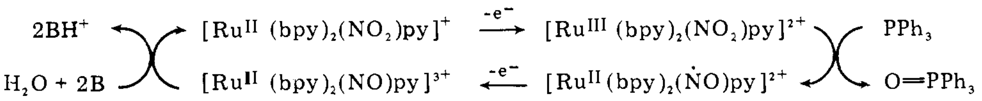
Scheme I (note Figure 2)



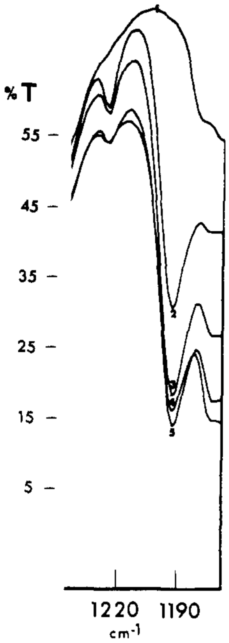


Figure 2. Infrared spectra following electrolysis of an acetonitrile solution containing initially $[Ru(bpy)_2(NO_2)py]^+$ (1.2×10^{-3} M), PPh_3 (7×10^{-3} M), 1% 2,6-lutidine, and 1% water in 0.1 M $[N(C_4H_9)_4]PF_6$. ν(PO) in $O{=}PPh_3$ occurs at 1194 cm^{-1}. The lower energy band arises from $[Ru(bpy)_2(NO_2)py]^+$: (1) before electrolysis; (2) electrolysis to 25% completion based on the initial amount of PPh_3; (3) electrolysis to 50% completion; (4) electrolysis to 60% completion; (5) electrolysis to 75% completion.

Rather than thermodynamic driving force, the origin of the relatively rapid rates of disproportionation and of PPh_3 oxidation may lie in the existence of two one-electron acceptor sites (Ru(III) and $Ru\text{-}^+NO$) in the oxidant rather than a single two-electron site and in the ability of the oxidant to donate an oxide ion. Kinetic barriers to electron transfer at both Ru(III)[8] and $Ru(^+NO)$[2] sites are known to be low and there are no profound changes in coordination environment on reduction except for the loss of O^{2-}.

$[Ru(bpy)_2(NO_2)py]^+$ and $[Ru(bpy)_2(NO)py]^{3+}$ are interrelated by the acid-base equilibrium in eq 8 and in water, the two ions are present in equimolar amounts at pH 3.8.[1,9]

$$[Ru(bpy)_2(NO)py]^{3+} + 2OH^- \rightleftharpoons [Ru(bpy)_2(NO_2)py]^+ + H_2O \qquad (8)^1$$

$$K(25.0\ ^\circ C;\ 1.0\ M\ NaCl) = 1 \times 10^{20}\ M^{-2}$$

In slightly basic solution the nitrosyl complex once formed (eq 6 and 7) is converted into the nitro complex. The nitro complex reenters the oxidation sequence in reactions 5–7, which means that the oxidation of PPh_3 can be made catalytic. Exhaustive electrolysis (at 1.15 V) of an acetonitrile solution containing $[Ru(bpy)_2(NO_2)py]^+$ (1×10^{-3} M), PPh_3 (1×10^{-2} M), H_2O (1%), and 2,6-lutidine (1%) gave $n = 21.1$ by coulometry. The final ruthenium product was $[Ru(bpy)_2(NO_3)py]^{2+}$ (by cyclic voltammetry). The results are consistent with the catalytic cycle in Scheme I ($n = 20$) followed by reaction 9 ($n = 3$) when the $PPh_3 \rightarrow O{=}PPh_3$ conversion (Figure 2) is complete.

$$[Ru^{II}(bpy)_2(NO_2)py]^+ + 2B + H_2O \xrightarrow{-3e^-} [Ru^{III}(bpy)_2(NO_3)py]^{2+} + 2BH^+ \qquad (9)^1$$

The electrolytic chemistry observed here is the chemically catalyzed, net electrochemical oxidation of PPh_3 to $O{=}PPh_3$.

$$PPh_3 + H_2O + 2B \rightarrow O{=}PPh_3 + 2BH^+ + 2e^- \qquad (10)$$

In an acetonitrile solution containing $[Ru(bpy)_2(NO_2)Cl]$, water, and triethylamine, the oxidation of PPh_3 is also catalytic. Under these conditions cyclic voltammetry shows only a distorted wave for the $[Ru^{II}(bpy)_2(NO_2)Cl] \rightarrow [Ru^{III}(bpy)_2(NO_2)Cl]^+$ oxidation and no rereduction wave, nor does a wave for $[Ru(bpy)_2(NO)Cl]^{2+}$ appear. The experiment shows that the chemical steps in Scheme I are rapid and that the *rate determining step in the catalyzed oxidation of* PPh_3 *is diffusion of* $[Ru(bpy)_2(NO_2)Cl]$ *to the electrode.*

The Ru(III)-nitro intermediates appear to have an extensive oxidase-like redox chemistry and their reactions with various reagents are currently under investigation. They are promising as oxidants, since in contrast to commonly used inorganic oxidants like Cr(VI) or MnO_4^-, their reactivity properties can be varied systematically by controlled chemical synthesis, and their reactions can be made catalytic.

Acknowledgment is made to the National Science Foundation under Grant MPS75-11867 and to the Materials Research Center of The University of North Carolina under Grant DAHC15 73 G9 with the National Science Foundation for support of this research.

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(1) F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 2384 (1977).

(2) T. J. Meyer, R. W. Callahan, and G. M. Brown, *J. Am. Chem. Soc.*, **97**, 894 (1975); R. W. Callahan and T. J. Meyer, *Inorg. Chem.*, **16**, 574 (1977).

(3) Unless otherwise noted electrochemical results were obtained in solutions 0.1 M in $[N(n\text{-}C_4H_9)_4]PF_6$ at 22 ± 2 °C vs. the saturated sodium chloride calomel eletrode (SSCE). Platinum bead electrodes were used in cyclic voltammetry and platinum gauze electrodes for electrolyses. *n* values were obtained by coulometry, where *n* is the number of electrons passed per Ru in a constant potential electrolysis.

(4) Disproportionation gives nitrosyl *and* nitrato complexes as products and $n = 3.0$ (eq 1 and 2).[1]

(5) Ca. 7% ^{18}O-enriched $[Ru(bpy)_2(NO_2)Cl]$ was prepared by treating a suspension of $[Ru(bpy)_2(NO)Cl](PF_6)_2$ with base in ^{18}O-enriched water.[6]

(6) T. J. Meyer and J. B. Godwin, *Inorg. Chem.*, **10**, 2150 (1971).

(7) Quantitative IR experiments were carried out using a Digilab FTS-14 spectrometer.

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(9) For the $[Ru(bpy)_2(NO)Cl]^{2+}$–$[Ru(bpy)_2(NO_2)Cl]$ equilibrium, *K* is 1.4×10^9 under the same conditions.[6]

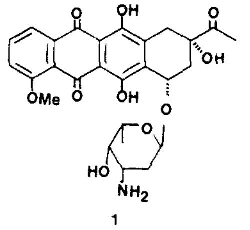
F. Richard Keene, Dennis J. Salmon, Thomas J. Meyer*
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received November 8, 1976

An Anionic Equivalent of the Friedel-Crafts Cycloacylation

Sir:

Our interest in the potent anticancer agent daunomycin[1] (**1**) has led us to consider possible synthetic routes[2] to this and other anthracycline antibiotics.[3] The problem, as we see it, is to develop methods for ring building as in eq 1 wherein the alicyclic ring possesses the desired functionality. In this manner one may reduce the regiospecificity problems[2] associated with anthracycline synthesis to that of constructing simply substituted anthraquinones. The traditional solution to the above transformation (eq 1) revolves around Friedel-Crafts chemistry and is essentially inconsistent with the presence of any degree of functionality on the ring being formed. We herein report what is essentially an anionic equivalent of the Friedel-Crafts cycloacylation that shows some promise as a synthetic entry into this class of compound.



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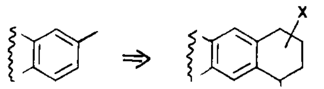
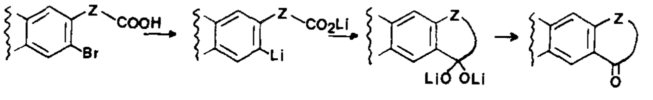


(1)

Treatment of o-bromophenylalkanoic acids (or lithium salts with 2.1-2.5 equiv of n-butyllithium (or 1.2-3 equiv of *tert*-butyllythium) in tetrahydrofuran (THF) at temperatures ranging from −110 to 0 °C affords the expected benzocycloalkenones in good yields. The reaction presumably proceeds[4] as in eq 2. The starting materials are available from o-bromobenzyl bromides by standard methods.[5] Thus the following compounds were prepared (acid or lithium salt, organolithium reagent, time, temperature, isolated yield): 1-indanone[6] (acid, n-C_4H_9Li, 5 min, −80 °C, 65%); 1-tetralone (salt, t-C_4H_9Li, 1 h, −80 to −35 °C, 73% as 2,4-DNP); benzsuberone (salt, t-C_4H_9Li, 2 h, −80 to −20 °C, 48%); **2** (acid, n-C_4H_9Li, 5 min, −80 °C, 67%); anthrone (**3**) (acid,[7] n-C_4H_9Li, 10 min, −80 °C, 74%); and **5** (eq 3)[8] (acid, n-C_4H_9Li, 2 h, −110 to −0 °C, 55%). By-products are usually the debrominated starting acids which presumably arise by competing enolization reactions. Butyl ketones, which would arise from intermolecular reactions, are produced to only a small extent. While **5** is produced smoothly from the bromo acid[9,10] **4** the corresponding cyclization of anthraquinone **6** failed, apparently owing to competing electron transfer and addition of the organometallic reagent to the quinone carbonyls.



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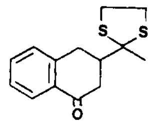

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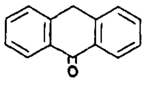

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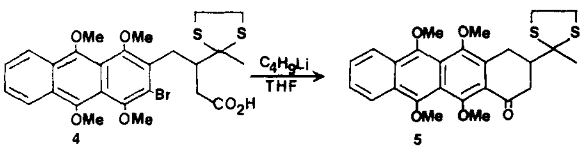

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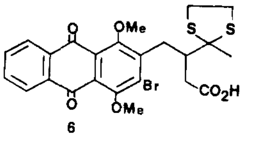
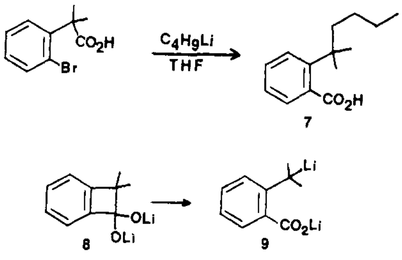


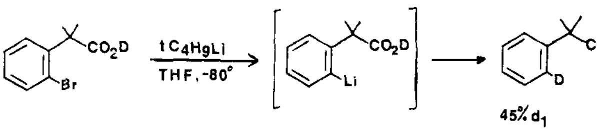
6

The attempted cyclization of o-bromophenylacetic acid with n-butyllithium afforded only phenylacetic acid. Deuterium labeling showed that isomerization of lithium o-lithiophenylacetate to the enol lithium α-lithiophenylacetate was responsible. To circumvent this, the cyclization of o-bromophenyldimethylacetic acid was attempted with the results shown in eq 4. The product, **7**,[11] presumably arises as shown, **9** being captured by the butyl bromide produced in the reaction. Ring openings as in **8** → **9** are precedented.[12]



(4)

Use of *tert*-butyllithium afforded only phenyldimethylacetic acid. Deuterium-labeling studies gave the result of eq 5. The fact that *tert*-butyllithium is a stronger kinetic base toward bromine than toward carboxylic acid protons is a striking but not totally unprecedented result.[13]



(5)

The experimental procedures employed may be illustrated by the conversion **4** → **5**. To a stirred solution of 1.10 g (1.90 mmol) of **4** in 50 mL of THF at ca. −100 °C (liquid nitrogen, ether bath) was added dropwise 2.1 equiv (2.45 mL of a 1.57 M hexane solution) of n-butyllithium. The reaction mixture was then allowed to warm to room temperature over 2 h. Workup afforded 550 mg of neutral and 421 mg of acidic material. Routine chromatography and recrystallization of the neutral fraction afforded 508 mg of **5**: mp 173-175 °C; δ ($CDCl_3$) 8.32 (2 H, m, Ar H), 7.51 (2 H, m, Ar H), 3.8-4.0 (13 H, OCH_3 + CH), 3.35 (4 H, s, SCH_2CH_2S), 2.4-3.3 (4 H, m), 1.91 (3 H, s, CH_3); λ_{max}^{MeOH} 444 (5100); m/e 484.13729 (calcd for $C_{26}H_{28}O_5S_2$ 484.13780). Anal. Calcd for $C_{26}H_{28}O_5S_2$: C, 64.44; H, 5.82. Found: C, 64.21, 64.02; H, 5.9, 5.87. The acidic fraction is principally "debrominated acid" (ii[10]), mp 158.5-160 °C.

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(2) (a) A. S. Kende, Y. Tsay, and J. Mills, *J. Am. Chem. Soc.*, **98**, 1967 (1976); (b) C. M. Wong, D. Popien, R. Schwenk, and J. TeRaa, *Can J. Chem.*, **49**, 2712 (1971); (c) T. R. Kelly, J. W. Gillard, and R. N. Goerner, Jr., *Tetrahedron Lett.*, 3873 (1976); (d) A. S. Kende, J. L. Bellitire, and E. Hume, *ibid.*, 2117 (1974).

(3) H. Brockmann, *Fortschr. Chem. Org. Naturst.*, **21**, 121 (1963).

(4) (a) W. F. Parham and Y. A. Sayed, *J. Org. Chem.*, **39**, 2051 (1974); (b) W. F. Parham and L. P. Jones, *ibid.*, **41**, 2704 (1976).

(5) All new compounds gave satisfactory elemental and spectral analyses.

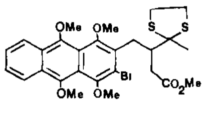
(6) W. F. Parham, L. D. Jones, and Y. A. Sayed, *J. Org. Chem.*, **40**, 2394 (1975).

(7) From o-(o-bromobenzyl)benzoic acid, this being prepared from o-bromobenzoic acid via sequential treatment with n-C_4H_9Li/THF, $(Bu_3P)_2CuI$, and o-bromobenzyl bromide.[14]

(8) The conversion **6** → **4** is achieved in 80-88% yield by treatment of **6** with sodium dithionite, aqueous potassium hydroxide, and dimethyl sulfate in dimethylformamide. Quinone **6** may in turn be prepared from 1,4-dimethoxy-2-methyl-3-bromoanthraquinone in an overall yield (purified material) of 70-79% via sequential bromination with NBS, reaction with di-*tert*-butyl acetylsuccinate/NaH/DMF, deesterification-carboxylation with pTSA in benzene, and thioketalization.

(9) This cyclization is quite slow at −78 °C and proceeds rapidly only at 0 °C. This is due presumably to steric problems involving the methoxys and the tertiary butyloidal dithiane group.

(10) Treatment of methyl ester i with *tert*-butyllithium at −100 °C also affords **5**. The efficacy of reductive methylation as a technique for "blocking" anthraquinones is illustrated by the fact that ii may be cyclized to **5** in quantitative yield by trifluoroacetic anhydride at −40 °C.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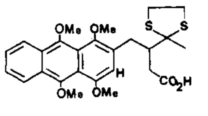
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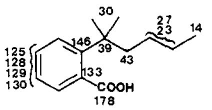
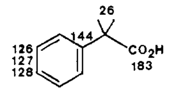
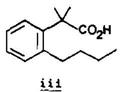
(11) Structure 7 is preferred rather than the isomeric iii on the basis of ^1H and ^{13}C NMR and mass spectral fragmentation. The ^{13}C NMR assignment is as shown below:






iii

(12) I. Fleming and T. Mah, *J. Chem. Soc. Perkin Trans. 1*, 964 (1975).
(13) C. Y. Stein and T. H. Morton, *Tetrahedron Lett.*, 4934 (1973).
(14) We thank Ms. Alexandra Brown for a sample of *o*-(*o*-bromobenzyl)benzoic acid.
(15) Partial support of this work by NIH is acknowledged.

R. J. Boatman, B. J. Whitlock, H. W. Whitlock, Jr.*[15]
Department of Chemistry, University of Wisconsin—Madison
Madison, Wisconsin 53706
Received January 17, 1977

Sequential Two Photon Photoredox Chemistry of Transition Metal Compounds. Nonlinear Intensity Effects in Photochemistry of the Reineckate Ion[1]

Sir:

Two photon photochemical effects appear to play a major role in the photochemistry of chlorophyll.[2] Two photon processes have been investigated in the luminescence of some dye molecules,[3] in the spectroscopy of a variety of substrates,[4,5] and in gas phase photochemical studies.[6] There have been few systematic investigations of two photon photochemical processes with condensed phase substrates.[7-9]

The reineckate ion, $Cr(NH_3)_2(NCS)_4^-$, has become an important chemical actinometer for visible radiation.[10] The use of the reineckate ion as a chemical actinometer depends upon the photoaquation of NCS^- (eq 1). However, near-ultraviolet excitations of $Cr(NH_3)_2(NCS)_4^-$ do lead to the formation of $(NCS)_2^-$ and Cr^{2+} in small yields ($\phi \sim 10^{-3}$) (eq 2).[11,12] Thus using $Co(NH_3)_5F^{2+}$ (7×10^{-3} M) to scavenge for Cr^{2+} (eq 3)[13-15] we find that $\phi_{Co^{2+}} = 3.4 \times 10^{-3}$ for 337-nm irradiations (xenon lamp with cut-off filter and monochromator) and 7.7×10^{-3} for 254-nm excitations (low pressure mercury lamp). In these same experiments, we found the quantum yields for NCS^- aquation to be 0.25 and 0.30,[15,16] respectively.

$$Cr(NH_3)_2(NCS)_4^- + h\nu \xrightarrow[H_2O]{} Cr(NH_3)_2(NCS)_3(OH_2) + NCS^- \quad (1)$$

$$Cr(NH_3)_2(NCS)_4^- + h\nu \xrightarrow[H^+]{} Cr^{2+} + 2NH_4^+ + (NCS)_2^- + 2NCS^- \quad (2)$$

$$Cr^{2+} + Co(NH_3)_5F^{2+} \xrightarrow[H^+]{k_3} CrF^{2+} + 5NH_4^+ + Co^{2+} \quad (3)$$

While investigating the suitability of the reineckate ion as an actinometric reference for visible-near-UV laser and dye laser systems, we have found that both these product yields increase for 337-nm pulsed nitrogen laser excitations (1 MW, 10-ns pulse width). For example, at the highest power levels[17] we found $\phi_{NCS^-} \simeq 0.5$ and $\phi_{Co^{2+}} \simeq 0.015$.[18] Under these conditions both ϕ_{NCS} and $\phi_{Co^{2+}}$ are intensity dependent, the former decreasing with I_a and the latter increasing with I_a (Figure 1). For moderate intensities $\phi_{Co^{2+}}$ is proportional to I_a, but at the highest power levels $\phi_{Co^{2+}}$ approaches an intensity independent limit (Figure 1). This is suggestive of a "saturation" effect of the sort expected when the ^2E concentration is significantly depleted by the absorption of a second photon and the accompanying photoredox processes. Such a "saturation" effect could only be important when the rate of excited-state light absorption becomes equal to or greater than the normal rate of excited state decay.

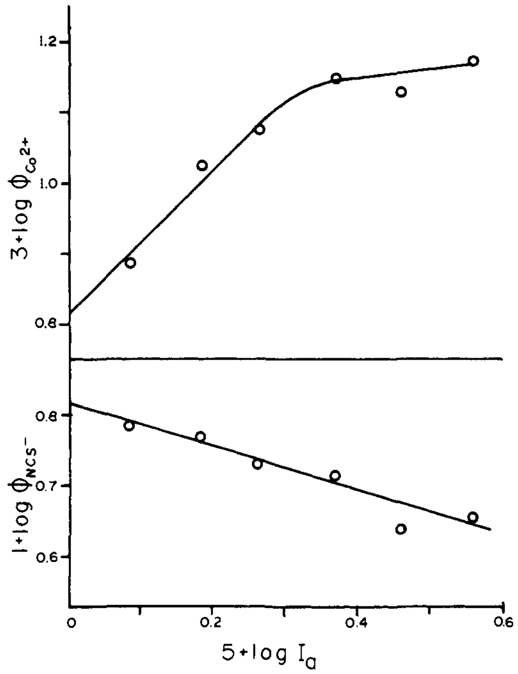


Figure 1. Variations of product quantum yields for redox (upper curve) and for NCS^- aquation (lower curve) with intensity during the 337-nm laser photolysis of *trans*-$Cr(NH_3)_2(NCS)_4^-$ in the presence of $Co(NH_3)_5F^{2+}$ in 0.01 M $HClO_4$.

If we take the NCS^- aquation process to be a characteristic reaction of quartet ligand field excited states,[19-21] then the laser induced processes may be described by eq 4-11 and

$$Cr(NH_3)_2(NCS)_4^- + h\nu \xrightarrow{I_a} {}^4CT^* \quad (4)$$

$$^4CT^* \longrightarrow Q^* \quad (5)$$

$$^4CT^* \xrightarrow[H^+]{\phi_0} Cr^{2+} + 2\,NH_4^+ + (NCS)_2^- + 2NCS^- \quad (6)$$

$$Q^* \longrightarrow Q_0 + \text{heat} \quad (7)$$

$$Q_0 \overset{K_8}{\rightleftharpoons} {}^2E \quad (8)$$

$$^2E + h\nu \xrightarrow{\phi' I_a'} Cr^{2+} + (NCS)_2^- + 2NCS^- + 2NH_4^+ \quad (9)$$

$$Q_0 \xrightarrow{k_{10}} Cr(NH_3)_2(NCS)_3OH_2 + NCS^- \quad (10)$$

$$Q_0 \xrightarrow{k_{11}} Cr(NH_3)_2(NCS)_4^- + \text{heat} \quad (11)$$

$$\phi_{Cr^{2+}} = \frac{\phi' \epsilon_D I_0 \delta \tau_D}{1 + \phi' \epsilon_D I_0 \delta \tau_D} + \phi_0 \quad (12)$$

$$\phi_{NCS^-} = \frac{k_{10} \tau_D}{1 + \phi' \epsilon_D I_0 \delta \tau_D} \quad (13)$$

Figure 2 where Q^* designates ligand field states of quartet spin multiplicity, and Q_0 the thermalized state of the quartet