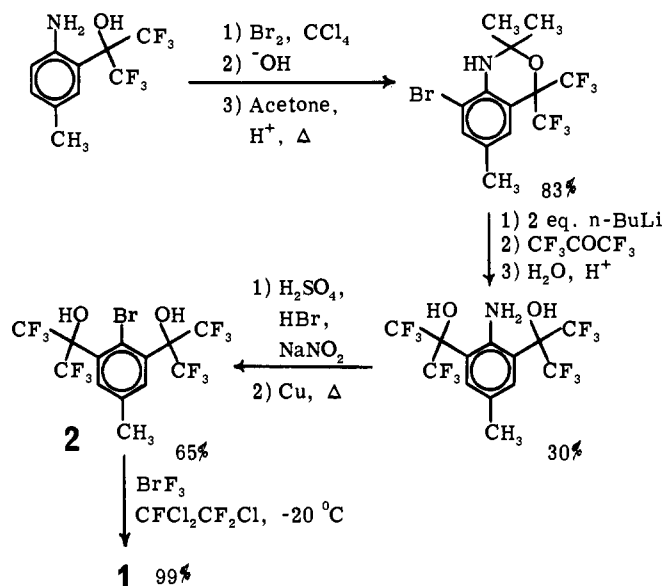
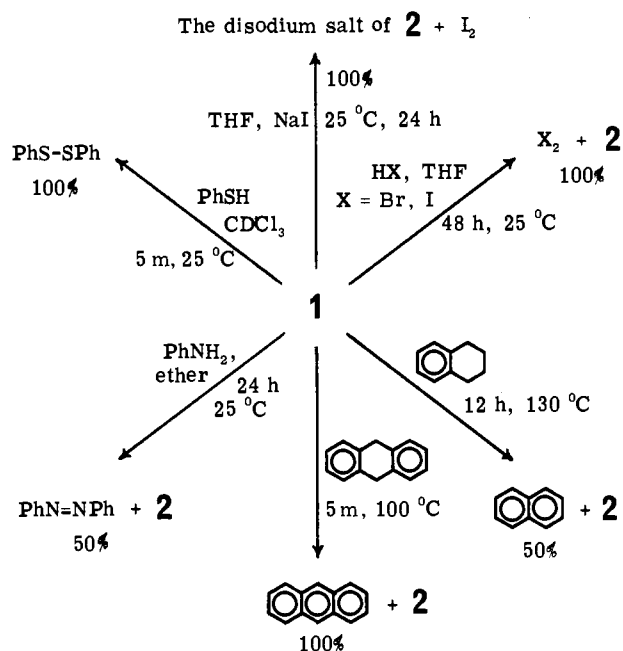


Scheme I



Scheme II



The synthesis of **1** was effected by the route of Scheme I.^{6,7} Crystalline **1**, mp 153–154 °C, is stable indefinitely at room temperature and may be sublimed at 60 °C (3 torr). The ¹⁹F NMR singlet at –75.8 ppm⁸ assigned to the equivalent CF₃ is upfield from that of the bromo diol **2** (–73.0 ppm). The infrared spectrum shows no hydroxy absorption. The mass spectrum shows a sizable molecular ion, *m/e* 502, and 500, and a prominent fragmentation peak at *m/e* 433, and 431 corresponding to the loss of one CF₃ group. The solid brominane **1** is unreactive toward atmospheric moisture. A sample of **1** in tetrahydrofuran did not show any change in the ¹⁹F NMR spectra in the presence of water,

(6) The details of the synthesis of this generally useful tridentate ligand, used here for brominane **1**, will be published elsewhere: Nguyen, T. T.; Amey, R. L.; Martin, J. C. *J. Org. Chem.*, manuscript in preparation.

(7) Anal. ($\text{C}_{13}\text{H}_2\text{O}_2\text{BrF}_{12}$) C, H, Br, F; IR (CHCl₃) 1239 (m), 1084 (s), 1049 (m), 855 (s) cm^{-1} ; ¹H NMR (CDCl₃) δ 2.65 (s, 3, CH₃), 7.7 (s, 2, Ar H); ¹⁹F NMR (CDCl₃) δ –75.8 (s); mass spectrum (10 eV) *m/e* (relative intensity) 502, 500 (1.7, M⁺), 431, 435 (100, M⁺ – CF₃), 295, 293 (7.0, M⁺ – 3CF₃).

(8) Chemical shifts are reported in ppm downfield of CFCl₃. Negative values are therefore upfield of CFCl₃ in accord with IUPAC recommendations: *Org. Magn. Reson.* 1978, 11, 267.

dilute HCl, or dilute aqueous NaOH at room temperature for 1 day. The brominane **1** is a mild oxidizing reagent. Some of its reactions are shown in Scheme II.⁹

The spectroscopic and chemical evidence presented here provides a compelling case for the proposed structure for brominane **1**. Further studies on the structure and reactivity of brominanes are currently under way in this laboratory.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, CHE-7905692. We acknowledge the contributions of Dr. Ronald L. Amey in working out the earlier steps in the synthesis of the tridentate ligand used here.

(9) The yields shown here were obtained by NMR. The products were identified by comparison with authentic samples.

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Highly Luminescent Polypyridyl Complexes of Osmium(II)

Sir:

Transition-metal complexes which have low-lying metal to ligand charge-transfer (MLCT) excited states have played a pivotal role in demonstrating the use of molecular excited states in light energy conversion processes.^{1,2} Experiments so far have relied primarily on Ru(bpy)₃²⁺ (bpy is 2,2'-bipyridine), Ru(phen)₃²⁺ (phen is 1,10-phenanthroline), and their ligand-substituted derivatives. The ruthenium complexes have many desirable features including high chemical and photochemical stability, a high light absorptivity in the visible region, the existence of relatively long-lived MLCT excited states, and chemically accessible ground- and excited-state redox properties.

One noticeable absence in this area has been the systematic development of new, stable chemical systems having exploitable excited states whose properties can be modified by simple alterations of the ligands. The development of new systems is essential in order to uncover new reaction pathways and to help define the fundamental photochemical and photophysical properties of MLCT excited states.

An obvious place to search for new MLCT excited states is in the chemistry of osmium where ground-state redox properties are similar to those of related ruthenium complexes and chemical stability is higher. However, spin-orbit coupling is considerably greater for osmium compared to ruthenium which is expected to enhance both radiative and nonradiative decay rates for triplet-singlet transitions and thus shorten excited-state lifetimes.³ In fact, lifetimes for the MLCT excited states of Os(bpy)₃²⁺, Os(phen)₃²⁺, and related substituted ligand derivatives are considerably shorter than those of their ruthenium analogues.⁴ We report that the lifetimes of osmium(II) MLCT excited states can be enhanced remarkably by replacing one of the polypyridyl ligands by stronger π acceptors such as acetonitrile or alkyl-

(1) (a) Balzani, V.; Bolletta, F.; Gandolphi, M. T.; Maestri, M. *Topics Curr. Chem.* 1978, 75, 1. (b) Sutin, N. *J. Photochem.* 1979, 10, 19. (c) Meyer, T. J. *Acc. Chem. Res.* 1978, 11, 94. (d) *Isr. J. Chem.* 1977, 15, 200. (e) Whitten, D. G. *Acc. Chem. Res.* 1980, 13, 83.

(2) See, for example: (a) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* 1979, 101, 4007. (b) Durham, B.; Dressick, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* 1979, 8, 381. (c) Kalyanasundaran, K.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 701. (d) Lin, C. T.; Sutin, N. *J. Phys. Chem.* 1976, 80, 97.

(3) Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962.

(4) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* 1980, 102, 1309.

Table I. Spectral and Electrochemical Properties of Osmium Complexes

complex ^a	$E_{1/2}^b$ ($B_2OsL_2^{3+} \rightarrow$ $B_2OsL_2^{2+}$)	$E_{1/2}^b$ ($B_2OsL_2^{2+} \rightarrow$ $B_2OsL_2^+$)	λ_{max}^{em} , nm ^c	λ_{max}^{abs} , nm ^c	τ_0 , μs^d	$E_{1/2}^{b,e}$ ($B_2OsL_2^{2+*} \rightarrow$ $B_2OsL_2^+$)	$E_{1/2}^{b,e}$ ($B_2OsL_2^{3+} \rightarrow$ $B_2OsL_2^{2+*}$)
(bpy) ₃ Os ²⁺	+0.81	-1.29	723	640	0.02 ^f	+0.50	-0.98
(bpy) ₂ Os(CH ₃ CN) ₂ ²⁺	+0.91	-1.35	673	555	0.07	+0.59	-1.03
(bpy) ₂ Os(Ph ₂ PCH ₂ PPh ₂) ₂ ²⁺	+1.27	-1.26	622	475	0.30	+0.83	-0.82
(bpy) ₂ Os(Ph ₂ PCH=CHPPh ₂) ₂ ²⁺	+1.40	-1.26	609	466	0.50	+0.88	-0.74
(phen) ₃ Os ²⁺	+0.82	-1.21	690	650	0.08	+0.57	-0.96
(phen) ₂ Os(Me ₂ PhP) ₂ ²⁺	+1.09	-1.28	661	603	0.39	+0.70	-0.89
(phen) ₂ Os(Ph ₂ PCH ₂ PPh ₂) ₂ ²⁺	+1.32	-1.24	610	500	1.13	+0.90	-0.82
(phen) ₂ Os(Ph ₂ PCH=CHPPh ₂) ₂ ²⁺	+1.41	-1.22	596	455	1.84	+0.96	-0.77

^a All complexes were used as PF₆⁻ salts. ^b Volts vs. SCE in CH₃CN with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as electrolyte. ^c In CH₃CN, position of lowest energy band in the charge transfer absorption or emission manifolds. ^d Measured by laser flash photolysis in deaerated CH₃CN at room temperature. ^e The excited-state potentials were estimated as described in footnote 8. ^f Measured in H₂O solution. See: Cruetz, C.; Chou, M.; Netzel, L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* 1980, 102, 1309.

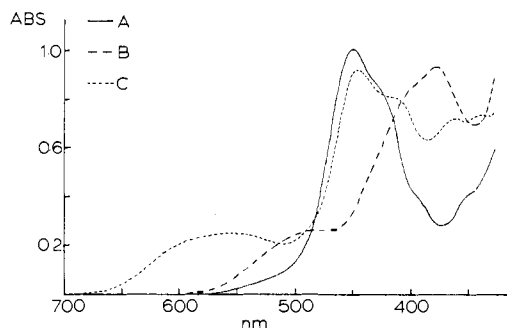
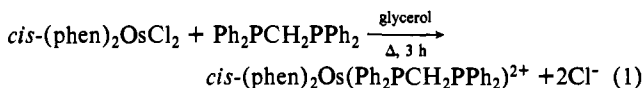


Figure 1. Visible absorption spectra of (A) (bpy)₃Ru²⁺, (B) (bpy)₂Os(Ph₂PCH₂PPh₂)₂²⁺, and (C) (bpy)₂Os(CH₃CN)₂²⁺. All complexes are PF₆⁻ salts dissolved in CH₃CN solution.

arylphosphines and that the chemical and physical properties of the resulting excited states vary systematically with the π -accepting ability of the added ligand.

The mixed-ligand bis(bipyridyl) or bis(phenanthroline) complexes of osmium (see Table I) can be prepared in >90% yield by a simple modification of the procedure of Buckingham et al.,⁵ (reaction 1) followed by metathesis to form the PF₆ salts. Pu-



rification⁶ was achieved by using nonaqueous chromatographic methods previously reported for the ruthenium analogues.⁷ The complexes are dark red to red-orange in the solid state and green to orange in solution. In the case of (bpy)₂Os(CH₃CN)₂²⁺ and (phen)₂Os(Me₂PhP)₂²⁺, a dull red solution luminescence is visible to the eye even under normal room fluorescent lighting. Typical absorption spectra of several of these new complexes are illustrated in Figure 1 and emission spectra in Figure 2.

Lifetime and emission data (see Figure 2) for the osmium complexes are collected in Table I along with measured ground-state and estimated excited-state redox potentials.⁸ The data show clearly that excited-state lifetimes are progressively enhanced by ligands that are increasingly effective as π acceptors.¹⁰

(5) Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* 1964, 17, 325.

(6) Elemental analyses on all the new complexes reported here gave satisfactory results. Examples are Anal. Calcd for [(bpy)₂Os(CH₃CN)₂](PF₆)₂: C, 32.95, H, 2.52, N, 9.61. Found: C, 32.79, H, 2.25, N, 9.50. Calcd for [(phen)₂Os(PMe₂Ph)₂](PF₆)₂: C, 39.26, H, 2.76, N, 5.73. Found: C, 39.83, H, 2.30, N, 5.61.

(7) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* 1978, 17, 3334.

(8) Excited-state redox potentials were estimated by the method given in ref 1a. In our case the spectroscopic zero-zero energy, $E_{00}(\text{Os}/\text{Os}^*)$, was taken as the energy of the emission maximum + 0.1 eV. The estimate of 0.1 eV for the vibrational distortion energy is reasonable, given the conclusions reached for the MLCT excited state of Ru(bpy)₃²⁺.⁹

(9) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* 1979, 101, 4815.

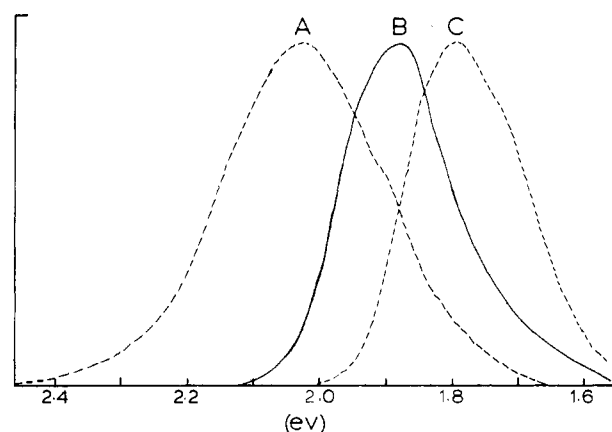


Figure 2. Emission spectra of (A) (bpy)₂Os(Ph₂PCH=CHPPh₂)₂²⁺, (B) (phen)₂Os(Me₂PhP)₂²⁺, and (C) (phen)₃Os²⁺. These spectra are uncorrected and shown normalized to the same emission response at λ_{max} .

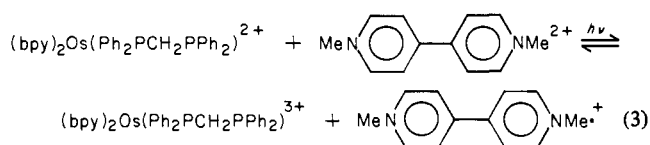
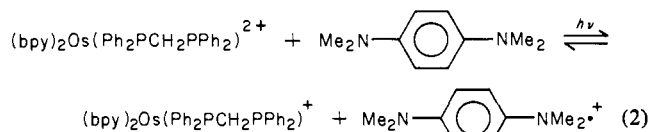
It is also true that the 1,10-phenanthroline complexes have lifetimes which are nearly four times longer than lifetimes for the analogous 2,2'-bipyridine complexes. Thus, by making relatively simple chemical modifications, it is possible to obtain a graded series of MLCT excited-state lifetimes which extend from tens of nanoseconds to lifetimes which are even longer than those of Ru(bpy)₃²⁺ or Ru(phen)₃²⁺ (855 ± 20 and 500 μ s, respectively, under the same conditions). Luminescence quantum yield measurements at 608 ± 5 nm show that both (bpy)₂Os(*cis*-Ph₂PCH=CHPPh₂)₂²⁺ (~0.9 of Ru(bpy)₃²⁺) and (phen)₂Os(Ph₂PCH₂PPh₂)₂²⁺ (1.8 times Ru(bpy)₃²⁺) are comparable or even better emitters than Ru(bpy)₃²⁺ ($\Phi \sim 0.06$).¹¹

The excited states of the complexes can clearly function as reversible redox reagents. Solution stable, oxidized and reduced forms of the ground states can be generated by controlled potential electrolysis, and the excited states are quenched in the presence of redox quenchers. For example, initial flash photolysis studies in deaerated acetonitrile demonstrate that net electron-transfer quenching does occur as shown by the appearance of the expected redox products following the flash, e.g., (2), (3).

When taken as a series, the luminescent osmium complexes are remarkable for at least two reasons: (1) There appears to be considerable synthetic flexibility in terms of the ligands added at the two *cis* positions in the complexes and in the Os-polypyridyl chromophore. The role of the ligand in determining excited-state lifetimes appears to be in its electronic effect on the metal. (2) Relatively simple chemical modifications result in large systematic

(10) On the basis of redox potential measurements and MLCT absorption band maxima on the related ruthenium complexes of the type (bpy)₂RuL₂²⁺, the order of increasing π -acceptor ability for the series of ligands appears to be CH₃CN < dialkylarylphosphine < alkylarylphosphine < vinylarylphosphine.⁷ Our results indicate the same order for the osmium complexes.

(11) Young, R. C. Ph. D. Dissertation, The University of North Carolina, 1977.



variations in excited-state energies, lifetimes, and redox potentials. Comparison with related MLCT excited states of other metals should give general insight into the photochemical and photophysical properties of MLCT excited states and, therefore, into the factors at the molecular level needed to synthesize long-lived excited states.

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(12) Sullivan, B. P.; Kober, E. M., work in progress.

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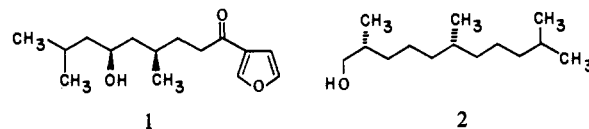
Received June 2, 1980

Remote Asymmetric Induction. A Stereoselective Approach to Acyclic Diols via Cyclic Hydroboration¹

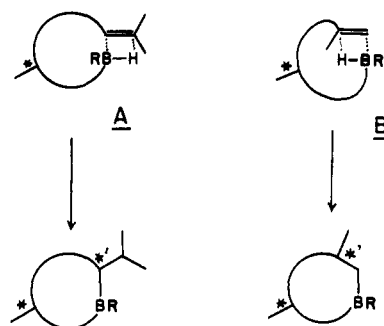
Sir:

When the synthesis of stereochemically complex acyclic molecules is considered, two synthetically significant types of diastereomeric relationships may be distinguished. Pairs of asymmetric centers may be either directly connected (adjacent) or separated by one or more atoms (remote). The efficient addition of new asymmetric centers relative to preexisting ones (relative asymmetric induction) is one of the most important problems facing would-be architects of complex acyclic structures,² and although several useful methods for building up adjacent stereocenters with high 1,2-asymmetric induction have been devised,³ general approaches to the construction of remote asymmetric relationships by efficient 1,>2-asymmetric induction are rare.⁴ Previous solutions to the remote stereochemistry problem have largely avoided remote asymmetric induction and have relied on the coupling of optically active fragments⁵ or on increasing the

separation of proximate asymmetric centers by some form of chirality transfer.⁶ Recently, however, Bartlett's phosphate chain extended epoxidation⁷ (1,3-asymmetric induction) and Kishi's bis(homoallylic) alcohol epoxidation⁸ (1,4-asymmetric induction) demonstrated that general methods for acyclic remote asymmetric induction were within grasp and could be synthetically useful processes. In this paper we wish to describe interesting preparations of nonvicinal, acyclic diols which proceed stereoselectively with 1,3-, 1,4-, and 1,5-asymmetric induction. The methodology involves the cyclic hydroboration⁹ of nonconjugated dienes, and its utility is illustrated by stereoselective synthesis of racemic forms of a naturally occurring dihydromyoporone (1)¹⁰ and the vitamin E side chain (2).^{5b,6b}

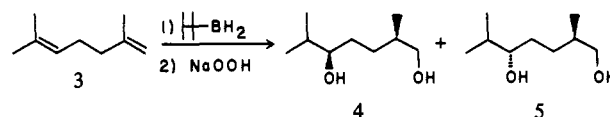


The effect upon which we wish to focus is the asymmetric induction which occurs during an intramolecular hydroboration where the cycle being closed contains one or more asymmetric centers (*). As illustrated, this operation can create new asymmetry (*') and may proceed via either fused or bridged intermediates (A or B, respectively). Since the object of this study



was exploration of methodology for the remote control of stereochemistry, we hoped that the diastereomeric relationship of asymmetric centers thus produced could be made to rely less on a direct and necessarily weak interaction between widely separated substituents and more on the overall conformation(s) of the transition state(s) leading to the boracycles. Factors which determine the detailed geometry of such transition states are not well understood; however, first approximation considerations may include the energetically accessible conformations of the ring being closed and any stereoelectronic constraints inherent to hydroboration itself.

The cyclic hydroboration of diene 3 was particularly instructive.



Although 3 reacted rapidly with borane (THF, -78 °C) almost

(1) This work was presented at the Bürgenstock Stereochemical Conference at Bürgenstock, Switzerland, on April 28, 1980, and at the Third IUPAC Symposium on Synthesis at Madison, WI on June 16, 1980.

(2) Relative and internal asymmetric induction is discussed in a recent review on acyclic stereochemical control: P. A. Bartlett, *Tetrahedron*, **36**, 2 (1980).

(3) For example: B. E. Rossiter, T. R. Verhoeven, and K. B. Sharpless, *Tetrahedron Lett.*, 4733 (1979); E. D. Mihelich, *ibid.*, 4729 (1979); P. A. Bartlett and J. Myerson, *J. Am. Chem. Soc.*, **100**, 3950 (1978); W. C. Still and J. H. McDonald, *Tetrahedron Lett.*, 1031 (1980); W. C. Still and J. Schneider, *ibid.*, 1035 (1980), and references cited therein.

(4) A few specific transformations by remote asymmetric induction are known and include such operations as stereoselective reduction of 15-keto-prostaglandins: E. J. Corey, K. B. Becker, and R. K. Varma, *J. Am. Chem. Soc.*, **94**, 8616 (1972); E. J. Corey and J. Moinet, *ibid.*, **95**, 6831 (1973).

(5) For example: (a) E. J. Corey, H. Shirahama, H. Yamamoto, S. Terashima, A. Venkateswarlu, and T. K. Schaaf, *J. Am. Chem. Soc.*, **93**, 1490 (1971); (b) N. Cohen, W. F. Eichel, R. J. Lopresti, C. Neukom, and G. Saucy, *J. Org. Chem.*, **41**, 3505 (1976); (c) G. Stork, Y. Nakahara, Y. Nakahara, and W. J. Greenlee, *J. Am. Chem. Soc.*, **100**, 7775 (1978); (d) D. B. Collum, J. H. McDonald, and W. C. Still, *ibid.*, **102**, 2117, 2118, 2120 (1980).

(6) For example: (a) G. Stork and S. Raucher, *J. Am. Chem. Soc.*, **98**, 1583 (1976); (b) K.-K. Chan and G. Saucy, *J. Org. Chem.*, **42**, 3828 (1977); (c) B. M. Trost and T. P. Klun, *J. Am. Chem. Soc.*, **101**, 6756 (1979).

(7) P. A. Bartlett and K. K. Jernstedt, *J. Am. Chem. Soc.*, **99**, 4829 (1977).

(8) T. Fukuyama, B. Vranesic, D. P. Negri, and Y. Kishi, *Tetrahedron Lett.*, 2741 (1978).

(9) For a review of the nonstereochemical aspects of cyclic hydroboration, see H. C. Brown and E.-I. Negishi, *Tetrahedron*, **33**, 2331 (1977). See also T. A. Bryson and W. E. Pye, *J. Org. Chem.*, **42**, 3214 (1977).

(10) L. T. Burka and J. Iles, *Phytochemistry*, **18**, 873 (1979).