 4 days at 20 °C the yellow color of **1** faded—a quantitative isomerization of the 3*H*-pyrazole **1** to the aromatic 1,3-dicarboxylic ester **5** was observed. Obviously, we are dealing with a phenyl isothiocyanate catalysis. The catalyst takes over the ester group from C-3 of **1**, carries it in a conducted tour to the other side, and delivers it to the nitrogen atom.

Phenyl isothiocyanate is a weaker acylating reagent than the isocyanate; i.e., it reacts more slowly with **1**. On the other hand, the thiolcarbonic acid group in **8** exceeds the oxygen analogue **7** in acylating strength; biological acylation by acyl coenzyme A may be quoted for comparison. Thus, with phenyl isothiocyanate, formation of **8** is so slow and intramolecular acylation on N-2 to give **5** so fast that the intermediate does not become detectable ($k_1 \ll k_2$).

Kinetic experiments with NMR analysis of **1** and **5** revealed that the isomerization is first order in **1** and in phenyl isothiocyanate. The influence of solvent polarity is rather modest; 10^4k_2 (l mol^{-1} s^{-1}) at 25 °C = 1.6 in $CDCl_3$, 3.9 in benzene, 6.4 in acetonitrile, and 10.7 in nitrobenzene. It may well be that the zwitterion **2**, S^- instead of O^-, is not a discrete intermediate in the pathway to **8**.

Carbon disulfide exerts a similar, though less efficient catalysis. After 10 days at 25 °C the isomerization **1** → **5** was complete.

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(1) Huisgen, R.; Reissig, H.-U.; Huber, H. *J. Am. Chem. Soc.*, preceding paper in this issue.
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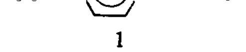
Intramolecular Energy-Transfer Reactions in Mixed Metal Dimers. $(NH_3)_5Ru^{II}LRh^{III}(NH_3)_5$

Sir:

The photochemistry of unsaturated, nitrogen-coordinated, heterocyclic complexes of ruthenium(II) has been extensively studied recently.[1-5] These complexes display intense metal-to-ligand charge-transfer (MLCT) bands in the visible spectral region and, therefore, have the potential for generation of chemical potential energy from the absorption of sunlight. To convert the radiant energy into usable chemical potential energy, the absorbing molecule must either undergo direction reaction[4] or transfer its energy[6,7] or an electron[8-11] to a second, reacting molecule. These latter processes are plagued by the inefficiency inherent to bimolecular quenching processes in dilute aqueous solutions. Here we present evidence for the first intramolecular energy-transfer reaction in dilute aqueous solution using a Ru(II)–Rh(III) mixed metal dimer as a model compound.

Malouf and Ford[5] have demonstrated that $(NH_3)_5Ru^{II}L$ complexes (L = substituted pyridine or pyrazine) display MLCT maxima sensitive to L. Electron-withdrawing substituents lower the MLCT maxima and modify the photochemical reactivity of the complex. Photochemical aquation of L can be drastically reduced when the MLCT maxima is shifted below ~2.1 μm^{-1}, which places the MLCT state at an energy lower than the ^3LF state.[5] For this work, we have prepared and studied $(NH_3)_5Ru^{II}LRh^{III}(NH_3)_5$ complexes where the nature of L places the MLCT maxima, localized mainly on the Ru(II) fragment,[12] below 2.1 μm^{-1} to reduce possible photosubstitution reactions at Ru(II). Rh(III) was selected as the other half of the binuclear complex because the $(NH_3)_5Rh^{III}L$ monomers are known to undergo facile photoaquation reactions[13] and low temperature emission studies[13,14] enabled approximate calculations of the Rh(III) ^3LF excited-state energies.

The two binuclear complexes studied in this work are the pyrazine and 4-cyanopyridine Ru(II)–Rh(III) bridged dimers (**1** and **2**), respectively. The former complex has an MLCT maximum at 528 nm (1.89 μm^{-1}), while the same band for the latter complex occurs at 488 nm (2.05 μm^{-1}). The energies of these MLCT maxima are lower than 2.1 μm^{-1} and little or no photoaquation of Ru(II) is observed in either compound. In fact, extensive irradiation of the pyrazine dimer at 2.29 and 1.83 μm^{-1} leads only to a small decrease in the intensity of MLCT band, and a calculated upper limit quantum yield of 7×10^{-5} and 3×10^{-6} mol/einstein, respectively, for disappearance of starting material.



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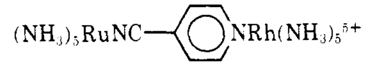
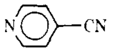
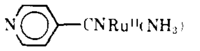


2

The photolysis of the 4-cyanopyridine bridged dimer differs from the pyrazine complex. The 4-cyanopyridine Rh(III) monomer and Ru(II)–Rh(III) dimer photolysis results appear in Table I. Ligand field irradiation of the Rh(III) monomer leads to cleavage of the Rh(III)–pyridine bond (Φ_L = 0.06 mol/einstein), which is characteristic of similar Rh(III) compounds.[13] MLCT irradiation of the 4-cyanopyridine bridged dimer at 436 or 546 nm (2.29 and 1.83 μm^{-1}, respectively) leads to cleavage of the same Rh(III)–pyridine bond. This photolysis reaction is not characteristic of the MLCT (Ru(II) → 4-CNpy) state and we propose that internal conversion from Ru(II) localized excited states to the reactive LF excited state associated mainly with the Rh(III) metal

Table I. Spectroscopic Quantum Yields for the Photoaquation of L from $(NH_3)_5Rh^{III}L^a$

L	E_{max} (Ru(II) → 4-CNpy, MLCT)^b	$E_{irr}{}^b$	$\Phi_L{}^c$
		3.19^d	$6 \pm 2 \times 10^{-2}$
	2.05	3.19^e	$2.2 \pm 0.2 \times 10^{-2}$
		2.29^f	$3.3 \pm 0.4 \times 10^{-3}$
		1.83^f	$3.0 \pm 0.3 \times 10^{-4}$

[a] pH 6.0, $HClO_4$ in H_2O. [b] In units of reciprocal micrometers. [c] For loss of L in units of moles/einstein. [d] Corresponds to ^1E, $^1A_2 \leftarrow {}^1A_1$ Rh(III)LF shoulder on higher energy internal ligand band. [e] Predominantly internal ligand ($\pi^* \leftarrow \pi$) character. [f] Corresponds to MLCT $\leftarrow {}^1A_1$ transition localized mainly on Ru(II) and 4-CNpy.[12]

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