Although inaccessible via the double Stobbe condensation with pival aldehyde, the diester (7) could be obtained in high yield by pyrolysis of the known sulfone **6**.[5] Selective photosensitized isomerization[9] of **7** does not proceed quantitatively, but a photostationary state can be achieved consisting of 25% of isomer **8**,[5] which is separable by preparative TLC on silica gel. Whereas reduction of esters **7** and **9** with diisobutylaluminum hydride occurs cleanly to produce alcohols **12** and **13**, respectively, similar reduction of **8** is accompanied by extensive rearrangement.

Isolation of diol **10** can be accomplished by preparative TLC;[10] however its NMR spectrum was found to consist of three singlets in $CDCl_3$, CCl_4, CS_2, benzene-d_6, and pyridine-d_5, due to accidental equivalence of the diastereotopic methylene protons.[11] Splitting of the *tert*-butyl singlet is observed in the presence of the chiral shift reagent $Eu(tfc)_3$,[12] indicating that **10** is chiral at room temperature, as expected.

An estimate of the racemization barrier in ester **8** can be made based on the temperature dependence of its NMR spectrum measured in the presence of chiral shift reagent, $Eu(tfc)_3$.[13] At 150° (the highest temperature attainable using bromobenzene-d_5 as the solvent) the peaks corresponding to the diastereomeric association complexes show incipient coalescence, placing a lower limit of ~24 kcal/mol on $\Delta G^{\ddagger}$ for compound **8**. In contrast, the isomeric ester **7** does not show evidence of diastereomeric complexes with $Eu(tfc)_3$ at room temperature (although large pseudo-contact shifts are observed), indicating that the energy barrier for **7** is less than ~13 kcal/mol. A closer approach to the value could not be made because of spectral broadening which occurred as the probe temperature was decreased.

The tertiary alcohol (**11**) also displays only three singlets in the NMR, and readily cyclodehydrates to the isomerized tetrahydrofuran (**14**), in which all four α-methyl groups are nonequivalent. Thermal instability of **14** precluded determination of its $\Delta G_c^{\ddagger}$.

Synthesis and resolution of other systems **1**, are planned.

References and Notes

(1) For part III see preceding paper in this issue.

(2) (a) D. S. Bomse and T. H. Morton, *Tetrahedron Lett.*, 3491–3494 (1974); (b) A. Mannschreck, V. Jonas, H.-O. Bödecker, H.-L. Elbe, and G. Köbrich, *ibid.*, 2153–2156 (1974); (c) H.-L. Elbe and G.Köbrich, *Chem. Ber.*, **107**, 1654–1666 (1974); (d) W. Z. M. Rhee and J. J. Zuckerman, *J. Am. Chem. Soc.*, **97**, 2291–2293 (1975).

(3) M. Rösner and G. Köbrich, *Angew Chem., Int. Ed. Engl.*, **13**, 741–742 (1974).

(4) (a) C. G. Overberger and C. W. Roberts, *J. Am. Chem. Soc.*, **71**, 3618–3621 (1949); (b) H. Stobbe, *Chem. Ber.*, **38**, 3673–3682 (1905).

(5) R. M. Kellogg and W. L. Prins, *J. Org. Chem.*, **39**, 2366–2374 (1974). We are deeply indebted to Professor Kellogg for a generous gift of the dihydrothiophene precursor of compound **6**.

(6) The crystal structure of **3** has been previously reported: T. Ottersen, L. W. Jelinski, E. F. Kiefer, and K. Seff, *Acta Crystallogr., Sect. B*, **30**, 960–965 (1974).

(7) J. P. Schaefer, J. G. Higgins, and P. K. Shenov, "Organic Syntheses", Coll. Vol., V, Wiley, New York, N.Y., 1973, pp 249–251.

(8) Spectra were recorded on Varian XL-100 or HA-100 spectrometers equipped with variable temperature units. Temperatures were calibrated against standards and are considered accurate to ±1°. All coalescence phenomena were fully reversible. $\Delta G^{\ddagger}$ values were calculated at the coalescence temperature from the Eyring rate equation: J. M. Lehn and J. Wagner, *Tetrahedron*, **26**, 4227–4240 (1970).

(9) V. Ramamurthy, Y. Butt, C. Yang, P. Yang, and R. S. H. Liu, *J. Org. Chem.*, **38**, 1247–1249 (1973), and references cited therein.

(10) That **10** is the correct geometric isomer was established by the observation of a 20% nuclear Overhauser enhancement of the vinyl proton intensity upon irradiation at the methylene frequency. The isomeric alcohol **13** shows no corresponding NOE.

(11) The same perverse spectral behavior was shown by Pasto's cyclic *vic*-dialkylidene compounds; see discussion and references in the preceding communication.

(12) $Eu(tfc)_3$ is tris(3-(trifluoromethylhydroxymethylene)-*d*-camphorato)europium(III) derivative.

(13) Determination of internal rotational rates in the presence of optically active shift reagents and solvents has been described and appears to produce values of $\Delta G^{\ddagger}$ ~5% greater than those determined in the absence of chiral interactions: (a) A. Mannschreck, V. Jonas, and B. Kolb, *Angew. Chem., Int. Ed. Engl.*, **12**, 909–1910 (1973); (b) L. D. Colebrook, S. Icli, and F. H. Hund, *Can. J. Chem.*, **53**, 1556–1562 (1975); (c) S. S. C. Yang and R. S. H. Liu, *Tetrahedron Lett.*, 4811–4814 (1973).

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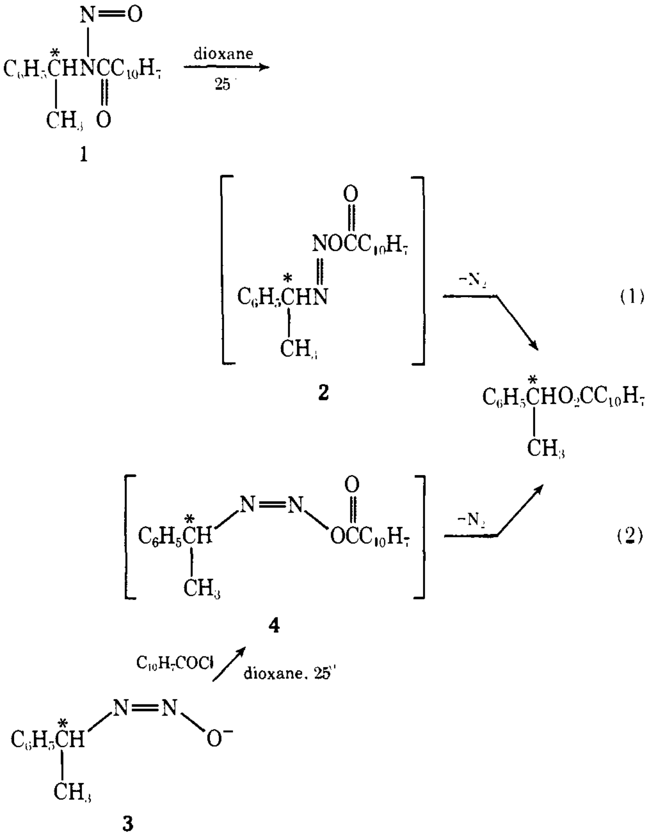
The Ethylation of *syn*- and *anti*-1-Phenylethane Diazotate. Dependence of Reaction Stereochemistry on Configuration at the Diazo Linkage[1,2]

Sir:

The thermolysis of nitrosoamide **1**, via *anti*-diazo ester **2** (eq 1), and the acylation of *syn*-1-phenylethane diazotate (**3**), via *syn*-diazo ester **4** (eq 2), yield 1-phenylethyl 2-naphthoate in similar yields, and with comparable stereochemistry (~73% overall retention).[3] It was concluded that "the stereochemistry of the diazo species is not an important variable".[3] This conclusion need not be general. The potential carboxylate counterion is large and resonance stabilized; these factors could inhibit its ability to quickly collapse with 1-phenylethyl cation, and favor geometrical equilibration of the ion pairs arising from **2** and **4**.



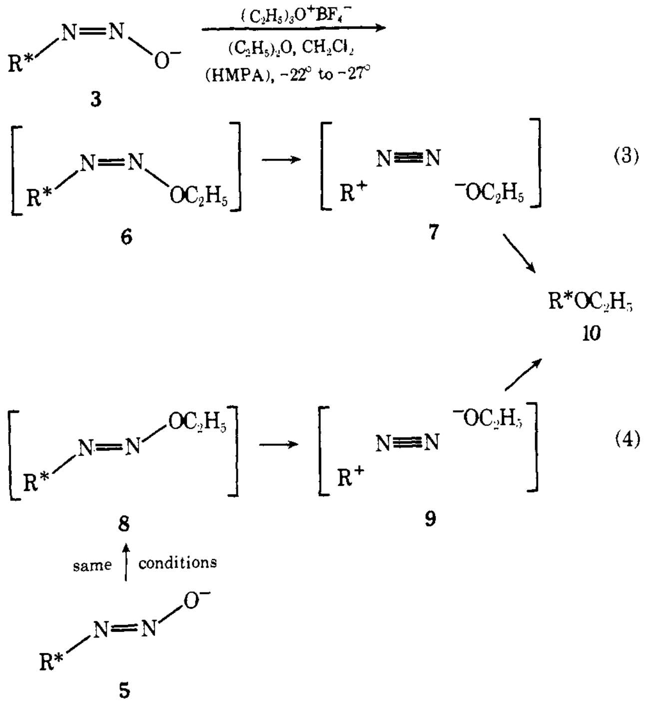
We now report the first *stereochemical studies* carried out *directly* on an *anti*-diazotate. Comparison of the ethylation of *anti*-1-phenylethane diazotate (**5**) (eq 4), with that of its syn isomer, **3** (eq 3), shows that the stereochemistry of the diazo species *is an important variable*.

anti-1-Phenylethane diazotate (**5**) was prepared from 1-phenylethylhydrazine,[2,4] KOC_2H_5-C_2H_5OH, and isoamyl nitrite.[3,5] Removal of volatile constituents (0.25 mmHg) afforded **5** (ir, Nujol[3]) free of alcohols, although isoamyloxide (and ethoxide) must have been present. Treatment of **5** (suspension in ether or solution in 15% HMPA-ether) with

Table I. Stereochemical Course of Formation of 1-Phenylethyl Ethyl Ether

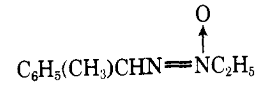
Case	Diazotate	Conditions[a]	α_D deg (temp °C)/optical purity (%)			Reaction stereochem, % net retn
			Initial RNH_2	Derived $RNHNH_2$	Product 10	
1	5	Direct, no HMPA	−36.89 (23)[b]/96.3[c]	−29.19 (25)[d]/96.3[e]	−7.24 (22)[b]/8.31[f]	8.63[g]
2	5	Direct, HMPA	−36.89 (23)/96.3	*h*	−3.54 (33)/4.06	4.22
3	5	Inverse, HMPA	−36.89 (23)/96.3	*h*	0.00 (22)/0.00	0.00
4	3[i]	Direct, no HMPA[j]	−37.43 (22)/97.7	*k*	−48.43 (22)/55.6	56.9
5	3[l]	Direct, HMPA	−37.19 (24)/97.1	*k*	−33.35 (23)/38.3	39.4

[a] Direct addition: $(C_2H_5)_3O^+BF_4^-$–CH_2Cl_2 was added to a suspension (no HMPA) or a solution (15 vol % HMPA) of diazotate in ether. Inverse addition: the diazotate was added to the oxonium salt solution. [b] Neat liquid, l = 1 dm. [c] The optically pure amine has $\alpha^{22}D$ −38.30° (neat, 1 dm).[12] [d] $[\alpha]^{25}D$ (c 1.391, benzene). [e] The optically pure hydrazine has $[\alpha]^{25}D$ −30.3° (c 0.784, benzene).[2,13] [f] Optically pure 10 has $\alpha^{28}D$ −87.04° (neat, 1 dm).[14] Control experiments showed that 10 retains 97% of its optical activity upon exposure to twofold excess $(C_2H_5)_3O^+BF_4^-$, under reaction conditions, for 12 h. [g] Corrected for the optical purity of the initial amine. In the 1-phenylethyl system, amino and ethoxyl derivatives of analogous configuration exhibit identical rotational signs.[15] [h] Not measured. [i] From ref 11. [j] CH_2Cl_2 was the solvent; the temperature was −40° to −20°. At +3° to +18°, 10 was formed with 53.0% net retention.[11] [k] Not applicable. [l] This work.



$(R^* = C_6H_5(CH_3)\overset{*}{C}H-)$

4 equiv of $(C_2H_5)_3O^+BF_4^-$ in CH_2Cl_2 at −22° to −27° gave smooth nitrogen evolution (92%), complete at the end of reagent addition (21 min). An aqueous work-up, followed by GC isolation, afforded styrene (9.6%), 1-phenylethyl ethyl ether (**10**) (24%), and 1-phenylethyl isoamyl ether (35%).[6] Neither 1-phenylethanol nor azoxyalkane **11**[7] were present.



$$C_6H_5(CH_3)CHN\overset{\overset{O}{\uparrow}}{=}NC_2H_5$$

11

Optically active 1-phenylethylhydrazine was stereospecifically prepared from 1-phenylethylamine,[8] converted to **5**,[9] and ethylated. Table I delineates the stereochemical course of the ensuing **5** → **10** conversion, together with parallel results for the ethylation of **3**.[9,11]

Alkylations **3** → **6**, eq 3,[11] and **5** → **8**, eq 4, should be fully stereoconservative.[16] Racemization attending conversions **3** → **10** and **5** → **10** can therefore be attributed to the respective intermediate nitrogen-separated ion pairs, **7** and **9**.[17] Comparisons of cases 1 with 4 or 2 with 5 (Table I) show that loss of stereochemical "memory" is 6.6 or 9.3 times greater, respectively, in conversion of **8** → **10** (via **9**) than in conversion of **6** → **10** (via **7**).[19] One interpretation holds that collapse of **9** → **10** is slower than that of **7** → **10**, giving more time for "cation rotation" [20] within the former ion pair, and hence greater racemization. This is compatible with the greater C*-O separation[21] in precursor **8** (3.5 Å), relative to **6** (2.7 Å), and with an intuitive expectation of greater interference to collapse by the interposed nitrogen molecule in **9**, relative to **7**.[22]

Alternative, less economical interpretations are possible, but the significant dependence of reaction stereochemistry on diazo configuration appears definite. Why conversion **8** → **10** is so much less stereoconservative than **2** → 1-phenylethyl 2-naphthoate[3,23] is presently unclear.

Note, finally, that N-alkylation of *anti*-**5** does not occur; **11** is not formed. This contrasts with facile formation of **11** by N-alkylation of *syn*-**3**.[7,24] These results parallel the contrasting alkylations of sodium *Z*-benzaldoximate (analogue of **3**), in which only nitrones (analogues of **11**) are formed, and of sodium *E*-benzaldoximate (analogue of **5**) in which benzaldoxime ethers (analogues of **8**) are the dominant products.[25] Steric selection of alkylation site[25] may be operative in these examples.

Acknowledgments. We thank the National Science Foundation and the Public Health Service (Research Grant CA-14912 from the National Cancer Institute) for financial support.

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(1) Alkane Diazotates, Part XX.

(2) For Part XIX, see R. A. Moss and C. E. Powell, *J. Org. Chem.*, **40**, 1213 (1975).

(3) E. H. White, T. J. Ryan, and K. W. Field, *J. Am. Chem. Soc.*, **94**, 1360 (1972).

(4) C. G. Overberger and A. V. DiGiulio, *J. Am. Chem. Soc.*, **80**, 6562 (1958).

(5) J. Thiele, *Chem. Ber.*, **41**, 2806 (1908); *Justus Liebigs Ann. Chem.*, **376**, 239 (1910). The molar ratio of reagents was 1:2:4.3, respectively.

(6) (a) Consonant ir, NMR, and exact mass (M^+) spectra were obtained for **10**, C_2H_5 = *i*-C_5H_{11}. Its origin must lie in reaction of **5** with (e.g.) (*i*-$C_5H_{11})_2C_2H_5O^+BF_4^-$ formed by rapid reactions of $(C_2H_5)_3O^+BF_4^-$ with the excess *i*-$C_5H_{11}O^-$ present. Other products were identified by spectral comparisons with authentic samples. Yields (Gc, hexadecane standard) are relative to 1-phenylethylhydrazine. (b) In "direct addition" (see Table I, note *a*), *i*-C_5H_{11} is the dominant alkyl group available during much of the alkylation process. This accounts for the high yield of **10**, C_2H_5 = *i*-C_5H_{11}, relative to **10** itself.

(7) R. A. Moss and M. J. Landon, *Tetrahedron Lett.*, 3897 (1969).

(8) E. Schmitz and D. Habisch, *Chem. Ber.*, **95**, 680 (1962).

(9) *syn*-Octane 2-diazotate is configurationally stable (at C*) to *tert*-butoxide;[10] **3** should be similarly stable.[11] Diazotate **5** should also be configurationally stable to generative conditions; prepared in C_2H_5OD, its NMR[3] revealed <7% H–D exchange at carbinyl carbon. Because integration overestimates the broad phenyl signal, relative to the carbinyl quartet, exchange must have been considerably less than 7%, and may have been nil.

(10) R. A. Moss and G. M. Love, *J. Am. Chem. Soc.*, **95**, 3070 (1973).

(11) R. A. Moss and M. J. Landon, *J. Am. Chem. Soc.*, **92**, 5755 (1970).

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(13) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969).

(14) K. Mislow, *J. Am. Chem. Soc.*, **73**, 4043 (1951).

(15) J. A. Mills and W. Klyne, *Prog. Stereochem.*, **1**, 194 (1954).

(16) It is unlikely that **6** and **8** interconvert; cf. ref 3, note 11.

(17) (a) Repetition of case 2 using **5** prepared with CH_3O^- CH_3OH gave **10** with 4.29% net retention. (In this experiment, **10**, C_2H_5 = CH_3, was formed with 0.1% net retention.) Close agreement with results obtained using **5** prepared with $C_2H_5O^-$–C_2H_5OH eliminates the possibility that **10**, formed solvolytically *during the preparation* of **5** has biased the observed stereochemistry. (b) Exclusion of $C_6H_5(CH_3)C{=}N_2$ as a racemizing intermediate (from **6** or **8** by loss of ethanol) is necessary because **10** is formed by reaction of $C_6H_5(CH_3)C{=}N_2$ and $(C_2H_5)_3O^+BF_4^-$.[18] However, nitrogen-evolution controls show that the latter reaction occurs either very slowly, or not at all, at −22° to −27°; i.e., conditions under which reactions of **3** or **5** with $(C_2H_5)_3O^+BF_4^-$ are fast and near quantitative. (c) Alternative mechanisms which feature bimolecular reactions of **5** with itself, or with oxonium ions derived from **10**, are inconsistent with the similar stereochemical results of direct and inverse addition experiments (Table I, note *a*, and runs 2 and 3). Specifically, such mechanisms predict more inversion for **10** formed in direct addition. This is not observed.

(18) R. A. Moss, C. E. Powell, and K. M. Luchter, unpublished observation.

(19) Both reactions are less stereoconservative in the presence of HMPA, consistent with their ionic nature.

(20) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N.Y., 1968, especially pp 449–452.

(21) Separations were measured from Dreiding models.

(22) Reasons for excluding alkyldiazonium ions in eq 3 or 4 are discussed in R. A. Moss, *Acc Chem. Res.*, **7**, 421 (1974).

(23) Parallel reactions of the syn analogues are almost identical: **6** → **10**, 78% (overall) retention, Table I, case 4; **4** → 1-phenylethyl 2-naphthoate, 73% retention.[3]

(24) R. A. Moss, M. J. Landon, K. M. Luchter, and A. Mamantov, *J. Am. Chem. Soc.*, **94**, 4392 (1972).

(25) E. Buehler, *J. Org. Chem.*, **32**, 261 (1967).

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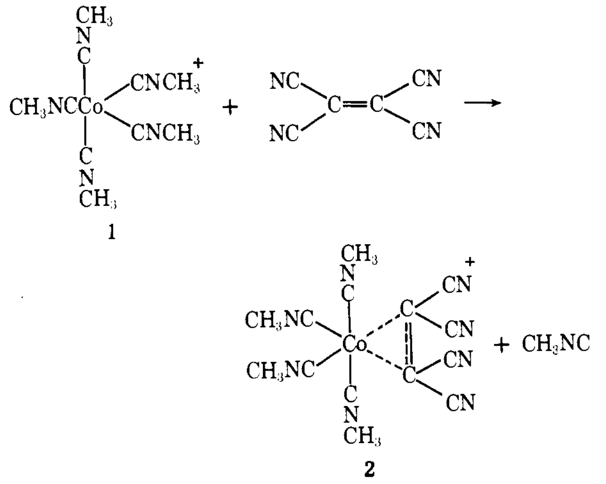
Evidence for Radical Intermediates in the Addition of Tetracyanoethylene to Pentakis(methyl isocyanide)cobalt(I)

Sir:

A number of reports of the involvement of free radicals in reactions of both d^8 and d^{10} transition metal complexes has recently appeared.[1-7] The involvement of electron-transfer steps is most probable in cases where the specific metal concerned is known to undergo one-electron transfer to give a stable complex with a d^7 or d^9 electronic configuration. Consequently, of the various group 8 metal complexes with a d^8 electronic configuration, those of Co(I) are the most likely to undergo a one-electron oxidation, since Co(II) is the most commonly encountered d^7 ion within this group. Many previous studies of Co(I) reactions have stressed the role of Co(I) as a nucleophile;[8] here are presented data which suggest that outer-sphere electron-transfer may also be involved in reactions of Co(I) complexes.

The reaction of tetracyanoethylene with $[Co(CNCH_3)_5][PF_6]$ (**1**)[9] in a variety of solvents including acetone, dichloromethane, and acetonitrile produces via eq 1 the yellow cation **2** which has been isolated as the hexafluorophosphate in yields of 90% (Anal. found for $C_{14}H_{12}CoN_8PF_6$, C, 33.93; H, 2.49; N, 22.36. Ir (Fluorolube mull) 2275, 2255, 2230 cm^{-1} ($\nu_{C\equiv N}$); ^{1}H NMR (CD_3COCD_3) τ 6.26 (6 H, $^2J_{NH}$ = 2.4 Hz), 6.12 (6 H, $^2J_{NH}$ = 2.4 Hz). Mixing the reactants of eq 1 produced a transient brown color. The evidence reported below suggests that the transient arises via reaction 2, an outer sphere, electron-transfer step and that this is followed by reaction 3 which generates the final products. Both of the products of reaction 2—tetracyanoethylene radical anion[10] and $Co(CNCH_3)_5^{2+}$ [11]—are known, isolable species. Thermodynamically, the electron transfer of eq 2 is favored as demonstrated by electrochemical measurements. In acetonitrile solution with 0.1 M $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte and an aqueous calomel reference electrode, tetracyanoethylene undergoes a one-electron reduction with a half-wave potential of +0.22 V. Under similar conditions $Co(CNCH_3)_5^+$ undergoes a one-electron oxidation with a half-wave potential of +0.10 V. Cyclic voltammetry demonstrates that this process is quasi-reversible with equal anodic and cathodic peak currents but with the peak separation of 120 mV. The identity of the electrochemical oxidation product as $Co(CNCH_3)_5^{2+}$ has been established; this complex undergoes one-electron reduction with a half-wave potential of +0.10 V.



(1)

$$Co(CNCH_3)_5^+ + (CN)_2C{=}C(CN)_2 \rightarrow Co(CNCH_3)_5^{2+} + (NC)_2C{=}C(CN)_2^- \quad (2)$$

$$Co(CNCH_3)_5^{2+} + (NC)_2C{=}C(CN)_2^- \rightarrow \mathbf{2} + CNCH_3 \quad (3)$$

Through the use of a flow system in conjunction with electron spin resonance (ESR) spectroscopy it has been possible to detect the tetracyanoethylene radical anion during reaction **1**. When a 5 mM dichloromethane solution of **1** and a 5 mM dichloromethane solution of tetracyanoethylene are mixed in a flow system with a flow rate of 25 ml/min through a tube with 3 mm i.d., it has been possible to detect the characteristic 11-line ESR spectrum[12] (a(N) = 1.5 g) of the tetracyanoethylene radical anion. This could only be observed under the conditions of rapid flow. When the flow was stopped, the ESR spectrum of the radical anion vanished. No ESR signal due to $Co(CNCH_3)_5^{2+}$ could be observed. The inability to observe such a signal is not surprising in view of the low concentration and the line width of the ESR spectrum of $Co(CNCH_3)_5^{2+}$. The observation of the ESR spectrum of the tetracyanoethylene radical appears to be the result of eq 1 only. Under similar circumstances the reactions of methyl isocyanide, pentakis(methyl isocyanide)cobalt(II), or **3** with tetracyanoethylene do not produce the tetracyanoethylene radical anion.

Finally the separate occurrence of reaction 3 has been verified. When $[Co(CNCH_3)_5]^{2+}$ and $K[(NC)_2C{=}C(CN)_2]$[9] are mixed in acetonitrile solution **2** is formed in greater than 85% yield.

Although tetracyanoethylene undergoes addition to a variety of d^8 and d^{10} metal complexes,[14] the reaction reported here is the first in which the transient appearance of radicals has been observed. By way of comparison the addition of tetracyanoethylene to $Rh(CNR)_4^+$ has been examined; products analogous to **2** are formed.[13] However, no evidence for paramagnetic intermediates has been found and electrochemical examination of these and other Rh(I) com-