continuing our study of this approach with indoles and are extending it to other heterocycles.

Acknowledgment. We wish to thank Reta H. Roth for carrying out certain experiments.

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On the Effect of *trans* Ligands on the Rate of Some Bridged Electron-Transfer Reactions[1]

Sir:

In 1956 Orgel[2] suggested that the rates of electron-transfer reactions which go *via* a bridged activated complex should depend on the nature of the group *trans* to the bridging group. Outward motion of the *trans* ligand should facilitate electron transfer by lowering the energy of the orbital which receives the transferred electron.

Using conventional spectrophotometric methods, we have measured the rates of Cr(II) reduction of *cis*- and *trans*-Co(en)$_2$A(H$_2$O)$^{+3}$ where en is ethylenediamine and A is either NH$_3$ or H$_2$O. In perchlorate media at 7 and 30°, these rates were inversely proportional to [H$^+$], which was varied between 0.1 and 1 M. The first acidity constant of each aquo ion was measured by pH titration under similar conditions. The observed [H$^+$] dependence indicates that the predominant path for the reaction is an attack of Cr(II) on the conjugate base of the aquo ion. Kruse and Taube[3] have shown that a single oxygen atom is transferred in the Cr(II) reduction of *cis*-Co(en)$_2$(H$_2$O)OH^{+2}; this supports the bridged electron-transfer mechanism for these reactions.

In Table I our results are listed as the second-order rate constants, k_2, for the Cr(II) reduction of the

Table I. Kinetica Data for Reduction of *cis* and *trans* Aquo and Ammine Bis(ethylenediamine)cobalt(III) Complexes in Perchlorate Media (1 M)

Oxidant	Cr(II) reductant[a] $k_2 \times 10^{-6}$, M^{-1} sec.$^{-1}$	E_2, kcal./ mole	Fe(II) reductant[b] $k_2 \times 10^4$, M^{-1} sec.$^{-1}$
cis-Co(en)$_2$(H$_2$O)X^{+2}	0.79	6.4	4.6
trans-Co(en)$_2$(H$_2$O)X^{+2}	2.6	2.6	2400
cis-Co(en)$_2$(NH$_3$)X^{+2}	0.20	5.8	0.18
trans-Co(en)$_2$(NH$_3$)X^{+2}	0.22	2.4	0.66

[a] X^{-1} = OH$^-$, 25.5°. [b] X$^-$ = Cl$^-$, 25° (see ref. 4).

hydroxo ions, and the corresponding activation energies, E_2. For comparison, we have listed the recently published results of Benson and Haim[4] on the Fe(II) reductions of the corresponding chloro complexes. The bridge mechanism is a reasonable assumption for the Fe(II) reactions.

The rates of Cr(II) reduction of the Co(en)$_2$-(NH$_3$)OH^{+2} oxidants are about 10^{10} faster than the

(1) Supported by the U. S. Air Force Office of Scientific Research.
(2) L. E. Orgel, *Rept. Xe Consiel, Inst. Intern. Chim. Solvay*, 289 (1956).
(3) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **82**, 526 (1960).
(4) P. Benson and A. Haim, *ibid.*, **87**, 3826 (1965).

rates of Fe(II) reductions of the Co(en)$_2$(NH$_3$)Cl^{+2} oxidants. The principal difference between the two systems resides in the difference of about 1.2 v. (27.6 kcal./mole) in the potentials of the Cr(II) → Cr(III) and Fe(II) → Fe(III) couples. For a pair of outer-sphere electron-transfer reactions for which all factors other than difference in free energy of reaction are either unimportant or constant, Marcus' theory predicts[5]

$$\log \frac{k_{Cr(II)}}{k_{Fe(II)}} \approx \frac{1}{2} \frac{\Delta(\Delta F)}{2.303 RT} = 10$$

It is interesting that this is the same factor observed for these inner-sphere reactions.

In the Cr(II) reductions, there seems to be no marked correlation of rate with the field strength of the *trans* ligand. The rate of reduction of the *trans* aquo complex is somewhat larger than the other rates in the Cr(II) series, but much larger in the Fe(II) series. This smaller effect implies that outward motion of the *trans* ligand is involved in both cases but is much more important in the slower Fe(II) reductions and agrees with the low isotopic fractionation factor for *trans* nitrogen observed in Co(III)–Cr(II) reductions.[6] Since the activation energies, E_2, are the same for *trans* aquo and *trans* ammine oxidants, the relatively small increase in rate for the Cr(II) reduction of the *trans* aquo species must reside in an entropy effect, possibly involved with partial release of the water molecule into the solvent sheath.

The small but real difference between the activation energies of Cr(II) reductions of oxidants which have a chelated nitrogen atom *trans* to the bridge and those with a monodentate ligand in that position agrees with the suggestion that the chelate attachment restrains motion of the nitrogen atom.[6]

It may be concluded that factors involved with outward motion of the *trans* ligand are not totally absent in the Co(III)–Cr(II) system, but they are much less important than in the Co(III)–Fe(II) reductions which proceed at slower rates because of less favorable free-energy change.

(5) R. Marcus, *J. Chem. Phys.*, **43**, 679, (1965); *J. Phys. Chem.*, **67**, 853 (1963).
(6) M. Green, K. Shug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

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Photochemistry of Cyclopropylacrylic Esters

Sir:

Current interest in the photochemistry of cyclopropanes[1] prompts us to disclose some preliminary results concerning the photolytic behavior of a cyclopropyl group residing in conjugation with an α,β-unsaturated ester chromophore.

Irradiation[2] of ethyl 3-cyclopropyl-2-butenoate (I)

(1) See, *inter alia:* (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.* **87**, 1410 (1965); (b) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963); (c) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964); (d) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964); (e) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).
(2) Ether solution, Hanovia 450-w. lamp, and Vycor filter were employed. The benzophenone-sensitized reaction in benzene with Pyrex

to 32% conversion yields,[3] in addition to 5% of the expected[4] β,γ isomer, ethyl 3-cyclopropyl-3-butenoate (IV), a mixture of three products.[5] The major component, formed in 42% yield, was shown to be ethyl 2-methyl-2-cyclopentene-1-carboxylate (V).[6] Ester V is also obtained by the thermal rearrangement of 1. The thermal vinylcyclopropane rearrangement is well documented.[7]

Two additional products are formed from a more complex reaction involving ring opening and loss of two carbons. These products are assigned structures VIII and X on the basis of the following evidence. Ethyl 2-methyl-2-cyclopropene-1-carboxylate (VIII), formed in 5% yield, shows infrared absorption at 1820 cm.$^{-1}$, typical of a cyclopropene double bond.[8] In addition to the ethyl ester signals it exhibits the following n.m.r. absorption: τ^{CCl_4} 3.75 (one-proton multiplet), 7.85 (three-proton doublet, $J = 1.2$ c.p.s.), and 8.0 (one-proton doublet, $J = 1.6$ c.p.s.). Compound VIII rapidly and quantitatively absorbs 1 mole of hydrogen in the presence of palladium on carbon, yielding ethyl cis-2-methylcyclopropanecarboxylate, which was unambiguously synthesized from cis-2-methylcyclopropanecarboxylic acid.[9]

2-Ethoxy-4-methylfuran (X), formed in 1.5% yield, was characterized by the following spectral properties: λ_{max}^{EtOH} 221 mμ (log ϵ 3.7); $\nu_{max}^{CCl_4}$ 1570 and 1610 cm.$^{-1}$; τ^{CCl_4} 3.5 (one-proton quartet, $J = 1.0$ c.p.s.), 5.12 (one proton, broad), 6.03 (two-proton quartet, $J = 6.5$ c.p.s.), 8.10 (three-proton doublet, $J = 1.0$ c.p.s.), and 8.66 (three-proton triplet, $J = 6.5$ c.p.s.). The structure of compound X is assigned on the basis of the spectral evidence; the location of the ethoxy group is corroborated by the unambiguous structure proof of the related furan X1 (vide infra).[10]

Irradiation of esters II and III demonstrates that the relative yield of cyclopentene, cyclopropene, and furan is remarkably dependent on the degree of substitution about the double bond. Irradiation of ethyl 3-cyclopropyl-2-methyl-2-butenoate (III) results in a 13% yield of ethyl 1,2-dimethyl-2-cyclopropene-1-carboxylate (IX) [ν^{CCl_4} 1800 and 1720 cm.$^{-1}$, τ^{CCl_4} 3.67 (one proton, broad), 6.03 (two-proton quartet, $J = 6.5$ c.p.s.), 7.95 (three-proton doublet, $J = 1.4$ c.p.s.), 8.75 (three-

proton, broad), and 8.85 (three-proton triplet, $J = 6.5$ c.p.s.)]. Only 6% of the cyclopentene derivative VII was formed, and no furan could be detected. Preliminary experiments indicate that the major products in the irradiation of ethyl 3-cyclopropyl-2-propenoate (II) are ethyl 2-cyclopentene-1-carboxylate (VI) and 2-ethoxyfuran (XI). Compound XI was identified by comparison with an authentic synthetic sample.[11] No ethyl 2-cyclopropene-1-carboxylate formation has been observed.

Attractive mechanisms for the formation of cyclopropenes, ethoxyfurans, and cyclopentenes involve either pathway A or B in Scheme I. Path A leads via a concerted extrusion of ethylene to a vinylogous carbethoxycarbene represented also as the dipolar resonance form XIII which can be equally derived by a stepwise fragmentation process involving species XII.[12,13] The production of ethoxyfurans and cyclopropenes from the dipolar ion XIII bears close resemblance to the reported formation of similar cyclopropenes and corresponding ethoxyfurans in the addition of carbethoxycarbene to acetylenes[14] where XIII could have similar transitory existence. Experiments are in progress to define further the mechanistic sequence of the photolytic pathway.

Scheme I

I, R = CH$_3$; R′ = H
II, R = R′ = H
III, R = R′ = CH$_3$

XII

V, R = CH$_3$; R′ = H
VI, R = R′ = H
VII, R = R′ = CH$_3$

XIII

VIII, R = CH$_3$; R′ = H
IX, R = R′ = CH$_3$

X, R = CH$_3$; R′ = H
XI, R = R′ = H

filter led, in a fast reaction, only to high molecular weight products. However, control experiments showed that the products resulting from the unsensitized reaction were not stable under the sensitized conditions.

(3) Yields are based on converted ester (cis and trans, present in a photostationary ratio of 50:50). Satisfactory elemental analysis and mass spectral molecular weights were obtained for all new compounds.

(4) M. J. Jorgenson, Chem. Commun., (7) 137 (1965).

(5) The proportion of these compounds appeared to be constant during the photolysis.

(6) Related photochemical vinylcyclopropane rearrangements have been reported in the bicyclo[3.1.0]hexene system [H. Prinsbach and E. Druckrey, Tetrahedron Letters, 34, 2959 (1965)] and in the rearrangement of 1,2-diphenylcyclopropane to 1-phenylindan.[1a] We thank Prof. G. W. Griffin for pointing out the relevance of his observation to our results.

(7) See, inter alia: (a) C. G. Overberger and A. E. Borchert, J. Am. Chem. Soc., 82, 4896 (1960); (b) M. C. Flowers and H. M. Frey, J. Chem. Soc., 3547 (1961); (c) A. D. Ketley and J. L. McClanahan, J. Org. Chem., 30, 940 (1965).

(8) A. Krebs, Angew. Chem. Intern. Ed. Engl., 4, 10 (1965); G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 83, 1003 (1961).
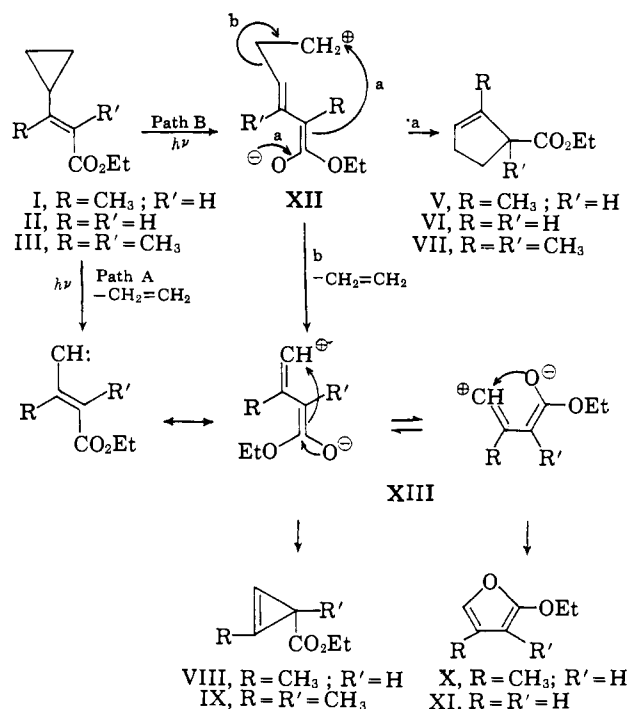
(9) D. E. Applequist and A. H. Peterson, J. Am. Chem. Soc., 82, 2372 (1960). We are indebted to Prof. Applequist for providing a sample of cis-2-methylcyclopropanecarboxamide which was employed as starting material for this synthesis.

(10) Furan X was shown not to be 2-ethoxy-5-methylfuran. Of the two remaining methyl-2-ethoxyfuran structures, the n.m.r. spectrum is consistent only with the 4-methyl isomer.

(11) D. G. Manley and E. D. Amstutz, J. Org. Chem., 21, 516 (1956).

(12) For convenience the polarization of a $\pi \rightarrow \pi^*$ excited state is employed in the derivation of this species, although no evidence exists that the critical excited state is, in fact, of that nature.

(13) The concerted formation of a carbene finds a close analogy in the recent report of the generation of methylene in the photolysis of cyclopropane derivatives [D. B. Richardson, L. R. Durett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, J. Am. Chem. Soc., 87, 2763 (1965)].

(14) (a) R. Breslow and D. Chipman, Chem. Ind. (London), 1105 (1960); (b) I. A. Dyakonov, et al., Zh. Obshch. Khim., 29, 1749, 3848 (1959); 31, 3881 (1961); 32, 923 (1962).

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Existence of the Planar ⇌ Tetrahedral Equilibrium in Solutions of Cobalt(II) Complexes

Sir:

A problem still largely unsolved in metal complex stereochemistry is that of the preferential stabilization of the planar or the tetrahedral stereoisomer in quadri-coordinate complexes of a given metal or in a series of complexes with the same ligand but different metals. From investigations of nickel(II) complexes it is recognized that the free-energy difference between planar and tetrahedral conformers can be adjusted by appropriate substitution on a parent ligand system to a point at which detectable concentrations of both exist in equilibrium in solutions of noncoordinating solvents.[1–4] Thus far the planar ⇌ tetrahedral equilibrium has been detected only in nickel(II) complexes of four general structural types, one of which is a group of bis(β-ketoamino) complexes recently studied.[3] We now report the existence of this configurational equilibrium for some bis(β-ketoamino)cobalt(II) complexes **1** in solution. Other structural equilibria of cobalt complexes in solution are known[5] but do not involve the planar and tetrahedral forms in equilibrium.

1
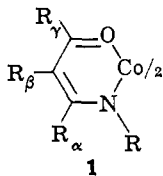
Bis(β-ketoamino)cobalt(II) complexes were prepared by a nonaqueous chelation procedure.[3] All are orange crystalline solids which gave satisfactory microanalyses. The complexes may be divided into two groups.

I $\begin{cases} R_\alpha = R_\gamma = CH_3; & R_\beta = H; & R = CH_3, n\text{-}C_3H_7, i\text{-}C_3H_7, C_6H_5 \\ R_\alpha = CH_3; & R_\beta = H; & R_\gamma = C_6H_5; & R = CH_3, n\text{-}C_3H_7, i\text{-}C_3H_7 \\ R_\alpha = R_\beta = H; & R_\gamma = CH_3; & R = CH_3 \end{cases}$

II $\begin{cases} R_\alpha = R_\gamma = CH_3; & R_\beta = H; & R = H \ (2) \\ R_\alpha = CH_3; & R_\beta = H; & R_\gamma = C_6H_5; & R = H \ (3) \\ R_\alpha = H; & R_\beta = R_\gamma = CH_3; & R = H \ (4) \end{cases}$

At room temperature crystalline group I complexes

(1) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964); A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010, (1964); A. Chakravorty, J. P. Fennessey, and R. H. Holm, *ibid.*, **4**, 26 (1965); L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); L. Sacconi and M. Ciampolini, *ibid.*, **85**, 1750 (1963); L. Sacconi, M. Ciampolini, N. Nardi, *ibid.*, **86**, 819 (1964); L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(2) D. R. Eaton, D. J. Caldwell, and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(3) G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964); *J. Am. Chem. Soc.*, **87**, 2117 (1965).

(4) R. H. Holm, A. Chakravorty, and L. J. Theriot, to be published.

(5) (a) CoL₂X₂ + 2L ⇌ CoL₄X₂; *cf.*, *e.g.*, H. C. A. King, E. Koros, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963); 4832 (1964); (b) tetrahedral ⇌ square pyramidal ⇌ octahedral: L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965); (c) low spin (penta-coordinate dimer) ⇌ high spin (tetrahedral): M. Nicolini, C. Pecile and A. Turco, *J. Am. Chem. Soc.*, **87**, 2379 (1965).

have magnetic moments in the range 4.22–4.44 B.M., and in solutions of noncoordinating solvents such as chloroform and toluene moments of 4.30–4.50 B.M. The ligand-field spectra of these complexes are identical in the solid and in chloroform solutions, exhibiting bands at 8500 and 10,500 cm.$^{-1}$ and 19,100 cm.$^{-1}$, which may be assigned as (components of) ν_2 and ν_3, respectively, in idealized tetrahedral symmetry. Both the magnetic moments and optical spectra of these complexes are nearly identical with those of the analogous bis(N-substituted salicylaldimino)cobalt(II) complexes,[6] several of which have been shown by X-ray results to possess a pseudo-tetrahedral configuration.[7] We conclude that all group I complexes, which have for nitrogen substituents methyl or larger groups, are pseudo-tetrahedral in the solid and completely in this form in solution.

Group II complexes exhibit a distinctly different behavior. In the solid these complexes have moments of 2.17–2.33 B.M. indicating low-spin planar Co(II). In chloroform solutions containing $\sim15\%$ v./v. TMS and *prepared with rigorous exclusion of oxygen and moisture*, the following results were obtained at $\sim25°$: **2**, 4.00 B.M.; **3**, 3.60 B.M.; **4**, 2.88 B.M. The moment of each complex increases with increasing temperature (*e.g.*, for **3**, 3.25 B.M. at $-40°$ and 3.75 B.M. at 58°) and the magnetic changes have been shown to be *reversible* with temperature. The ligand-field spectra of the solid complexes (hydrocarbon mull) show a relatively narrow band at 8500 cm.$^{-1}$ (~1100-cm.$^{-1}$ half-width) and no shoulder at $\sim10,500$ cm.$^{-1}$, a feature clearly evident in all group I complexes. The narrow 8500-cm.$^{-1}$ absorption must be considered characteristic of low-spin Co–N₂O₂ complexes inasmuch as it is found in the solid and solution spectra of N,N′-bis-(salicylidene)ethylenediaminocobalt(II)[8] and bis-(benzoylacetone)ethylenediiminocobalt(II). The solution spectra of the group II complexes contain an 8500-cm.$^{-1}$ absorption and the shoulder at 10,500 cm.$^{-1}$, both of which are reduced in intensity proportionate to the fraction of planar form (obtained from the magnetic data at a given temperature). Associated species are ruled out by the excellent Beer's law dependence[9] of the three group II complexes in chloroform at 25° in the 0.005–0.040 M range, which overlaps with that used in the magnetic measurements. We conclude that the data are consistent only with the equilibrium

planar $(S = {}^1\!/_2, \sim2.2\text{ B.M.}) \rightleftharpoons$ tetrahedral $(S = {}^3\!/_2, \sim4.4\text{ B.M.})$

Thermodynamic data for the equilibrium of **2**, **3**, and **4** have been obtained by magnetic susceptibility measurements (n.m.r. method) of chloroform solutions containing 15% v./v. TMS over the range -40 to 70°. Taking $K_{eq} = N_t/N_p = [(2.2)^2 - \mu^2{}_{obsd}]/[\mu^2{}_{obsd} - (4.4)^2]$, in which 2.2 and 4.4 are the limiting moments of the planar and tetrahedral forms, respectively, the calculated free-energy changes are found to vary linearly with temperature. Least-mean-squares treat-

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(7) E. Frasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961); L. Sacconi and P. L. Orioli, *Ric. sci. rend.*, **32**, 645 (1962).

(8) H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Japan*, **37**, 8 (1964).

(9) Osmometric measurements of molecular weights were vitiated by the extreme sensitivity of the solutions to oxygen.