compd no.	R_f with		
	CHCl$_3$	CHCl$_3$-EtOAc[a]	EtOAc
4a	0.73	0.83	0.85
4b	0.73	0.84	0.86
2a	0.49	0.78	0.83
2b	0.03	0.47	0.63
3b	0.63	0.85	0.87
1a	0.42	0.77	0.86
1c	0.02	0.24	0.51

[a] 1:1 by volume.

$-NO_2-CO$), 151 (25%), 150 (58%, M $- HNO_4S$), 139 (37%), 115 (86%), plus fragments <100.

Cyclic voltammetry was conducted in a three-compartmental H-cell bearing two Pt foil electrodes (1 cm^2 each), a ground-glass Luggin capillary insert (into the working-electrode chamber) for connection to a reference electrode, and a solvent-electrolyte of 0.1 M reagent-grade, anhydrous LiClO$_4$ in purified[14] CH$_3$CN in all compartments. Compartments were separated by glass frits (G-4). The reference electrode consisted of an Ag wire in 0.1 M reagent-grade Ag salt (usually *p*-toluenesulfonate, but nitrate was used in a few oxidative runs). The solvent-electrolyte was preelectrolyzed[5] so as to remove extraneous peaks in the potential range to be investigated. The substrate (5-13 mg) was added to the working electrode compartment (bearing 7-9 mL of solvent-electrolyte), air in the compartment was displaced by nitrogen, and the voltammogram was obtained by means of a Princeton Applied Research modular instrument (units 173, 175, 176, and 178) which generates a time-dependent triangular voltage input at the working electrode and transmits a voltage output to an X-Y recorder (a Houston Instrument Omnigraph 2000). Reductive cyclic voltammograms were also recorded after addition of varying amounts (1-15 vol %) of purified Ac$_2$O to the cathode chamber. Data obtained are presented in Table I.

Synthetic electrochemical reductive acetylation was conducted in a larger three-compartmental H-cell whith the following items placed in the cathode chamber: 14 mL of Hg (cathode), a 2.5-cm magnetic stirring bar, 100 mL of 0.72 M NaClO$_4$ in MeCN-Ac$_2$O (10:1 v/v), and a Ag/0.1 M AgOTs in MeCN reference electrode insert. The anode was Pt foil. The same solvent-electrolyte (prepared from anhydrous NaClO$_4$,[15] laboratory reagent CH$_3$CN, and Ac$_2$O—mixture dried over 4-Å molecular sieves for at least 3 days before use) was also placed in the other compartments. Preelectrolysis was continued at a constant cathode potential of -1.3 V until the background current fell to a low value (2-4 mA). The substrate was then added to the cathode chamber and electrolysis was conducted in a nitrogen atmosphere at -1.1 to -1.3 V with vigorous stirring at room temperature and an initial current of 50-90 mA. Coulometry was obtained by plotting the current as a function of time.

2-(*N,O*-Diacetylhydroxylamino)dibenzothiophene 5,5-Dioxide (2b). Electrolysis of 310 mg of 2a occurred over a period of 128 min (coulomb uptake 479, 104% of theory). The catholyte was filtered by suction to collect precipitated NaOAc (washed with MeCN, dried in vacuo, yield 391 mg, 100%; identified by infrared spectrum). The filtrate was rotoevaporated at 40 °C to remove MeCN, diluted with 100 mL of CH$_2$Cl$_2$, allowed to stand for 30 min, and refiltered to remove salts. Rotoevaporation of the filtrate (40 °C) gave a yellow liquid which crystallized on standing. Washing the crystals with ethyl acetate and reworking the mother liquors (evaporation at 50 °C (1 torr)) gave a total yield of 326 mg (83%) of orange product, mp 212-219 °C, converted to white needles on recrystallization from absolute ethanol (charcoal): mp 218-219.5 °C dec; IR (vida supra); ^{1}H NMR δ 2.39 (s, NAc), 2.55 (s, OAc), 7.7-8.8 (m, aromatic H); mass spectrum, *m/z* 332 (26%, M + 1), 331 (0.4%, M), 290 (26%), 289 (100%, M $- CH_2$=C=O), 272 (23%), 248 (22%), 247 (100%, M $- 2$

CH_2=C=O), 231 (29%), 139 (25%), 43 (100%, Ac).
Anal. Calcd for C$_{16}$H$_{13}$NO$_5$S: C, 58.00; H, 3.95; N, 4.23; S, 9.7. Found: C, 57.94; H, 4.11; N, 4.20; S, 9.5.

Compound **2b** was dried and stored in the dark, for it appeared to undergo photooxidation (to a cream or orange product) on the laboratory bench.

4,4'-Bis(*N,O*-diacetylhydroxylamino)diphenyl Sulfone (1c). By the foregoing procedure 299 mg of **1a** was electrolyzed for 290 min (103% coulomb uptake) to yield 534 mg (84%) of NaOAc and 323 mg (74%, mp 183.5-186.5 °C) of **1c**: orange prisms, mp 184.5-185.5 °C from absolute ethanol (charcoal) (lit.[2] mp 186-188 °C); IR (vide supra); ^{1}H NMR δ 2.36 (s, 6 H, NAc), 2.57 (s, 6 H, OAc), 8.07 (dd, J_{AB} = 9 Hz, $\Delta\delta$ = 24.4 Hz, 8 aromatic H); mass spectrum (15 eV, 200 °C probe), *m/z* 449 (0.5%, M + 1), 448 (not observed, M), 406 (15%, M $- CH_2$=C=O), 364 (26%, M $- 2$ CH$_2$=C=O), 348 (11%), 322 (8%, M $- 3$ CH$_2$=C=O), 320 (16%, M $- 2$ Ac $- CH_2$=C=O), 306 (24%), 304 (21%), 60 (22%), 43 (100%, Ac).

For a larger run, electrolysis was repeated with a suspension of 1.03 g of **1a** in 100 mL of 0.72 M NaClO$_4$ in MeCN-Me$_2$SO-Ac$_2$O (5:5:1). After 22 h (without coulometry) the reaction was stopped (3 mA) and the catholyte was poured directly into 1.5 L of water. The beige precipitate of **1c** was collected and dried in the dark, yield 1.20 g (80%), mp 175-180 °C.

Chromatography. TLC data for **1c, 2b**, and the compounds studied in cyclic voltammetry are shown in Table II. It is apparent that the diacetylhydroxylamino sulfones should be easily separable from precursory nitro sulfones on a silica gel column with chloroform as an eluting solvent.

Photolysis of *cis*-1,2,6-Octatriene

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The photochemistry of allenic compounds has drawn little attention; the first report of allene photolysis appear in the work of Collin and Lossing.[1] Ward and Karafiath[2] reported the first benzene-sensitized photolysis of allenes, 1,2,6-heptatriene and 1,2,6-cyclononatriene, and observed a single primary product for each reaction. Betouski and Deyrup[3] reported the photolysis of *trans*-1,2,6-cyclononatriene to study the photochemical Cope rearrangement. Although other allenes such as derivatives of 1,2,6-heptatriene and 2,3,7-octatriene have been reported as intermediates of oxy-Cope rearrangements,[4] their photochemistry has not been studied extensively. In the present work, *cis*-1,2,6-octatriene was prepared in order to study further the mechanism of allene photochemistry. The benzene-sensitized photolysis of *cis*-1,2,6-octatriene gave not only the trans isomer but also several other primary products which were identified as all having the same molecular weight (*m/e* 108).

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(15) Lund, H. *Acta Chem. Scand.* **1957,** *11,* 491.

Table I

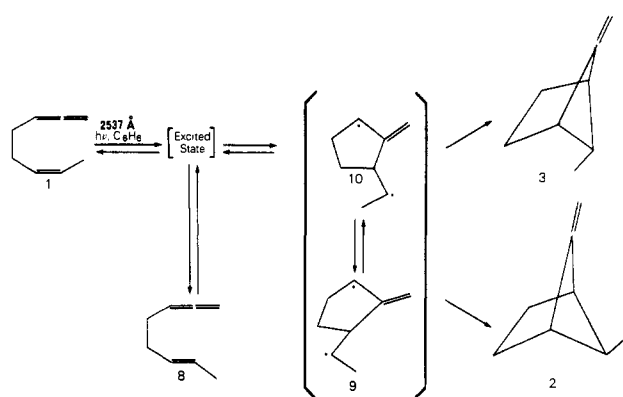|		t_R on column				
		C	E	F	G	
no.	compd	60 °C	40 °C	90 °C	40 °C	Φ
2	*exo*-5-methyl-6-methylenebicyclo-[2.1.1]hexane	0.369	0.52	1.52		0.0130 ± 0.0007
3	*endo*-5-methyl-6-methylenebicyclo-[2.1.1]hexane	0.475	0.648	1.67		0.023 ± 0.001
4	2-methyltricyclo[4.1.0.0^{1,3}]heptane	0.568	0.74	1.00		0.006 ± 0.001
5	3-methyl-4-methylene-1,5-hexadiene	0.67	0.807	2.25		0.0068 ± 0.0006
6	5-methyl-1,2,6-heptatriene	0.69	1.00	2.46		0.042 ± 0.003
7	3-methylene-1,5-heptadiene	0.915	1.16	2.91	1.59	0.011 ± 0.001
8	*trans*-1,2,6-octatriene					0.150 ± 0.002

Scheme I
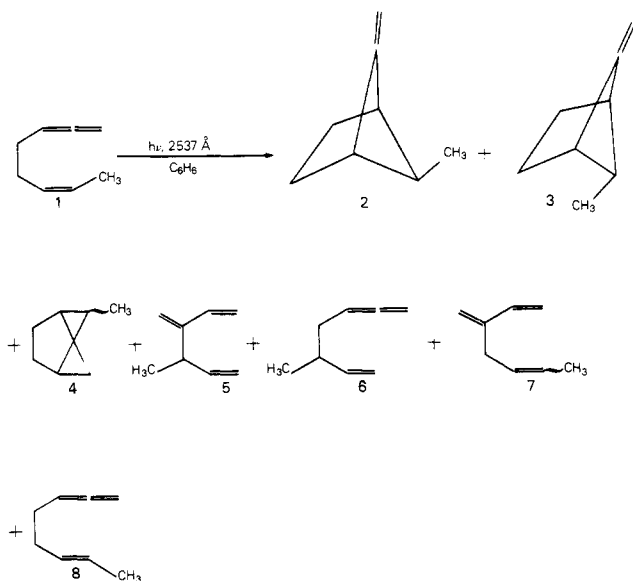
Scheme II

Results and Discussion

The gas-phase benzene-sensitized photolysis of *cis*-1,2,6-octatriene (1) led to the formation of trans isomer 8 and six other primary products (2–7, Scheme I). A percentage of product distribution of products 2–7 vs. time (duration of photolysis) showed a linear relation. The quantum yields of products which are independent of percent conversions are shown in Table I. Mass spectra of all products showed a parent peak at m/e 108. When 1 was photolyzed to higher conversion, 2, 3, and 4 became the major products in the photolysate and a large amount of polymer formation was observed. The photolysis of 1 without benzene gave none of these products. The pyrolysis of 1 at 200 °C for 1.5 h gave only one major product which was identified as 5 from its mass and NMR spectra. The yield of 5 was 53%. Compound 1 was photolyzed under conditions identical with the actinometric measurements with the same amount of benzene (17 mmHg).[5]

The major primary reaction appears to be a cis–trans isomerization. The photosensitized cis–trans isomerization of olefins and conjugated dienes has been studied in detail.[6-11] It is generally accepted that triplet states of ac-

ceptors are involved in the process of cis–trans isomerization,[10] and a "diradical pathway" was suggested as a reasonable mechanism for this reaction.[11] By analogy to the olefin and conjugated diene cases, a triplet-state involvement will account for the cis–trans isomerization of 1. The observed quantum yield of 8 was 0.15 or about one-half of the quantum yield of cis–trans isomerization of isolated olefins such as 2-butene and 2-pentene (Φ = 0.26–0.28). This may be explained by intramolecular energy transfer or a difference in the excited-state decay modes of 8.

A reasonable reaction pathway from 1 to 2 and 3 proceeds in a stepwise manner through an α–δ diradical intermediate. The intermediates 9 and 10 will close the ring to form 2 and 3, respectively,[11,12] or open the ring to form cis- or trans-1,2,6-octatriene (Scheme II). The difference in quantum yield of 2 and 3 shows that the latter reaction is more efficient than the former, although compound 3 probably is less stable thermodynamically because of steric interaction between the endo-methyl group and hydrogen atoms at the C-2 and C-3 positions.

Although an attempt to trap the cyclopropylidene-carbene was not successful, a reaction pathway for the conversion of 1 to 2-methyltricyclo[4.1.0^{1,3}]heptane (4) may
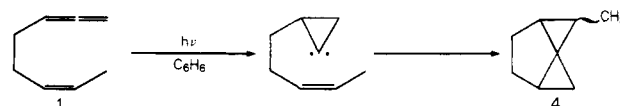
reasonably be explained by the closure of the allenic moiety in 1 to a cyclopropylidene, followed by carbene addition to the internal carbon–carbon double bond. An alternate mechanism to 4 is through diradical intermediates 9 and 10, but this requires rather complicated bond breaking and

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<div style="text-align:center">Table II</div>

compd	IR,[a] cm^{-1}
cis-1,2,6-octatriene	1660 (m), 1405 (m), ~700 (m)
cis-2-hexene	1660 (m), 1405 (m), ~700 (m)
trans-2-hexene	~1660 (w), ~965 (s)

[a] s, strong; m, medium; w, weak.

forming processes. The reverse thermal reaction from tricyclo[4.1.0.0^{1,3}]heptane to the mixture of 1,2,6-heptatriene and 3-methylene-1,5-hexadiene has been reported by Frey et al.[14]

The formation of 5-methyl-1,2,6-heptatriene (6) and 3-methylene-1,5-heptadiene (7) can be explained either by a "free-radical" pathway or by two independent modes of 1,3-sigmatropic shifts in 1. Although an excited triplet state could be responsible for both the "free-radical" and 1,3-sigmatropic rearrangements, the evidence of polymer formation seems to support the "free-radical" pathway more. However, the possibility of the latter cannot be completely eliminated.

Isomerization of 1 to 5 appears to be one of the minor processes in this reaction. Various reaction mechanisms for this process can be considered, including a 3,3-sigmatropic shift (the Cope rearrangement); however, further information is necessary for the accurate prediction of this reaction mechanism.

Experimental Section

Preparative gas chromatography was carried out on an Aerograph Model A-90 chromatograph. The aluminum columns used were as follows: A, 15% TCEP on Chromosorb W (100–120 mesh), $^3/_8$ in. o.d.; B, 20% TCEP on Chromosorb P (80–100 mesh), 0.25 in. o.d.; C, 15% Carbowax 20M on Chromosorb W (100–120 mesh), 0.25 in. o.d.

Analytical determinations were carried out on a Varian Aerograph Model 1200HY-F/III flame-ionization instrument, which was equipped with a gas sample valve.

NMR spectra were taken on a Varian A-60 spectrophotometer in carbon tetrachloride, using Me$_4$Si as an internal standard. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6D spectrometer by using a gas chromatograph–mass spectrometer combination.

Materials. 1,2,6-Octatriene (*cis*-1, 42%; *trans*-8, 6%) was prepared by treating 4,5-hexadienal with ethylidenetriphenylphosphorane at 0 °C.[15] 4,5-Hexadienal was prepared by pyrolyzing hexen-5-yn-3-ol which was synthesized by the method of Viola and MacMillan.[16] Cis and trans isomers were separated by preparative GLC, using columns A and B at 40 °C. Compounds 1 and 8 were identified by comparison of their IR (Table II) and NMR spectra (Figures 1 and 2) with those of model compounds, *cis*- and *trans*-2-hexene. Compound 1 was further purified (~99.7 to 99.9%) on preparative column B at 40 °C for the purpose of photolyses.

Preparation of 2-Methyltricyclo[4.1.0.0^{1,3}]heptane (4). The low-temperature (−20 °C) reaction of 1,5-heptadiene and bromoform with potassium *tert*-butoxide produced a colorless liquid of 1,1-dibromo-2-methyl-3-(but-3-enyl)cyclopropane (11)[17] by vacuum distilling the reaction mixture. Compound 11 was reacted with methyllithium in ether at −70 °C,[17] the reaction mixture was hydrolyzed, and then the ether layer was separated and dried over magnesium sulfate. The yield of 4 was 35%. All reactions were carried out under nitrogen. The pure sample of 4 was isolated by preparative GLC on a column C at 42 °C. The NMR spectrum of 4 showed absorptions at δ 1.88 (8 H, m) and 1.12 (4 H, d + m, CH$_3$ and tertiary H).

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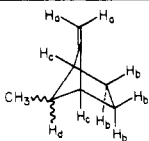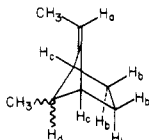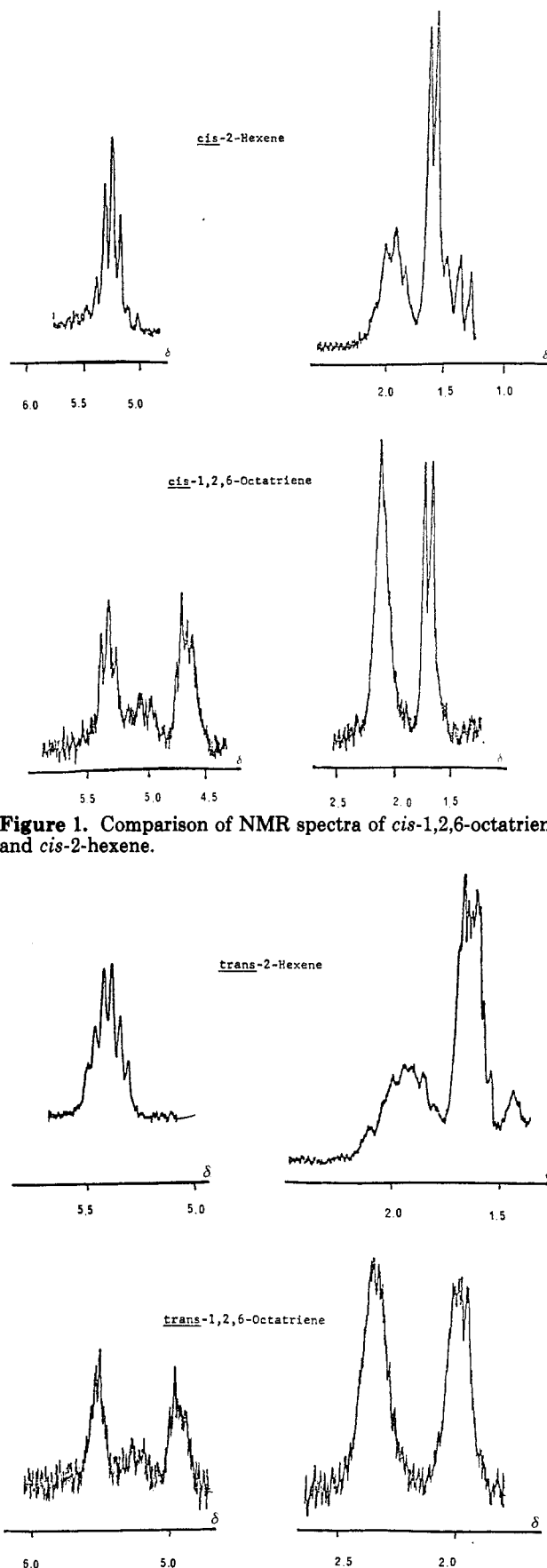(17) W. R. Moore and H. R. Ward, *J. Org. Chem.*, 27, 4179 (1962).

Figure 1. Comparison of NMR spectra of *cis*-1,2,6-octatriene and *cis*-2-hexene.

Figure 2. Comparison of NMR spectra of *trans*-1,2,6-octatriene and *trans*-2-hexene.

Preparation of 5-Methyl-1,2,6-heptatriene (6). 1,1-Dibromo-2-methyl-3-(but-3-enyl)cyclopropane (11) was reacted with methyllithium at −30 °C under nitrogen. The yield of 6 was

Table III

compd	NMR, δ

| 2 (exo) | 4.43 (s, H$_a$), 1.64 (s~d, H$_b$), 2.42 (~d, H$_c$), 1.34^a (~q, H$_d$), 1.32^a (d, CH$_3$) |
| 3 (endo) | 4.24 (s, H$_a$), 1.53 (s~d, H$_b$), 0.73 (d, CH$_3$), 2.55 (q, H$_c$), 1.09 (q, H$_d$) |

5-methyl-6-ethylidene-bicyclo[2.1.1]hexene[18]	
exo	4.85 (q, H$_a$), 2.0–1.6 (4 H$_b$ + H$_d$), 2.60–2.35 (H$_c$), 1.52 and 1.05 (2 d, 2 CH$_3$)
endo	4.65 (q, H$_a$), 2.3–1.5 (4 H$_b$ + H$_d$), 2.75–2.5 (H$_c$), 1.50 and 0.72 (2d, 2 CH$_3$)

^{a} Overlap.

~70%. Compound **6** was purified by preparative GLC on the column B at 40 °C. The NMR spectrum showed absorption at δ 5.8–4.6 (m, 6 H), 2.1 (m, 3 H), and 1.0 (d, CH$_3$) and the terminal vinyl absorptions were extremely similar to those of 4-methyl-1-pentene and 4-methyl-1-hexene.

Photolyses. The benzene-sensitized photolyses of **1** were carried out in a quartz cell (79.5 cm) with Vycor windows. The low-pressure mercury lamp (a helical Hanovia 69A-1, 7.56 × 13.86 cm) was positioned so as to pass light to the cell through a Vycor window at maximum efficiency. With this system, it was not necessary to remove the cell from the vacuum line during photolyses. Nitrogen gas was passed over the cell to remove ozone as formed and for cooling. In a typical photolysis, 5 μL of **1** and 5.5 μL of benzene (99.9% pure) were mixed. After irradiation the mixture was analyzed by GLC on the following aluminum columns ($^1/_8$ in. o.d.): D, 15% TCEP on Chromosorb P (80–100 mesh); E, 15% TEG on Chromosorb P (80–100 mesh); F, DU-RAPAK (*n*-octane) on Porasil C (120–150 mesh); G, 10% Carbowax 20M on Chromosorb W (100–120 mesh).

Identification of **2** and **3** was largely based on their mass and NMR spectra. The NMR spectra are also in good agreement with those of model compounds such as 5-methylenebicyclo[2.1.1]-hexane[18] and *exo*- and *endo*-5-methyl-6-ethylidenebicyclo-[2.1.1]hexane[18] (Table III). Compounds **4** and **6** were identified on the basis of identity of GLC retention times (on three columns) (Table I) with those of independently synthesized samples. Identification of **5** was based on the identity of GLC retention times with those of an authentic sample isolated from the pyrolysate of **1**. Compound **7** was identified on the basis of the identity of GLC retention times (on the four columns, Table I) with those of the Cope rearrangement product which was obtained by the short-contact pyrolysis of **6**.

Pyrolysis. The pyrolyses of 1-hexen-5-yn-3-ol were carried out in a cylindrical Pyrex tube (3.0 × 10.2 cm) in which nitrogen gas was passed. Pyrex brand glass wool or helices (i.d. $^1/_8$ in.) was used as a packing agent. Temperatures were measured by a copper–constantan thermocouple. All analyses of pyrolysate were made by GLC using column D at 90 °C. Pyrolysates were analyzed by GLC, using column C at 60 °C and column D at 40 °C.

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Syntheses of Protoporphyrin IX Analogues Bearing Acetic and Butyric Side Chains

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Protoheme (**1**) is the prosthetic group in myoglobins, hemoglobins, and several other types of heme protein.[1] X-ray studies have shown[2] that the vinyl-bearing rings are the most deeply embedded in the protein pockets of myoglobin and hemoglobin and that the 6 and 7 propionic acid groups on rings C and D are consequently pointing to the outside of the protein cleft. It seems likely that the length of the 6 and 7 substituent side chains might affect physiological action because if the carboxylates are to be situated at the polar edge of the heme pocket then the number of connecting carbons will affect the depth of the heme within the cleft, and therefore the proximity of the iron-binding histidine imidazoles to the center of the heme.

In this paper we describe efficient syntheses of protoporphyrin IX analogues bearing 6 and 7 butyric side chains (i.e., one carbon lengthened over the natural heme ligand) and 6 and 7 acetic side chains (i.e., one carbon shortened). These compounds are required for X-ray structural investigations of heme proteins and reconstituted hemes and for studies on the oxygen and carbon binding characteristics of the resulting novel heme proteins. We also describe a modification of the 6,7-dibutyric synthesis to give the 6,7-di-*n*-propyl analogue which was required for clarification of certain problems associated with self-aggregation of magnesium(II) and zinc(II) porphyrins in solution.[3,4]

Synthesis of the Diacetic Porphyrin, 6,7-Bis-[(methoxycarbonyl)methyl]-1,3,5,8-tetramethyl-2,4-divinylporphyrin (2). The porphyrin **2** was synthesized directly from monopyrroles via the a,c-biladiene route.[5] Though approaches by degradation of commercial protohemin (**3**) were considered, we felt that the sensitive vinyl groups in **3** might cause undue problems; moreover, in the

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