(1978).

(27) P. J. Aparicio, D. B. Knaff, and R. Malkin, *Arch. Biochem. Biophys.*, **169**, 102 (1975).

(28) R. Deeg, H.-P. Kriemler, K.-H. Bergmann, and G. Müller, *Hoppe-Seyler's Z. Physiol. Chem.*, **358**, 339 (1977). The material described here as "Faktor II" is identical with sirohydrochlorin.[20,21]

(29) J. B. Paine III, W. B. Kirshner, D. W. Moskowitz, and D. Dolphin, *J. Org. Chem.*, **41**, 3857 (1976); D. O. Cheng and E. LeGoff, *Tetrahedron Lett.*, 1469 (1977).

(30) J.-H. Fuhrhop, *Z. Naturforsch. B*, **25**, 255 (1970).

(31) U. Eisner, A. Lichtarowicz, and R. P. Linstead, *J. Chem. Soc.*, 733 (1957).

(32) R. Bonnett, I. A. D. Gale, and G. F. Stephenson, *J. Chem. Soc. C*, 1168 (1967).

(33) (a) J. H. Furhop, P. K. W. Wasser, J. Subramanian, and U. Schrader, *Justus Liebigs Ann. Chem.*, 1450 (1974). (b) See note 3 in ref 14.

(34) B. J. Norris, M. L. Meckstroth, and W. R. Heineman, *Anal. Chem.*, **48**, 630 (1976).

(35) N. Sailasuta, F. C. Anson, and H. B. Gray, *J. Am. Chem. Soc.*, **101**, 455 (1979).

(36) H_2(TPiBC):[6] (λ_{max}, C_6H_6), 390, 408 (sh), 516, 552, 594 nm. Zn(TPiBC):[37] (λ_{max}, C_6H_6), 418, 498, 562, 607 nm.

(37) H. W. Whitlock and M. Y. Oester, *J. Am. Chem. Soc.*, **95**, 5738 (1973).

(38) R. B. Woodward and V. Škarić, *J. Am. Chem. Soc.*, **83**, 4676 (1961).

(39) A total of five diastereomers is possible if both cis and trans reductions of the pyrrolic rings are considered.

(40) H. Scheer and J. J. Katz, in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 10.

(41) H. Wolf and H. Scheer, *Justus Liebigs Ann. Chem.*, 1710 (1973).

(42) J.-H. Fuhrhop, *Struct. Bonding (Berlin)*, **18**, 1 (1974).

(43) R. H. Felton, in "The Porphyrins", Vol. V, Part C, D. Dolphin, Ed., Academic Press, New York, 1978, Chapter 3.

(44) Butyronitrile was employed in several cases in order to obtain adequate solubility.

(45) J.-H. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).

(46) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, **92**, 3451 (1970).

(47) J.-H. Fuhrhop, P. Wasser, D. Reisner, and D. Mauzerall, *J. Am. Chem. Soc.*, **94**, 7996 (1972).

(48) (a) λ_{max} (A_λ/A_{619}): 394 (6.9), 406 (6.3), 522 (0.28), 619 nm (1.0). (b) This spectrum (in chloroform containing HCl/methanol) differs somewhat in absorbance ratios from those obtained in this work in different media. λ_{max} (A_λ/A_{616}): 391 (5.0), 403 (4.0), 516 (0.20), 618 (1.0).[30]

(49) R. F. Nelson and R. N. Adams, *J. Am. Chem. Soc.*, **90**, 3925 (1968); F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. C*, 2719 (1969).

Communications to the Editor

Lifetime of Chlorophyll a Radical Cation in Water-Containing Acetonitrile

Sir:

Recently, in vitro properties of chlorophylls (Chl's) have drawn the attention of many workers in relation to modeling of photosynthetic primary processes as well as to construction of artificial solar conversion systems.[1-6] One of the most important, yet the least understood, processes in plant photosynthesis is the oxidation of water taking place within the photosystem II (PS II).[7] Here the primary oxidant, capable of initiating a chain of enzymic reactions leading finally to water splitting, is generally supposed to be a photooxidized reaction center ($P_{680}^{+\cdot}$) consisting of Chl *a*. Such an apparent complexity of PS II processes suggests an inefficiency of a reaction between *monomeric* Chl $a^{+\cdot}$ and H_2O *without assistance* by an enzyme. However, to our knowledge, no experimental verification for this presumption has been reported to date. In the present work we measured the lifetime of electrochemically generated Chl $a^{+\cdot}$ in water-containing acetonitrile. The experimental results enabled an estimation of the rate constant for a possible reaction Chl $a^{+\cdot}$ + H_2O.

Chl *a* was isolated from fresh spinach and purified chromatographically.[8] Acetonitrile (AN), which is sufficiently inert to most organic radical cations, was used as the solvent after dehydration and distillation treatments.[9] An optically transparent thin-layer electrochemical cell of conventional design[10,11] was fabricated by sandwiching a Pt grid working electrode (80 mesh, 20 × 10 mm, 0.15 mm thick, optical transmittance 55%) with a pair of Pyrex slide glasses (25 × 40 × 1 mm) using a Teflon spacer 0.16 mm thick. The potential of the working electrode was controlled potentiostatically against an Ag layer (~20 mm^2) vacuum deposited onto the inner face of a slide glass of the thin-layer cell. About 5 mL of Chl *a* solution (10^{-4}–10^{-3} M) was poured into a glass cup in which a Pt wire counterelectrode was immersed. The meniscus of the solution rose well above the Pt grid part when the thin-layer cell was set vertically and its lower end was dipped into the solution in the cup. The whole assembly was placed in the sample compartment of a Shimadzu spectrophotometer Model MPS-5000, and one could measure the spectral changes of the Chl *a* solution during and after electrolysis. The Karl Fischer titration was used to determine [H_2O] in AN, and all the measurements were conducted at room temperature (20 ± 3 °C).

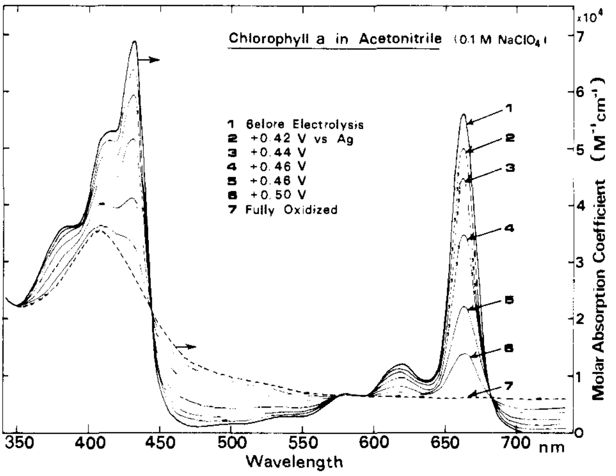


Figure 1. Change of the absorption spectrum of Chl *a* (original concentration, 5 × 10^{-4} M) in the course of electrochemical oxidation in AN. The supporting electrolyte is 0.1 M $NaClO_4$. The values of molar absorption coefficient (right ordinate) for Chl *a* and Chl $a^{+\cdot}$ in AN were calculated referring to the value ϵ_{662} = 8.63 × 10^4 M^{-1} cm^{-1} for Chl *a* in ether.[13] The electrooxidation of water does not proceed at potentials below +1.0 V vs. Ag.

Figure 1 shows the spectral changes of a Chl *a* solution during potential-controlled electrolysis ([H_2O] = 0.04 M). With rising anodic potential, the main peaks (432 and 663 nm) tended to decrease, while the absorbance in the 445-580- and >683-nm regions showed an increase, with isobestic points at 340-350, 445, 580-595, and 683 nm. This spectral change was reversible with respect to the electrode potential. At potentials higher than +0.50 V vs. Ag, the spectrum in the range of 650-730 nm became more and more flat against the wavelength.[12] Thus we assumed a flat absorbance for the oxidized Chl *a* in the above range and calculated the concentration ratio of oxidized to unoxidized Chl *a* at each potential, based on the peak absorbance (663 nm). The slope of the Nernstian plot[11] for this oxidation reaction was ~51-52 mV per decade change in the concentration ratio, being close to the theoretical one-electron value of 58 mV. This shows that the electrochemical process involved is a one-electron oxidation leading hence to the radical cation, Chl $a^{+\cdot}$. The broken curve in Figure 1 corresponds to the absorption spectrum of Chl $a^{+\cdot}$ thus determined in this particular solvent.

0002-7863/80/1502-0370$01.00/0

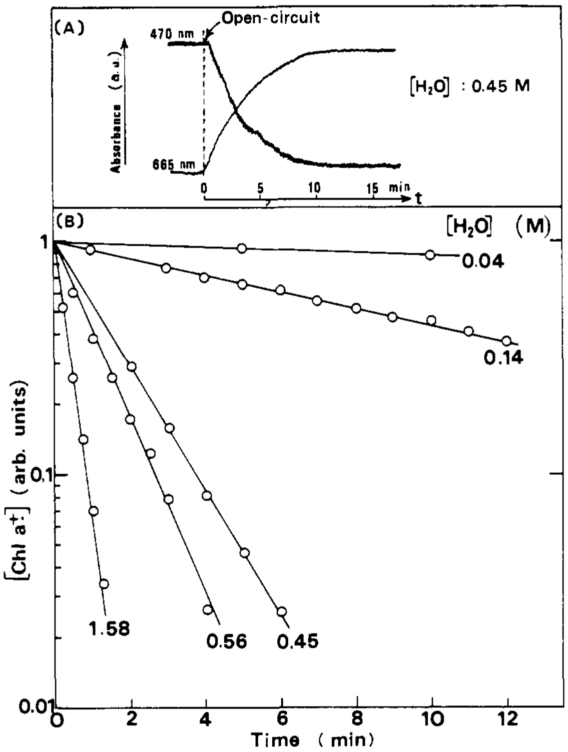


Figure 2. (A) Typical time courses of the absorbances at 470 and 665 nm after the external circuit was opened. (B) Semilogarithmic profiles for the decay of Chl $a^{+}\cdot$, derived from measurements as shown in A, at various water concentrations. At the end of the decay, the absorption spectrum of the solution was just the same as that before electrolysis (curve 1 in Figure 1).

When the external circuit was turned off after electrolysis at an appropriate anodic potential, the absorbances at ~470 and 665 nm showed a decrease and an increase with time, respectively, with nearly the same time constant. An example is shown in Figure 2A. At the end of this spectral change, the absorption spectrum of the solution in the cell perfectly coincided with that before electrolysis. Hence we can regard this spectral change as the decay of the electrogenerated Chl a^{+} resulting in the regeneration of Chl *a*. Figure 2B shows the decay profiles of Chl $a^{+}\cdot$ thus observed at different [H_2O]'s. As is seen this decay is approximately first order, with smaller time constant at higher [H_2O]. Based on this result one can determine the lifetime, τ, of Chl $a^{+}\cdot$, at which [Chl $a^{+}\cdot$] becomes $1/e$ of the original concentration, for each [H_2O].

Figure 3 shows the value of Chl $a^{+}\cdot$ lifetime (τ) thus determined as a function of [H_2O] in AN, in log-log scale. There seems to exist a regular relationship obeying an experimental formula

$$\tau = 1.0 \times 10^{2}[H_2O]^{-1}\ (s) \qquad (1)$$

The value of τ depended little on the initial Chl *a* concentration. These results make us suppose that the rate-determining step for the regeneration of Chl *a* is an attack of H_2O to Chl $a^{+}\cdot$. This reaction system is obviously pseudo first order because water is in great excess, and hence one obtains from eq 1 a value of 10^{-2} M^{-1} s^{-1} as the bimolecular rate constant for a possible reaction between Chl $a^{+}\cdot$ and H_2O. This value is incomparably smaller than the diffusion-controlled rate constant in AN at 20 °C (~10^{10} M^{-1} s^{-1}),[14] and by a factor of ~10^{3} smaller than the reported rate constants for the reaction of Chl $a^{+}\cdot$ with several alcohols,[2] indicating that a possible reaction between monomeric Chl $a^{+}\cdot$ and H_2O is an extremely slow process at least in this particular solvent. There remains a possibility that the regeneration of Chl *a* is occurring through electron exchange at the metal electrode surface. In that case, the rate constant for a direct interaction between Chl $a^{+}\cdot$ and H_2O should be smaller than 10^{-2} M^{-1} s^{-1}. For a remarkable enhancement of the reaction rate, a positive shift of the oxidation redox potential (by, e.g., aggregate formation of Chl a^{3}) and/or a decrease in the activation energy (by an appropriate redox catalyst) will be required. This might be one of the reasons why Nature had to invent a complicated system (PS II), which has to be elucidated in future researches, for an efficient oxidation of water.

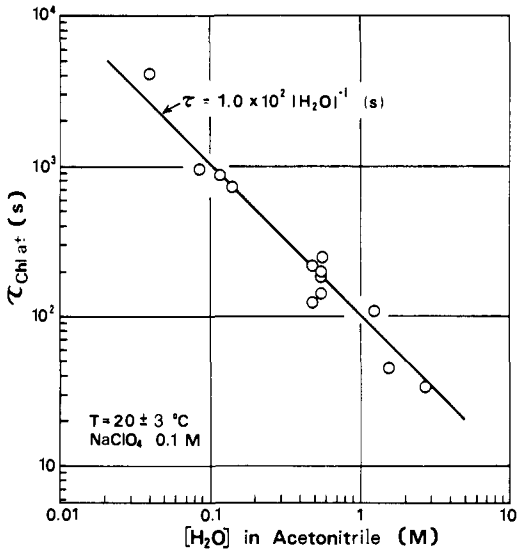


Figure 3. Lifetime of Chl $a^{+}\cdot$ as a function of water concentration in acetonitrile.

Though a detailed reaction scheme remains to be clarified, this is the first time where a rate constant for a reaction between Chl $a^{+}\cdot$ and H_2O has been experimentally deduced. Similar studies, using this simple method, on the reaction of water with the oxidized states of a variety of Chl *a* species (dimers, "special pairs",[3-5] protein complexes,[15] monolayers,[6] etc.) in different solvents with and without enzymic additives are expected to provide further information.

Acknowledgment. The authors are grateful to Dr. N. Murata for providing them with the method of Chl extraction-purification[8] as well as for valuable comments, to Professor M. Fragata, Université du Québec à Trois-Rivières, for useful discussions, and to Mr. M. Endo for taking part in the experiments.

References and Notes

(1) G. R. Seely, *Curr. Top. Bioenerg.*, **7**, 3 (1978).
(2) V. A. Kuz'min, A. K. Chibisov, and A. P. Vinogradov, *Dokl. Akad. Nauk SSSR*, **197**, 129 (1971).
(3) L. Galloway, J. Roettger, D. R. Fruge, and F. K. Fong, *J. Am. Chem. Soc.*, **100**, 4635 (1978).
(4) D. R. Fruge, G. D. Fong, and F. K. Fong, *J. Am. Chem. Soc.*, **101**, 3694 (1979).
(5) L. L. Shipman, T. M. Cotton, J. R. Norris, and J. J. Katz, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1971 (1976).
(6) T. Miyasaka, T. Watanabe, A. Fujishima, and K. Honda, *J. Am. Chem. Soc.*, **100**, 6657 (1978).
(7) R. Radmer and G. Cheniae, *Top. Photosynth.*, **2**, 303 (1977).
(8) T. Omata and N. Murata, *Photochem. Photobiol.*, in press.
(9) T. Watanabe, A. Fujishima, and K. Honda, *Chem. Lett.*, 735 (1978).
(10) R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, **39**, 1666 (1967).
(11) W. R. Heineman, *Anal. Chem.*, **50**, 390A (1978).
(12) When the anodic potential exceeded +0.6 V vs. Ag, the smoothening of the spectrum (in the region of 650–730 nm) was accompanied by a gradual decrease in the absorbance over the whole visible range. This might be due to the onset of the second oxidation stage leading to dication formation. In the present communication we limit our discussion to the one-electron oxidation process, by avoiding the potential range positive of +0.5 V vs. Ag. The second and further oxidation stages shall be considered in future studies.
(13) H. H. Strain, M. R. Thomas, and J. J. Katz, *Biochim. Biophys. Acta*, **75**, 306 (1963).

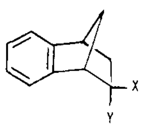
(14) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973, p 55.
(15) N. K. Boardman, J. M. Anderson, and D. J. Goodchild, *Curr. Top. Bioenerg.*, **8**, 35 (1978).

Tadashi Watanabe,* Kenichi Honda
Department of Synthetic Chemistry
Faculty of Engineering, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan
Received August 8, 1979

Intramolecular Aryl-Assisted Photolytic Cleavage of 2-Benzonorbornenyl Derivatives. A High Excited-State Exo/Endo Reactivity Ratio and a Novel Wagner-Meerwein Rearrangement[1]

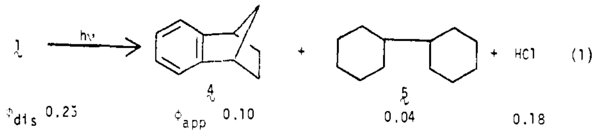
Sir:

Though the enhanced ground-state solvolyses rates of exo-2-substituted benzonorbornenyl derivatives are well documented,[2] the photochemical properties of these compounds have not hitherto been studied. We have been examining such compounds as part of our ongoing program in the photochemistry of bichromophoric molecules,[1,3] and have observed that (1) *photolysis of 2-benzonorbornenyl chlorides and mesylates* (**1–3**) *with 254-nm light results in cleavage of the C–Cl or C–O bonds,* (2) *there is a remarkable stereoelectronic preference for reaction at the exo position, and* (3) *one of the reaction paths involves a novel 1,2 shift of the C_9 bridge.*

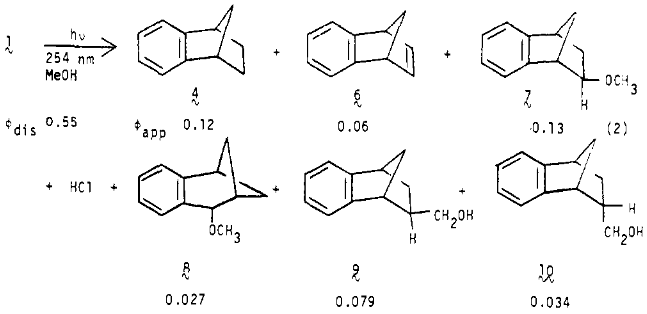


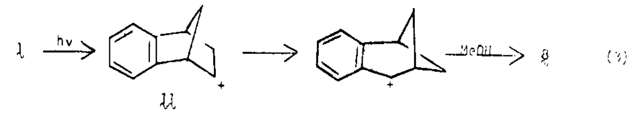
1 X = Cl, Y = H
2 X = H, Y = Cl
3 X = OMs, Y = H

Although the $S_0 \rightarrow S_1$ (B_{2u}) transition of **1** is only slightly perturbed by comparison with that of benzonorbornene (**4**),[4] and the C–Cl bond is virtually transparent at 254 nm,[5] photolysis of an argon-degassed 0.015 M cyclohexane solution of **1** at this wavelength results in the efficient loss of starting material (eq 1).[6] Under these photolytic conditions, *exo*-2-norbornyl chloride is photoinert, whether irradiated alone or in the presence of toluene. More striking is the 20-fold reduction in reactivity for the endo isomer (**2**), with ϕ_{dis} = 0.013! (Compounds **4**, **5**, and HCl are again formed.)

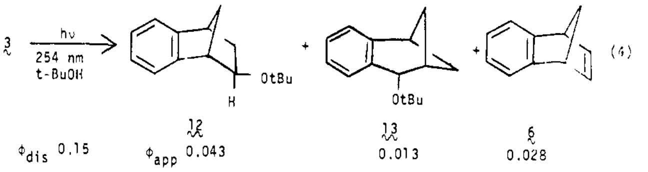


The free-radical chemistry evident in eq 1 becomes admixed with ionic chemistry when **1** is photolyzed in methanol (eq 2; note that ϕ_{dis} increases markedly).[7] Compound **8**[8] is the most unusual of the products formed, being an apparent consequence of a hitherto unobserved 1,2 migration of the C_9 bridge in the 2-benzonorbornenyl cation, **11** (eq 3).[10] Though bridge migration does not occur in ground-state solvolyses,[2,12] we have independent synthesized **8** by photolyzing an alkaline alcoholic solution of 2-benzonorbornenone tosylhydrazone, a reaction known to produce carbenium ions[11] (i.e., **11**).[13]





The aryl-sensitized reactivity at the 2 position is not unique to a chloro substituent, for photolysis of the mesylate (**3**) at 254 nm[14] likewise results in cleavage (eq 4). (In this case, facile ground-state solvolysis in methanol requires that *tert*-butyl alcohol be used for the photochemical experiment; ϕ_{dis} for **1** in *t*-BuOH is 0.38.) As with the chlorides, there is a large decrease in reactivity for the endo isomer of **3**.



There are a number of observations in the literature which are potentially related to this report. These include (1) the aryl-assisted photosolvolysis of 2-(3,5-dimethoxyphenyl)ethyl mesylate,[15] (2) the facile benzylic cleavage which occurs upon photolysis of various ϕ CH_2X species,[16] including benzyl chloride,[17] and (3) the radical and ionic products which result from the direct photolysis of alkyl bromides and iodides.[18] The most interesting mechanistic questions arising from these studies involve the excited state(s) responsible for ion formation[19] and the question of concomitant homolytic and heterolytic cleavage[20] vs. a sequential mechanism (wherein electron transfer occurs within an initially formed radical pair).[18] Our data which bear on these points and on the manner by which energy is transmitted to the C_2–X bond[21] will be discussed in the full paper.

Acknowledgments. We thank the Army Research Office for support of this research and the Dyson Perrins Laboratory of Oxford University for hospitality extended during the preparation of this manuscript. The 360-MHz NMR spectra were run on an instrument purchased through the National Institutes of Health Research Grant No. RR01077 from the Division of Research Resources.

References and Notes

(1) Organic Photochemistry. 44. Part 43: Morrison, H. *Acc. Chem. Res.*, in press. Part 42: Giacherio D.; Morrison, H.; *J. Am. Chem. Soc.* **1978**, *100*, 7109–7110. Presented, in part, at the Joint Regional Meeting of the Central and Great Lakes Sections of the American Chemical Society, May 24–26, 1978, Indianapolis, Ind.

(2) Goering, H. L.; Chang, C.-S., Masilamani, D. *J. Am. Chem. Soc.* **1978**, *100*, 2506–2510, and references therein.

(3) Nylund T.; Morrison, H. *J. Am. Chem. Soc.* **1978,** *100*, 7364–7374, and references therein.

(4) The B_{2u} band is red shifted by ~2 nm and slightly more intense, much as is observed for 2-methylenebenzonorbornene. Cf. Scully, F.; Nylund, T.; Palensky, F.; Morrison, H. *J. Am. Chem. Soc.* **1978,** *100*, 7352–7364.

(5) For example, the absorbance of 0.1 M 2-norbornyl chloride in a 1-cm cell is <0.02 at 254 nm.

(6) Additional high molecular weight products can be detected, the principal two being tentatively assigned as *exo*- and *endo*-2-cyclohexylbenzonorbornene on the basis of NMR and mass spectral data.

(7) ϕ_{dis} for **2** is 0.019 in methanol; the principal product is **7** (ϕ = 0.011) with only a trace of **8** and *endo*-**7.** It is noteworthy that C_9 migration is *not* favored; this suggests that rearrangement and cleavage do not proceed concertedly.

(8) (a) Satisfactory analytical data have been obtained for all new compounds. (b) Evidence for the structure of **8** derives from the virtual identity of its ^1H NMR with that of **13.** The structure of **13** follows from its 360-MHz ^1H NMR, i.e., for **13** (see numbering below): ^1H NMR ($CDCl_3$, 360 MHz) δ 6.75–7.35 (m, aromatic, 4 H), δ_3 4.83 (d, J_{32} = 3.2 Hz), δ_1 3.00 (q, $J_{12} \simeq J_{15} = J_{16} \simeq$ 5.8 Hz), δ_2 2.69 (m, J_{23} = 3.2, $J_{25} = J_{26} \simeq$ 7.0 Hz), δ_5 2.42 (m, $J_{51} \simeq$ 5.8, $J_{52} \simeq$ 7.0, $J_{54} \simeq$ 8.3 Hz), δ_6 2.26 (m, $J_{61} \simeq$ 5.8, $J_{62} \simeq$ 7.0, $J_{67} \simeq$ 8.3 Hz), δ_7 1.72 (t, $J_{74} = J_{76} \simeq$ 8.3 Hz), δ_4 1.53 (t, $J_{45} = J_{47} \simeq$ 8.3 Hz), δ 1.35 (s, *t*-butyl, 9 H). The chemical shifts and coupling constants match very well with those of **14.**[9]

0002-7863/80/1502-0372$01.00/0