

Dichlorocarbene Chlorination of Alcohols in an Alkaline Micelle

Sir:

Dichlorocarbene is often used for the introduction of a dichloromethylene function into an organic compound.¹ Especially, dichlorocarbene additions to double bonds are very successfully applied to prepare dichlorocyclopropanes. Among many procedures in the literature for generating dichlorocarbene, one reported by Makasza, *et al.*,² using an emulsifying system seems to be most convenient and efficient. Even for dichlorocarbene insertions, the procedure (with a slight modification using benzene) was found to give excellent results as reported by us recently.^{3,4}

Now we wish to report that dichlorocarbene reacts very readily with alcohols, leading to the corresponding chlorides. The reaction affords considerable preparative advantage⁵ (*e.g.*, preparation of a chloride in excellent yield under basic conditions and/or at room temperature) and mechanistic interest.

A mixture of 1-adamantyl alcohol (1.52 g, 0.01 mol), 20 ml of 50% aqueous sodium hydroxide solution, and 0.04 g of triethylbenzylammonium chloride was stirred vigorously at 40° to emulsify, and then 16 ml of chloroform was added dropwise into the emulsion during 2 hr and the mixture was stirred for a further 2 hr. Usual workup gave 1.60 g of practically pure 1-adamantyl chloride (94% yield), *m/e* 170; ir and nmr spectra were identical with those reported.

Dichlorocarbene chlorination of various alcohols proceeded similarly and the results are shown in Table I.

Table I. Dichlorocarbene Chlorination of Alcohols

Starting alcohols	Product (yield, %)
1-Adamantyl alcohol	1-Adamantyl chloride (94) 1-Adamantyl formate (sa) ^a
Benzyl alcohol	Benzyl chloride (90) Benzyl formate (sa)
<i>l</i> -Menthyl alcohol	<i>l</i> -Menthyl chloride ^b <i>d</i> -Menthyl chloride ^b
2- <i>exo</i> -Norbornyl alcohol	2- <i>exo</i> -Norbornyl chloride (90)
2- <i>endo</i> -Norbornyl alcohol	2- <i>exo</i> -Norbornyl chloride (47) 2- <i>endo</i> -Norbornyl chloride (44)
(1-Adamantyl)methyl alcohol	(1-Adamantyl)methyl chloride (40) Homoadamantyl chloride (13) (1-Adamantyl)methyl formate (35)

^a sa = small amount. ^b $\alpha_D = -23.6^\circ$.

The reaction was always very exothermic and practically complete within a few minutes at room temperature.

Since the major chloride obtained was that resulting from retention of configuration of the starting alcohol (see Table I), the S_Ni mechanism may be operative.

(1) *E.g.*, see W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(2) M. Makasza and M. Wawrzyniewicz, *Tetrahedron Lett.*, 4659 (1969).

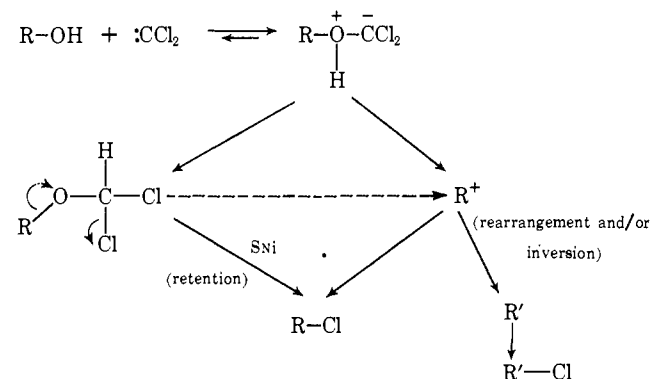
(3) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, **92**, 6670 (1970).

(4) Seyferth's procedure using trichloromethylmercuric reagents was also reported to give good results: D. Seyferth, *et al.*, *J. Org. Chem.*, **35**, 1989, 1993 (1970); *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

(5) The reaction of alcohols with dichlorocarbene in basic media afforded corresponding olefins, *e.g.*, P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959).

However, the rearrangement (from adamantylcarbonyl to homoadamantyl) and the inversion (from *endo*-2-norbornyl to *exo*-2-norbornyl or from *l*-methyl to *d*-methyl) observed suggest considerable leakage to a carbonium ion (as shown in Scheme I).

Scheme I



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Unusual Metalloporphyrins. VI. Metal Shuttling between Imidazole Nitrogens in a Ruthenium Porphyrin Imidazole

Sir:

The great biological significance of the iron(II)-porphyrins has caused substantial interest in their properties, structures, and mechanisms. The fact that imidazole derivatives are such frequent axial ligands in these complexes makes the iron(II)-porphyrin-imidazole complexes a subject of concern to the coordination chemist. Among the problems involved in the study of such compounds are both the ease of oxidation and the paramagnetism frequently found in iron(II) compounds. The only reported ruthenium porphyrin had been ruthenium(III) carbonyltetraphenylporphyrine chloride.¹ It was anticipated, however, that a porphyrin of ruthenium in the +2 state would eliminate these obstacles to the facile study of the metal-imidazole bond in heme-type compounds.

Ruthenium(II) carbonylmesoporphyrin IX dimethyl ester (I) was prepared by refluxing 0.50 g of mesoporphyrin IX dimethyl ester with 2.00 g of ruthenium dodecacarbonyl in benzene under nitrogen for 48 hr. The product, purified by chromatography with acetone on neutral alumina, is crystallized from tetrahydrofuran-hexane to give I, a brick red, air-stable solid, mp 290° dec. *Anal.* Calcd for $RuC_{37}H_{40}O_5N_4$: C, 61.57; H, 5.59; N, 7.76; Ru, 14.00; mol wt, 721.8. Found: C, 61.28; H, 5.75; N, 7.60; Ru, 13.80; mol wt (in benzene), 722. The product has a visible spectrum which is typical of metalloporphyrins² with α and β bands at 548 (ϵ 3.43×10^4) and 518 nm (1.53×10^4), respectively, and a Soret band at 393 nm (2.85×10^5) in tetrahydrofuran. The presence of a C=O ligand is confirmed by the ir spectrum which has a

(1) E. B. Fleischer, *Chem. Commun.*, 475 (1969).

(2) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964, p 75.

strong $C\equiv O$ stretching band at 1940 cm^{-1} . The sharp, well-resolved lines of the nmr spectra indicate a diamagnetic, low-spin Ru(II) complex.

The solid-state ir spectrum (KBr) has two bands of medium intensity in the ester carbonyl region, at 1690 and 1740 cm^{-1} . The material is only slightly soluble in noncoordinating solvents, but it dissolves readily in the presence of a suitable ligand (e.g., amines, alcohols, even atmospheric moisture). The resulting solutions show only the ir absorption at 1740 cm^{-1} . It seems likely that the solid-phase ir absorption at 1690 cm^{-1} is caused by the coordination of the ester carbonyl groups in the empty sixth coordination site of the ruthenium. Similar lowering of the frequency of an ester carbonyl group coordinated with a metal has been observed in titanium porphyrins³ and in chlorophyll aggregates.⁴ When the material is recrystallized, the ligand-free solid with the 1690 - and 1740-cm^{-1} bands is obtained.

The ruthenium carbonyltetraphenylporphine (II) was made in a similar manner. It is also a red, air-stable, diamagnetic solid, mp 200° dec . The visible spectrum has peaks at 528 and 412 nm . The ir spectrum shows a carbonyl stretching frequency at 1945 cm^{-1} .

An indication that the sixth coordination site in both I and II is either empty or at least in some sort of equilibrium with a five-coordinate species, is the fact that imidazole and similar bases immediately complex with both compounds upon simple mixing in benzene to form red, crystalline, diamagnetic solids. Since octahedral Ru(II) is substitution "inert," the rapid addition of a ligand can be presumed to involve the five-coordinate complex.

The imidazole-ruthenium carbonylmesoporphyrin IX dimethyl ester (III) has a typical metalloporphyrin spectrum with α and β bands at 554 ($\epsilon\ 8.54 \times 10^3$) and 522 nm (6.95×10^3), respectively, and a Soret band at 399 nm (1.14×10^5) in benzene. The ir spectrum of III (CHCl_3) shows -NH stretching at 3455 cm^{-1} , metal carbonyl absorption at 1940 cm^{-1} , and ester carbonyl absorption at 1740 cm^{-1} . *Anal.* Calcd for $\text{C}_{40}\text{H}_{44}\text{O}_5\text{N}_6\text{Ru}$: C, 60.82; H, 5.61; N, 10.64; Ru, 12.80; mol wt, 789.9. Found: C, 61.03; H, 5.80; N, 10.7; Ru, 12.58; mol wt in benzene, 791.

The imidazole-ruthenium carbonyltetraphenylporphine (IV) has a visible spectrum with peaks at 535 and 414 nm in benzene. Its ir spectrum (CHCl_3) has an N-H stretching frequency at 3455 cm^{-1} and a metal carbonyl absorption at 1945 cm^{-1} . *Anal.* Calcd for $\text{C}_{48}\text{H}_{32}\text{ON}_6\text{Ru}$: N, 10.38. Found: N, 10.33.

In coordinating solvents (tetrahydrofuran, methanol) the imidazole complex, III or IV, dissociates to give the same species as is formed by dissolving an authentic sample of I or II. Chromatography on alumina or silica gel with either methylene chloride or acetone and chromatography on talc with benzene removes the imidazole molecule from the complex. The metalloporphyrin eluted is, in all cases, the corresponding complex, I or II.

A possible explanation for the looseness with which the sixth ligand is held—and its possible absence in some cases—would be that the metal atom is located

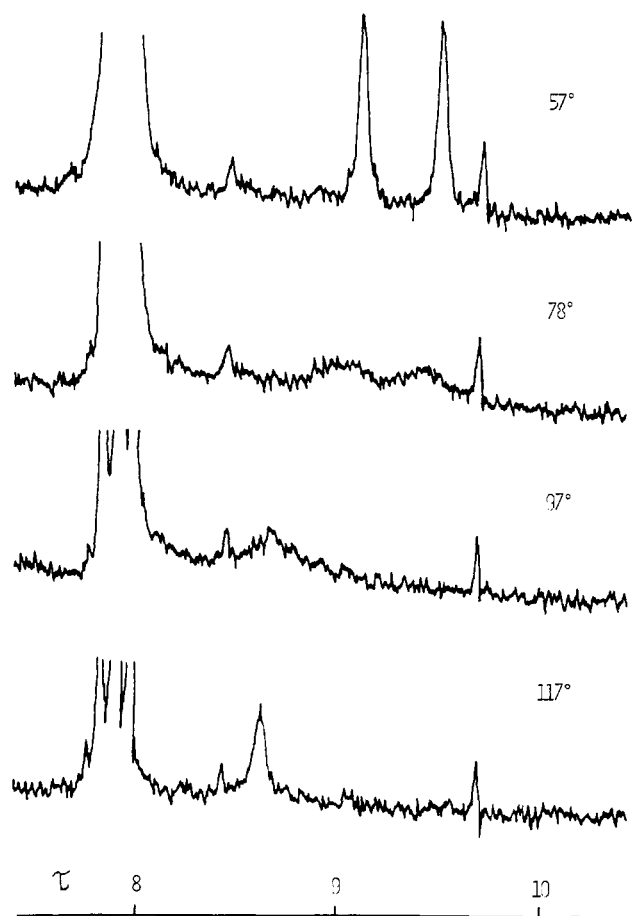


Figure 1. Pmr spectra of II (100 MHz) in *sym*-tetrachloroethane at various temperatures.

on the carbonyl side of the porphyrin plane. A weak ligand bond is also indicated by the relatively small changes in the visible spectrum and the carbonyl stretching frequency upon complexation of I with imidazole. Interpreting the change in chemical shift of the pyridine γ proton in the pyridine complex of I by the approximate method of Storm⁵ indicates that the metal is roughly 0.5 \AA out of plane toward the carbonyl side of the porphyrin ring.

Using III, it was hoped that certain aspects of the nature of the metal-imidazole bond could be elucidated. Chemical evidence⁶ plus a single crystal X-ray study⁷ have both shown that the imidazole bonds to metals through its "pyridine" nitrogen. Imidazole itself, of course, exists as a pair of identical tautomers, V.⁸ Recently, N-bonded trimethylsilylpyrazole was also found to exist as a pair of tautomers.⁹

The pmr spectrum of III (Figure 1) was therefore investigated to ascertain whether, under any circumstances, a similar tautomerism takes place.

At room temperature, the 100-MHz pmr spectrum of ruthenium carbonylmesoporphyrin IX dimethyl ester-imidazole (III) in *sym*-tetrachloroethane showed two peaks, with areas corresponding to one proton each, at $\tau\ 9.0$ and 9.4 . As the temperature is raised,

(5) C. B. Storm, *ibid.*, **92**, 1424 (1970).

(6) R. Driver and W. R. Walker, *Aust. J. Chem.*, **21**, 671 (1967).

(7) K. S. Lundberg, *Acta Crystallogr.*, **21**, 901 (1966).

(8) J. D. Roberts and M. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964, p 1006.

(9) D. H. O'Brien and C. P. Hsung, *J. Organometal. Chem.*, in press.

(3) M. Tsutsui, R. A. Velapoldi, K. Suzuki, F. Vohwinkel, M. Ichikawa, and T. Koyano, *J. Amer. Chem. Soc.*, **91**, 6262 (1969).

(4) J. J. Katz, G. L. Closs, F. C. Pennington, M. P. Thomas, and H. H. Strain, *ibid.*, **85**, 3801 (1963).

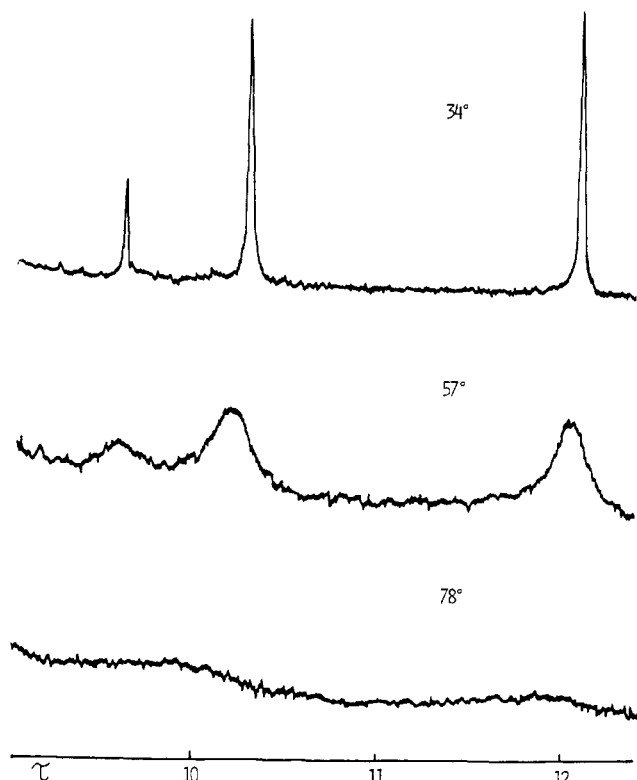
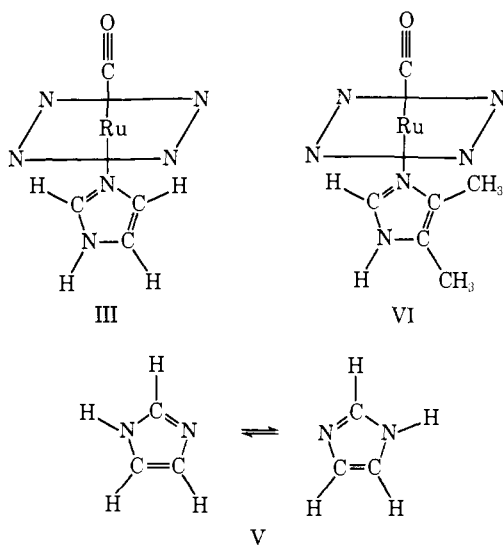


Figure 2. Pmr spectra (100 MHz) of III in benzene at various temperatures.

they first broaden and then coalesce to a singlet at τ 8.7 with an area corresponding to two protons, at 117° (Figure 1). The chemical shifts were determined relative to the solvent peak which was used as an internal lock.

The two high-field peaks in III were assigned to imidazole protons 4 and 5 by comparison with the



two similarly positioned methyl peaks in the spectrum of VI, ruthenium carbonylmesoporphyrin IX dimethyl ester (4,5-dimethylimidazole). The room temperature pmr spectrum of the latter contains two sharp singlets whose areas correspond to three protons each, at τ 10.0 and 11.4. These peaks also broaden at

higher temperature and, at 117° , they form a sharp singlet at τ 10.0 with an area corresponding to six protons.

Further confirmation of these assignments comes from the benzene solution of VI. Resonances corresponding to all three types of carbon-bonded protons are apparent in its pmr spectrum. The three peaks come at τ 9.6, 10.2, and 12.0 with areas corresponding to one, three, and three protons, respectively. As the temperature is raised, the three peaks are broadened until at 78° they are hardly distinguishable from the base line (Figure 2).

The striking upfield shifts of the imidazole resonances are caused by porphyrin ring currents and are in accord with the large shifts found in other metalloporphyrin complexes.⁵ Two observations which require explanation are the broadening of the resonance attributed to proton 2 of the imidazole, and the temperature-dependent movement of the two peaks at τ 9.0 and 9.4 up to their eventual coalescence to a singlet at τ 8.7. These two phenomena indicate that more than a simple averaging process is involved and are best explained by the supposition that as the temperature changes there is, in addition to the "shuttling," a rapid movement of the imidazole through several different orientations with respect to the porphyrin ring. Such a change in position should cause a substantial chemical-shift difference in all the imidazole protons, as well as a significant broadening of the 2 proton. It is likely that these different environments involve simple "wagging" of the σ -bonded imidazole, but one cannot exclude a change in the nature of the metal imidazole bond to one with greater π character. Indeed, even a π -bonded sandwich complex can be proposed as a limiting case.

Previous room temperature pmr studies on metal-imidazole complexes¹⁰ have used labile species such as Zn^{2+} or Co^{2+} in which any intramolecular effect making the imidazole nitrogens equivalent was masked by rapid intermolecular ligand exchange. To ascertain whether an intermolecular process was responsible for the temperature dependence in the spectra of II and III, an excess of 4,5-dimethylimidazole was added to a solution of III in benzene. A resonance at τ 8.0 was caused by the two methyl groups of the free imidazole. At 78° , in benzene, where the methyl resonances of the complexed imidazole are severely broadened, the free imidazole peak is broadened only slightly, if at all.

Fratiello, Schuster, and Bartolini,^{10c} by cooling a mixture of Co^{2+} and imidazole sufficiently, have been able to separate the pmr peaks of free and complexed imidazole. The "shuttling" mechanism proposed here would account for the unexplained equivalence of their 4 and 5 protons at -40° in acetone.

Further studies are now being undertaken to more fully elucidate the nature and scope of this "shuttling."

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(10) (a) S. M. Wang and N. C. Ki, *J. Amer. Chem. Soc.*, **88**, 4592 (1966); (b) R. H. Carlson and T. L. Brown, *Inorg. Chem.*, **5**, 269 (1966); (c) A. Fratiello, R. E. Schuster, and G. Bartolini, *J. Amer. Chem. Soc.*, **92**, 2304 (1970).

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The Structure of Peridinin, the Characteristic Dinoflagellate Carotenoid

Sir:

The principal carotenoid pigment of dinoflagellates (class, Dinophyceae; division, Pyrrophyta) is an important substance in the carbon economy and ecology of the world.¹ First isolated and named peridinin by Schütt in 1890,² it has since been isolated from various marine and fresh-water dinoflagellates^{3,4} including endozoic symbionts (zooxanthellae) of marine corals, clams,⁵ and sea anemones.^{4,6,7} A preparation from an anemone (*Anemonia sulcata*) was once called sulcatoxanthin.⁶

Peridinin, mp 107–109°, is an orange-red pigment (λ_{\max} (hexane) 455, 485 nm; (ethanol) 475 nm),⁷ readily separable from other carotenoids by chromatography. It is decolorized by alkalis^{4,7} and reacts slowly with acids, the absorption maxima being shifted hypsochromically 20 nm.⁴ Reduction with LiAlH_4 shifts the maxima to 329, 345, 364, and 390 nm in methanol.⁴ Earlier analyses indicated a molecular formula $\text{C}_{40}\text{H}_{52}\text{O}_8$, mol wt 660,⁶ but high-resolution mass spectrometry established⁸ the molecular formula as $\text{C}_{39}\text{H}_{50}\text{O}_7$ (630.3529).

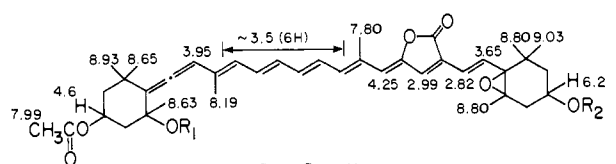
Current studies were carried out cooperatively in our four laboratories. For these studies, peridinin with identical properties was isolated from the zooxanthellae of the Pacific Coast sea anemone,⁷ *Bunodactis* (now *Anthopleura*) *xanthogrammica*, from a natural bloom or red tide of dinoflagellates, greater than 98% *Gonyaulax polyedra*, and from cultures of *Cachonina niei* and *Amphidinium operculatum*.

On the basis of detailed physical and chemical evidence, we now assign structure **1** to peridinin, a unique tricyclic carotenoid with a C_{37} skeleton. The terminal rings are linked by a chain differing from the usual carotenoid structure by the absence of two in-chain carbons and two branching methyl groups, one of the latter being replaced by a carboxylic function in the form of a butenolide unit which forms part of the chromophore.

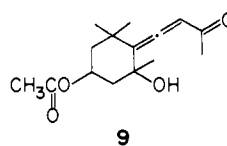
Peridinin (**1**), itself a monoacetate, on esterification yielded one further acetate (**2**), chloroacetate (**3**), or *p*-bromobenzoate (**4**). On silylation, it gave a di(trimethylsilyl) ether (**5**). The diacetate (**2**), on silylation, gave a mono(trimethylsilyl) ether (**6**). These results establish the function of four of the oxygen atoms: one acetate, one tertiary hydroxyl, and one esterifiable hydroxyl. The three remaining oxygen functions were assigned to one epoxy group and a butenolide group of the type encountered in tetrenolin (**7**)⁹ and free-lingyne (**8**).¹⁰

The location of three oxygen atoms in a terminal ring of known structure was established by ozonolysis of peridinin *p*-bromobenzoate (**4**). The resulting allenic ketone (**9**) was identical (uv, ir, nmr, mass spectra) with the ketone obtained on cleavage of fucoxanthin.^{11,12} This result defined one end of the peridinin molecule and accounted for three oxygen functions: one acetate and one tertiary hydroxyl.

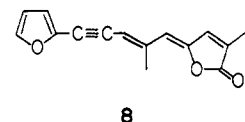
The pmr signal assignments of peridinin (recorded in CDCl_3 at 220 MHz) are given on structure **1** and



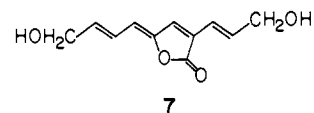
- 1, $\text{R}_1 = \text{R}_2 = \text{H}$
- 2, $\text{R}_1 = \text{H}; \text{R}_2 = \text{CH}_3\text{CO}$
- 3, $\text{R}_1 = \text{H}; \text{R}_2 = \text{ClCH}_2\text{CO}$
- 4, $\text{R}_1 = \text{H}; \text{R}_2 = \text{Br}-\text{C}_6\text{H}_4-\text{CO}$
- 5, $\text{R}_1 = \text{R}_2 = \text{Si}(\text{CH}_3)_3$
- 6, $\text{R}_1 = \text{Si}(\text{CH}_3)_3; \text{R}_2 = \text{CH}_3\text{CO}$



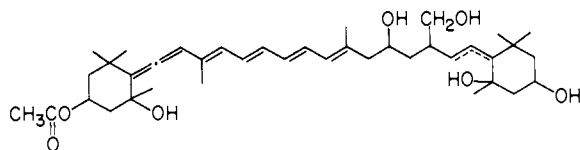
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agree with previous assignments for the allenic end group of fucoxanthin^{11,12} and the epoxy end group of violaxanthin¹³ and neoxanthin.¹⁴ The olefinic region

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- (6) I. M. Heilbron, H. Jackson, and R. N. Jones, *Biochem. J.*, **29**, 1384 (1935).
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- (8) H. H. Strain and W. A. Svec, *Advan. Chromatogr.*, **8**, 119 (1969); cf. p 172.

- (9) G. G. Gallo, C. Coronelli, A. Vigevani, and G. C. Lancini, *Tetrahedron*, **25**, 5677 (1969).
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