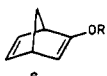
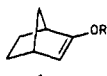
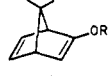
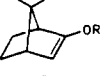


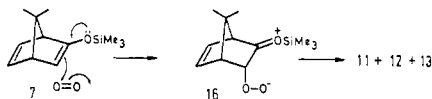
Table I. Relative Rates of Photooxygenation of 2-Siloxynorbornenes

acceptor ^a				
K_{rel}	17	8.4	4.2	1

^a R = SiMe₃.

quently, the peroxide ion has the choice of removing the easily detachable silyl group to give **8** or closing to the dioxetane **10**. The same process occurs to a lesser degree on the endo face of **6**. The endo zwitterionic peroxide gives mainly the product of silatropic rearrangement, **9**. The corresponding *endo*-dioxetane is simply not detected, presumably owing to its even lower concentration than that of **9**.

The action of the *gem*-dimethyl grouping at C-7 is to force singlet oxygen to approach the endo face of the norbornadiene skeleton. This time the resulting zwitterionic peroxide **16** has three avenues of reaction available. Silatropic shift, as before, is favored over dioxetane formation. However, an alternative



is provided, as charge is also conveniently annihilated by closure to the *endo*-peroxynorbornadiene derivative **12** which, incidentally, could be regarded as the consequence of a non-concerted homo-Diels-Alder addition. The isolation and stability of **11** and **12** at room temperature rule out concerted formation of **12** followed by equilibration to **11**.

One last, but important point, concerns reaction rates. Both **6** and **7** reacted rapidly with singlet oxygen; solutions (0.5 M) in deuteriochloroform containing *meso*-tetraphenylporphyrin (~10⁻³ M) were quantitatively oxidized in 5 min. Moreover, the usual tests confirmed the intermediacy of singlet oxygen as reagent.¹² Rates of **6** and **7** were also compared with their monoolefinic counterparts (Table I). It is significant that dienes react faster than monoenes and that the presence of methyl groups at C-7 is rate retarding.¹³ This behavior parallels exactly that of 2-methylnorbornadiene and its 7,7-dimethyl derivative, where singlet oxygen reacts to give the allylically rearranged hydroperoxide.¹⁴ Consequently, in the present case it can be similarly concluded that singlet oxygen is behaving as an electrophile and that the transition state is controlled essentially by the HOMO of the siloxy olefins, modified by a steric effect.

Acknowledgment. We thank the Swiss National Science Foundation for support of this work (Grant No. 2.430-0.75).

References and Notes

- Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133; Bartlett, P. D. *Chem. Soc. Rev.* **1976**, *5*, 149; Stephenson, L. M.; McClure, D. E.; Sysak, P. K. *J. Am. Chem. Soc.* **1973**, *95*, 7888.
- Saito, I.; Matsuura, T.; Nakagawa, M.; Hino, T. *Acc. Chem. Res.* **1977**, *10*, 346; Saito, I.; Imuta, M.; Takahashi, T.; Matsugo, S.; Matsumura, T. *J. Am. Chem. Soc.* **1977**, *99*, 2005; Nakagawa, M.; Okajima, H.; Hino, T. *ibid.* **1977**, *99*, 4424.
- Rousseau, G.; Le Perche, P.; Conia, J.-M. *Tetrahedron Lett.* **1977**, 2517; Jefford, C. W.; Rimbault, C. G. *ibid.* **1977**, 2375.
- McCapra, F.; Beheshti, I. *J. Chem. Soc., Chem. Comm.* **1977**, 517.
- For theoretical studies see Yamaguchi, K.; Fueno, T.; Fukutome, H. *Chem. Phys. Lett.* **1973**, *22*, 466; Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1975**, *97*, 3978; Politzer, P.; Daiker, K. C. "Excited States in Organic Chemistry and Biochemistry", Pullman, B., Goldblum, N., Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1977; pp 331-344; Harding, L. B.; Goddard, III, A. *Tetrahedron Lett.* **1978**, 747.
- Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 295; *ibid.*, in press.
- Treatment of norborn-5-en-2-one and its 7,7-dimethyl derivative⁸ with 1 equiv of lithium diisopropylamide in THF at -78 °C followed by quenching with trimethylchlorosilane gave the pure dienes **6** and **7** in ~60% yield.
- Jefford, C. W.; Wallace, T. W.; Nguyen thi Huong, C.; Rimbault, C. G. *J. Org. Chem.*, submitted for publication.
- Story, P. R.; Clark, Jr., B. C. "Carbonium Ions", Olah, G.; Schleyer, P. v. R., Ed.; Wiley-Interscience: New York, N.Y., 1973, Vol. 3, p 1007. Goering, H. L.; Chang, C.-S. *J. Am. Chem. Soc.* **1977**, *99*, 1547, and references cited therein. Sonney, J. M.; Vogel, P.; Burger, U. *Tetrahedron Lett.*, **1978**, 825.
- To our knowledge, only one case of a siloxydioxetane is known, prepared by ozonolysis of a vinylsilane (Büchi, G.; Wüest, H., *J. Am. Chem. Soc.* **1978**, *100*, 294). The *exo* and *endo* stereochemistries of dioxetanes **10** and **13**, respectively, were established by comparing their ¹H NMR spectra with that of **4**.⁹ **10** exhibits a typical triplet at δ 4.84 for its *endo* C-3 proton (³J_{3n,4} = ⁴J_{3n,7a} = 1.6 Hz); **13** shows a typical doublet at δ 5.58 for its *exo* C-3 proton (³J_{3x,4} = 5 Hz).
- ¹H NMR analyses are fully consistent with those previously reported for *exo*- and *endo*-α-silylperoxynorbornanones (see ref 6). **11** (CDCl₃): δ 0.2 (9 H, s, Si(CH₃)₃), 1.10 (6 H, s, 2CH₃), 2.8 (1 H, m, H-C(1)), 2.9 (1 H, m, H-C(4)), 4.72 (1 H, d, J_{3,4} = 3 Hz, H-C(3-*exo*)), 5.96 (1 H, dm, H-C(6)), 6.50 (1 H, dd, J_{6,5} = 6 Hz, J_{6,1} = 3 Hz, H-C(5)), **8** (CDCl₃): δ 0.2 (9 H, s, Si(CH₃)₃), 2.22 (1 H, dm, J_{7,7} = 10 Hz) and 2.42 (1 H, dm, J_{7,7} = 10 Hz) (H-C(7a, 7s)), 2.98 (1 H, m, H-C(1)), 3.38 (1 H, m, H-C(4)), 4.08 (1 H, dd, J = 3, 1 Hz, H-C(3n)), 6.21 (1 H, ddt, J_{5,6} = 6 Hz, J = 3, 1 Hz, H-C(6)), 6.44 (1 H, dd, J_{5,6} = 6 Hz, J = 3 Hz, H-C(5)), **9** (CDCl₃): spectrum identical with that of **11** except d at 4.48 (1 H, J = 3 Hz, H-C(3x)) instead of dd at δ 4.08. **11** and **9** are readily reduced to the corresponding α-siloxynorbornenones by treatment with 1 equiv of triphenylphosphine. The decoupled ¹H NMR spectrum for peroxide **12** is unambiguous: δ 0.2 (9 H, s, Si(CH₃)₃), 0.96 (3 H, s, CH₃), 1.16 (3 H, s, CH₃), 1.6 (1 H, dd, J_{1,6} = 6 Hz, J_{1,4} = 2.5 Hz, H-C(1)), 1.72 (1 H, dm, J_{1,6} = 6 Hz, H-C(6)), 2.32 (1 H, m, H-C(4)), 4.78 (1 H, d, J_{3,4} = 3 Hz, H-C(3)), 4.84 (1 H, dd, J_{4,5} = 3 Hz, J_{5,6} = 2 Hz, H-C(5)).
- Proof for reagent singlet oxygen was obtained by testing oxygenation in the absence of light, sensitizer, oxygen, and by adding Dabco as well as noting the effect of deuterated solvent.
- The relative rates of photooxygenation of olefins **1**, **6**, **7**, and **17** were determined by the competition method.¹⁴ The disappearance of acceptors was monitored either by NMR or GLC (OV 225 15%/Chrom W).
- Jefford, C. W.; Rimbault, C. G. *J. Org. Chem.* **1978**, *43*, 1908.

Charles W. Jefford,* Christian G. Rimbault

Department of Organic Chemistry, University of Geneva
1211 Geneva 4, Switzerland

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1,5-Diazabicyclo[3.3.0]octadienediones (9,10-Dioxabimanes). Strongly Fluorescent Syn Isomers

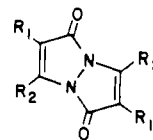
Sir:

We herewith report the existence of an essentially new class of stable heterocyclic molecules, of elegant and simple structures, derived by surprisingly straightforward means from commonly available compounds and marked, in one series of isomers, by a beautiful and striking fluorescence. We now describe the synthesis and some chemical reactions. The X-ray structural determinations¹ and the photophysical properties² will be reported later.

In attempts to prepare 2-octadecynoic acid via treatment of a dichloropyrazolone with strong base,^{3,4} we noted the formation of a strongly fluorescent compound in small yield. Spectroscopic and analytical data suggested an unusual structure, and we were able to develop a procedure (heterogeneous base treatment of a concentrated solution of halopyrazolone in a suitable organic solvent) which has given up to 67% yield of the fluorescent isomer along with up to 10% of the weakly fluorescent isomer. The isomeric compounds are 1,5-diazabicyclo[3.3.0]octadienediones, the syn isomer being strongly fluorescent (emission maxima 388-520 nm, depending upon substitution and solvent, quantum yields 0.7-0.9), and the anti isomer weakly fluorescent. The structures have been confirmed by X-ray crystallography. Since the compounds are usually quite symmetrical, we have adopted the brief name



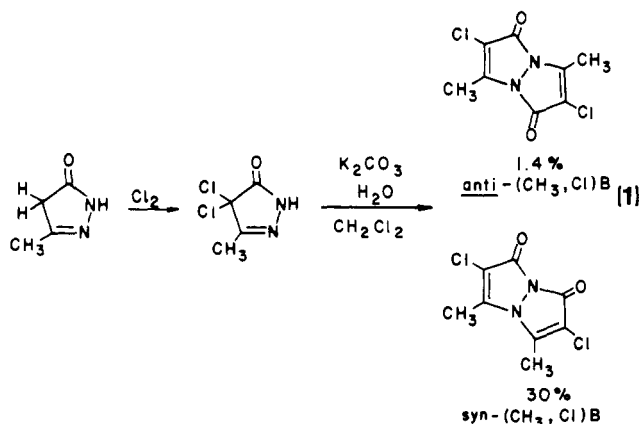
syn - (R₂, R₁) B



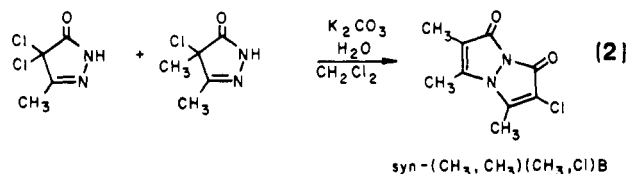
anti - (R₂, R₁) B

"bimane" (*bi*, two, and *manus*, hand) for the basic ring system, and use the shorthand, *syn*-(R₂, R₁)B or *anti*-(R₂, R₁)B, to denote the materials, which are 9,10-dioxabimanes.^{5,6}

The synthesis of *syn*-(CH₃, Cl)B and *anti*-(CH₃, Cl)B are accomplished with the reaction sequence shown in eq 1.



A mixed *syn*-bimane has been isolated from reaction mixtures containing two chloropyrazolones (eq 2). We may infer



a scheme (Scheme I) for the formation of *syn*- and *anti*-bimanes.

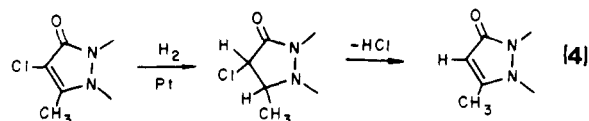
Both classes of bimanes are very stable compounds. *syn*-(CH₃, CH₃)B sublimes unchanged at 200 °C (760 mm) as does *syn*-(C₆H₅, Cl)B at 190 °C (0.1 mm). *anti*-(CH₃, CH₃)B sublimes unchanged at 120 °C (0.1 mm). Brief heating of the *syn*-bimanes above their melting points (some over 300 °C) had no apparent effect, nor did refluxing the same compounds in 1,2,4-trichlorobenzene (bp 210 °C) for 6 h lead to any change. However, *syn*-(CH₃, CH₃)B had a half-life of ~4.5 h at 285 °C in a sealed tube in the absence of oxygen. Irradiation of *anti*-(CH₃, CH₃)B in CH₃CN (0.25 M, 300 nm) for 5 h led to little change, but longer irradiation times did slowly

give rise to as yet unidentified products. Irradiation of *syn*-(CH₃, CH₃)B at 360 nm for 22 h in CH₃CN (0.05 M) led to only small changes, 95% of the starting material being recovered. However, irradiation of *syn*-(CH₃, CH₃)B at 254 nm for 24 h in CH₃CN (0.035 M) led to only 60% recovery of starting material.

Based on the results for a number of reactions, including reversible addition of methoxide and hydroxide ions, we may write eq 3 as a general description of the behavior of bimanes (B).



The hydrogenation of *syn*-(CH₃, Cl)B in KOAc/AcOH with Pd/C leads to two new fluorescent compounds, *syn*-(CH₃, H)(CH₃, Cl)B and *syn*-(CH₃, H)B, structures being based on NMR, mass spectra, X-ray crystallography, and fluorescence behavior. In this two-stage reaction (eq 4), the



AX added to the *syn*-bimane (AX = H₂) is not identical with the AX which is lost from the adduct (AX = HCl).

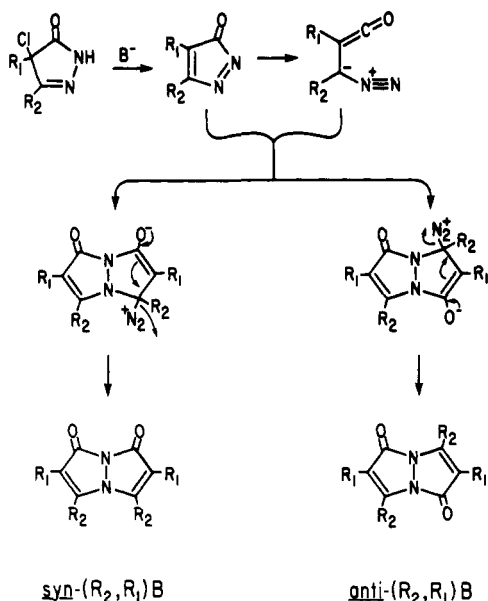
A dibromo compound can be easily isolated in pure form after reaction of *syn*-(CH₃, CH₃)B with bromine (initial step, addition), with structure *syn*-(BrCH₂, CH₃)B, as shown by NMR and mass spectra. Methoxide ion/CH₃OH converts the dibromide very rapidly into a dimethoxy compound, *syn*-(CH₃OCH₂, CH₃)B. The dibromo compound (*syn*-BBR₂) represents a functionalized *syn*-bimane which is likely to find many uses. We have utilized the compound in fluorescent labeling of proteins and cells (thus, sB-labeled proteins and cells)¹⁷ and in the preparation of a bispyridinium salt through reaction with methyl isonicotinate. Successful reduction of the latter to the bispyridinyl radical will be described elsewhere.¹⁸ Another useful class of new compounds, the μ -*syn*-bimanes, with a one-atom bridge replacing the two bromines, is readily synthesized from *syn*-BBR₂ and suitable nucleophiles.¹⁹ The monobromo (sBBR) derivative may also be isolated in pure form.

The availability of the starting materials, the ease of preparation of most of the bimanes, the stability of the bimanes, the striking fluorescence of the *syn*-bimanes, and the interesting and useful reactions which are possible for the bimanes suggest that a fertile new territory for chemical investigation has been revealed.

References and Notes

- (1) E. M. Kosower, J. Bernstein, I. Goldberg, B. Pazhenchevsky, and E. Goldstein, submitted for publication.
- (2) E. M. Kosower, H. Kanety, H. Dodiuk, and B. Pazhenchevsky, unpublished work.
- (3) L. A. Carpino, *J. Am. Chem. Soc.*, **80**, 599 (1958).
- (4) A. Silveira, Jr., T. J. Weslowski, T. A. Weil, V. Kumar, and J. P. Gillespie, *J. Am. Oil Chem. Soc.*, **48**, 661 (1971).
- (5) Systematic trivial names can be based on naming two ring systems, 2,8-bis(methylene)-1,5-diazabicyclo[3.3.0]octa-3,6-diene as *syn*-bimane and 2,6-bis(methylene)-1,5-diazabicyclo[3.3.0]octa-3,7-diene as *anti*-bimane. By numbering the methylene carbons as 9 and 10, the diones would then become 9,10-dioxo-*syn*-bimane and 9,10-dioxo-*anti*-bimane, but can be referred to briefly as "bimanes". The following examples illustrate the system. *syn*-(C₆H₅, Cl)B = 9,10-dioxo-*syn*-(phenyl, chloro)bimane = 3,7-dichloro-4,6-diphenyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione. The last, a completely systematic name, is clearer than a name based on pyrazolo[1,2-*a*]pyrazole, *anti*-(CH₃, CH₃)B = 9,10-dioxo-*anti*-(methyl, methyl)bimane = 2,3,6,7-tetramethyl-1,5-diazabicyclo[3.3.0]octa-2,6-diene-2,6-dione.
- (6) Carpino³ noted the formation of a yellow compound, probably *syn*-(C₆H₅, Cl)B from the result obtained in a similar experiment, but never published a promised structure. A number of *anti*-bimanes have been reported by Rees⁷ (*anti*-(C₆H₅, C₆H₅)B), Mosby⁸ (indazolo[2,1-*a*]indazole-6,12-dione (*anti*-(benzo, benzo)B) (cf. also Gibson and Lindsey⁹), and Spafte¹⁰ (*anti*-(benzo)(CH₃, Br)B), who obtained a structure through X-ray crystallography. Some of the small group of *anti*-bimanes were originally

Scheme I



isolated by Michaelis^{11,12} and further investigated by Velbel and co-workers¹³ before the structural confirmation by Sötofte.

Only four examples of *syn*-bimanes, *syn*-(benzo)(CH₃,H)B, *syn*-(benzo)(CH₃,Br)B, *syn*-(benzo)(CH₃,CH₂CH₂)B, and *syn*-(benzo)(C₆H₅,H)B, have previously appeared in the literature. The first two were characterized by Michaelis^{14,15} and the latter two by Velbel and Lillielund.¹⁶ The intense fluorescence was noted,¹⁴⁻¹⁶ but the syntheses were rather limited in applicability. The only chemical reactions mentioned were bromination, converting the first *syn*-bimane mentioned above to the second, and treatment with 0.1 N NaOH which caused ring opening to the 1-(2-carboxyphenyl)pyrazol-3-ones.¹⁶ The idea that a new and useful class of compounds was under study was not advanced and, indeed, became plausible only with our discovery of a reasonably general synthesis, illustrated as follows.

syn-(CH₃,CH₃)B is prepared by mixing 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (0.48 mol) in CH₂Cl₂ (500 mL) with K₂CO₃· $\frac{1}{2}$ H₂O (1 mol) and K₂CO₃ (0.36 mol) at 0 °C (1 h), stirring at room temperature for 18 h, filtering through Celite, evaporation with solvent, and crystallization from boiling CH₃CN (150 mL). Essentially pure *syn* isomer separates in 60% yield. Evaporation of filtrate and chromatography on alumina with CH₂Cl₂ yields *anti*-(CH₃,CH₃)B (~4.6% yield) and additional *syn* isomer (~9%). *syn*-(CH₃,CH₃)B: yellow-white crystals; mp 211–212 °C; UV λ_{\max} (dioxane) 359 nm (ϵ_{\max} 6500), 255 (sh, 5200), 235 (14 600); IR ν_{\max} (KBr) 2890, 1745, 1670, 1610, 1400, 1030 cm⁻¹; NMR (CDCl₃) δ 1.85 (s), 2.28 (s); ¹³C NMR δ 160.5, 146.1, 111.8, 11.9, 6.7; mass spectrum 192 (parent peak). *anti*-(CH₃,CH₃)B: white needles; mp 174 °C (EtOAc); UV λ_{\max} (dioxane) 322 nm (ϵ 15 100); IR (KBr) ν_{\max} 2930, 1750 (sh), 1695, 1630, 1415, 1275, 1170 cm⁻¹; NMR (CDCl₃) δ 1.80 (s), 2.40 (s); Anal. (C₁₀H₁₂N₂O₂, both isomers) C, H, N.

Among the bimanes which have been synthesized and characterized are *syn*-(CH₃,Cl)B, mp 253 °C; *syn*-(C₆H₅,CH₃)B, mp 308–310 °C dec; *syn*-(C₆H₅,C₆H₅)B, mp 312 °C; *syn*-(CH₃,C₆H₅)B, mp 284 °C; *anti*-(CH₃,Cl)B, mp 196–197 °C; *anti*-(C₆H₅,Cl)B, mp 236–237 °C; *anti*-(CH₃,C₆H₅)B, mp 265 °C.

- (7) C. W. Rees and M. Yelland, *J. Chem. Soc., Perkin Trans. 1*, 221 (1973).
- (8) W. L. Mosby, *Chem. Ind. (London)*, 17 (1957).
- (9) G. K. J. Gibson and A. S. Lindsey, *J. Chem. Soc. C*, 1792 (1967).
- (10) I. Sötofte, *Acta Chem. Scand.*, **27**, 661 (1973).
- (11) A. Michaelis and C. Eisenschmidt, *Ber.*, **37**, 2228 (1904).
- (12) A. Michaelis, *Justus Liebigs Ann. Chem.*, **373**, 129 (1910).
- (13) S. Velbel et al., *Acta Chem. Scand.*, **2**, 914, 921 (1948).
- (14) A. Michaelis, *Justus Liebigs Ann. Chem.*, **373**, 148 (1910).
- (15) A. Michaelis, *Justus Liebigs Ann. Chem.*, **373**, 202, (1910).
- (16) S. Velbel and H. Lillielund, *Tetrahedron*, **1**, 201 (1957).
- (17) N. S. Kosower, G. L. Newton, E. M. Kosower, and H. M. Ranney, Biophysics Congress, Kyoto, Japan, Sept 1978, Abstracts, p 387.
- (18) E. M. Kosower, A. Teuerstein, and B. Pazhenchevsky, unpublished results.
- (19) E. M. Kosower, B. Pazhenchevsky, and M. Parasol, unpublished work. The (CN)₂C-bridged compound structure has been established by X-ray crystallography.²
- (20) (a) Tel-Aviv University. (b) State University of New York. (c) 1977–1978: Departments of Chemistry, University of California, San Diego, La Jolla, Calif. 92093, and Berkeley, Calif. 94720. The J. S. Guggenheim Memorial Foundation is thanked for support.

Edward M. Kosower*^{20a}

Barak Pazhenchevsky,^{20a} Eli Hershkowitz^{20a}

Tel-Aviv University, Ramat Aviv, Tel Aviv, Israel, and the
Department of Chemistry, State University of New York
Stony Brook, New York 11794

Received April 27, 1978

Picosecond Studies of Excited-State Decay Kinetics in Chromium(III): *trans*-Diisothiocyanato-bis(ethylenediamine)chromium(III), Reinecke's Salt, and Hexaisothiocyanatochromium(III) in H₂O and D₂O at Room Temperature

Sir:

The interest in excited-state relaxation in Cr(III) complexes stems from the debate over the identity of the photoactive state in Cr(III) photochemistry. Early work by Plane and Hunt¹ and Schläfer² suggested that the lowest doublet state was the primary intermediate responsible for photochemistry. Subsequently, Chen and Porter³ established that at least some of the photoproduct in the photoaquation of *trans*-Cr(NH₃)₂-(NCS)₄⁻ must derive from sources other than the doublet. They suggested that the lowest quartet excited state was responsible. In addition, the lack of direct evidence for doublet photochemistry led them to suggest that all other photoproduct could be a consequence of thermally activated back intersystem

crossing from the doublet to the quartet similar to the process of E-type delayed fluorescence. Since then, it has been demonstrated that some, if not all, of the photochemistry for several complexes derives from the lowest excited quartet state.⁴ The quartet hypothesis is supported by the successful prediction of product stoichiometry by models based on the ligand field strength of the first coordination sphere. The first of the spectroscopic models was developed by Adamson.⁵ Models have since been developed to rationalize Adamson's rules which use MO theory to account for changes in the σ and π character of the metal ligand bonds as a result of the change in electronic configuration in the lowest excited quartet state.⁶ Even stereochemical changes have been rationalized.⁷ The similarity in formal electronic configuration between the ground and doublet states (t_{2g}^3) and the negligible Stokes shift of the doublet phosphorescence has suggested that there was negligible difference in geometry between the two states and that bond rupture in the doublet was therefore no more likely than in the ground state.⁸ However, this argument is weakened by the following considerations. Intensity progressions in the vibrational structure of the phosphorescence of Cr(CN)₆³⁻ have been interpreted as evidence for considerable distortion arising from compression of the metal-ligand bonds in the doublet relative to the ground state.⁹ In addition, configuration interaction ($t_{2g}^3-t_{2g}^2e_g$) could cause some increase in average bond lengths as the crystal field parameter (10 *Dq*) decreases and the excited quartet-doublet energy gap shrinks.¹⁰ Thus, doublet reactivity cannot, at present, be completely ruled out.

Excited-state kinetic and spectroscopic studies of Cr(III) complexes under photochemical conditions may contribute to the understanding of the mechanism of the photochemical reaction. Until recently, however, studies of the photophysics of excited states in Cr(III) have been limited to studies of ruby; observations of phosphorescence of complexes at low temperature; and to data obtained indirectly through studies of photochemistry, emission quenching or sensitization. Nanosecond pulsed laser studies of the decay of emission or excited state absorbance (ESA) in acidoammine complexes of Cr(III) may be helpful in assessing the role of the doublet state in photoreaction.¹¹⁻¹³ However, picosecond time resolution is needed to examine the role of the excited quartet state in Cr(III) photochemistry. Earlier studies in our laboratory, of picosecond excited-state relaxation in transition metal complexes, suggested that the excited quartet lifetime in Cr(III) complexes was too short to measure (<10 ps).¹⁴ We have extended this work. Repeated studies of *trans*-Cr(en)₂(NCS)₂⁺, *trans*-Cr(NH₃)₂(NCS)₄⁻ and Cr(NCS)₆³⁻ show that, while the rise time of transient absorbance is fast (11 ps < τ < 24 ps), it is within the time resolution of our picosecond flash system. We have also studied the influence of the medium on the rate of appearance of transient absorbance.

Excited-state spectroscopy and measurement of excited-state lifetimes were performed using the picosecond flash photolysis system described elsewhere.¹⁵ Solutions were prepared in H₂O and D₂O at the start of each experiment. The counterions were K⁺ and NH₄⁺ in Cr(NCS)₆³⁻ and *trans*-Cr(NH₃)₂(NCS)₄⁻, respectively. The counterions were Cl⁻ and ClO₄⁻ in the case of *trans*-Cr(en)₂(NCS)₂⁺, and the rise times of transient absorbance were equivalent in both media. Solutions of Cr(III) were typically 0.1 M, and a fresh solution was used for each flash. The transient spectra were identical with those observed in the earlier picosecond work¹⁴ as well as those reported for the excited doublet state in low temperature glassy media.¹⁶ Similar spectra were also observed in nanosecond room-temperature kinetic spectroscopy.^{12,13} We have estimated the extinction coefficients of the excited-state transitions by comparison with the excited singlet transition in Rhodamine 6-G ($\epsilon(S_1) = 4.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 450 nm¹⁷). The values all lie between 10³ and 10⁴ M⁻¹ cm⁻¹ and agree