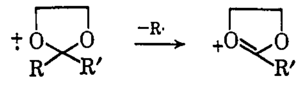


III, R = alkyl; R′ = H e, R′ = H
IV, R = alkyl; R′ = CH_3 f, R′ = CH_3

and f in the case of ketals) produced by elimination of a series of alkyl groups in each case it may be that one is witnessing here a comparison of radical stabilities. In contrast our results with ketones, Schiff bases, and ethers differ in that they are comparing the relative stabilities of the carbonium ions formed. When the positive charge is delocalized over only one heteroatom (as in ketones, Schiff bases, and ethers) carbonium ion stabilities may be more important than when the positive charge is distributed over two heteroatoms[8] as in acetals and ketals.

Experimental Section[14]

Ketones. All ketones were either obtained commercially and purified by vpc or prepared from commercially available alcohols by Jones' oxidation.[16]

Schiff Bases. The method of synthesis of these compounds has previously been described.[9] The mass spectra were determined on samples immediately after purification by vpc.

Ethers. All unbranched ethers were prepared according to the procedure described earlier.[12] Isopropyl *n*-pentyl ether and isopropyl *n*-hexyl ether have been described.[10] Isopropyl *sec*-butyl ether was prepared by heating 0.1-mole quantities of 2-propanol, *sec*-butyl alcohol, and 98% sulfuric acid for 30 min, on the steam bath. Subsequent dilution with water and ether extraction provided a mixture of products from which isopropyl *sec*-butyl ether was separated by vpc.

---

(14) All low-resolution mass spectra were determined with an Atlas CH-4 mass spectrometer using the TO-4 ion source (temperature 200°) and a gas cartridge. All low-voltage spectra correspond to nominal electron voltage values and were recorded with zero potential on the draw-out plates of the gas cartridge. Metastable peaks were observed with the aid of a logarithmic transfer recorder.[15] Where necessary isobaric ions were separated either by running at "medium resolution" (approximately 4000–5000) or at high resolution (15,000, 10% valley definition) by Mr. R. G. Ross using an A.E.I. MS-9 instrument.

(15) R. T. Aplin, H. Budzikiewicz, H. S. Horn, and J. Lederberg, *Anal. Chem.*, **37**, 776 (1965).

(16) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Magnetic Circular Dichroism Studies. III.[1] Investigation of Some Optically Active Chlorins[2]

Bernard Briat,[3] David A. Schooley, Ruth Records, Edward Bunnenberg, and Carl Djerassi

Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received May 20, 1967*

Abstract: The magnetic circular dichroism (MCD) of optically active molecules has been investigated for a number of chlorophyll-like derivatives (metal-free substituted chlorins). Their absorption, circular dichroism, and magnetic circular dichroism spectra have been recorded through the spectral range 700–240 nm and the results indicate that MCD is by far the most sensitive of the three spectroscopic techniques to detect the influence of various external substituents on the chlorin framework. Some theoretical comments and suggestions for further investigations are also made.

During the past decade optical rotatory dispersion (ORD) and circular dichroism (CD) have been widely applied to many problems in the structure elucidation of optically active materials.[4] This activity in turn has stimulated a recent resurgence of interest in the superficially similar phenomenon of magnetically induced optical activity (the so-called Faraday effect). This effect may be produced in all substances by a magnetic field coincident with the direction of propagation of a beam of linearly polarized light. As with natural optical activity, one observes "anomalous" magnetooptical rotatory dispersion (MORD) as well as magnetic circular dichroism (MCD) when measurements are made through absorption bands. It follows from the above definitions that MORD and MCD can be measured with an ordinary spectropolarimeter, provided that a magnetic field is introduced in the sample compartment. A number of devices have now become commercially available or have been described in the literature.[5–7] Moreover, as the observed phenomena are proportional to the magnitude of the magnetic field, the recent use of superconducting magnets has greatly increased the possibilities in this area of research. Since the data are usually easier extracted from MCD rather than MORD measurements, main emphasis has been given to the former in our laboratory.

Faraday effect measurements have been motivated by the potentiality of this technique as a spectroscopic tool[8] as well as a means of empirically obtaining an-

---

(1) Paper II: D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1377 (1966).

(2) We are indebted to the National Science Foundation (Grant No. GP-4304) and to the National Institutes of Health (Grants No. GM-12173 and CA 07195) for financial aid.

(3) Recipient of a NATO postdoctoral fellowship (1966–1967) and a Fulbright travel grant while on leave from the Laboratoire d'Optique Physique, E.S.P.C.I., Paris 5^e, France.

(4) (a) C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960; (b) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965; (c) L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press Inc., New York, N. Y., 1965.

(5) M. Billardon and J. Badoz, *Compt. Rend.*, **263**, 139 (1966).

(6) J. G. Forsythe, R. Kieselbach, and V. E. Shashoua, *Appl. Opt.*, **6**, 699 (1967).

(7) J. G. Foss, *Anal. Chem.*, **35**, 1329 (1963).

alytical or structural information regarding optically inactive or active substances.[9]

MORD and MCD have already given rise to a large number of applications. These include the investigation of individual absorption bands in solution[10,11] or in crystals,[12–14] qualitative and quantitative analysis of rare earth mixtures,[15] kinetic studies of biological samples,[16] and different correlations for numerous organic molecules.[17,18] An excellent review of the theory and applications of this technique has been published[8] and a development of the theory at an intermediate level has recently been given by Dratz.[19]

We wish to report here our MCD investigations through the visible and ultraviolet absorption bands for a series of optically active chlorophyll-like derivatives, namely, substituted, metal-free chlorins. Some experimental[16,19] and theoretical[11a] work has already been done on the Faraday effect of the closely related porphyrins. However, with a few exceptions[16] most of the studies previously published have been concerned with *optically inactive* materials. It seemed of interest to us to apply the same technique to *optically active* samples, in order to effect a direct comparison of MCD and CD results and to explore at the same time the analytical utility of MCD. Furthermore, the use of a high magnetic field has allowed us to extend the measurements to previously unexplored spectral regions[16,19] down to 240 nm. Our results show that substituted chlorins represent a good series for an approach to the theoretical study of the influence of external substituents on MCD spectra.

General Considerations

Characteristics of Absorption Spectra. Owing to the great biological interest of porphyrins, a large number of papers have been devoted to the study of molecules containing that skeleton. Their basic chemical properties are explained in terms of an 18-membered framework with strongly delocalized π electrons which provide the aromatic character. These π electrons are also responsible for the absorption of visible and ultraviolet light which is of fundamental importance in photosynthesis. Therefore it may be expected that physical and especially spectroscopic methods would provide information of great value about these molecules.[20]

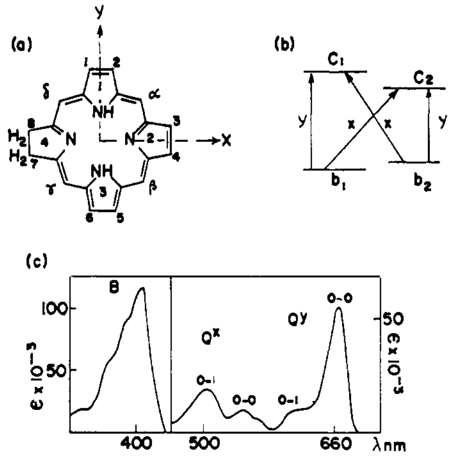


Figure 1. Characteristics of the absorption of chlorins: (a) formula and convention used for the denomination of the axis; (b) four-orbital model; (c) B and Q bands with vibrational components.

Chlorin-free bases are derived from metal porphyrins by protonation of two oppoite nitrogens and reduction of a double bond. The characteristics of the absorption spectra of these compounds may be explained simply by the use of a four-orbital model.[21,22] The four visible bands are ascribed to $\pi \rightarrow \pi^*$ transitions, polarized in the molecular plane and arising from the promotion of an electron from the two highest filled orbitals (b_1,b_2) to the two lowest empty orbitals (c_1,c_2). These four bands are composed of two pairs of bands which, in a metal porphyrin with planar nucleus and uniform substitution around the framework, would be superimposed. In metal-free porphyrins, neither b_1 and b_2 nor c_1 and c_2 have the same energy. In other words, the degeneracy is now lifted, which results in four bands, Q^x, Q^y, B^x, and B^y, although the B states remain nearly degenerate (B^x and B^y are sometimes unresolved and constitute the Soret band). These bands are associated with an electronic displacement toward the periphery, either along (x polarization) or perpendicular to the x axis.

Following Seely[23] and Platt,[24] this model also applies to the metal-free chlorins by treating reduction as a perturbation. The situation in this particular case is described in Figure 1, which illustrates the qualitative features of the absorption spectra. The notations are taken from the literature[22a]—the double bond of the fourth pyrrole ring is reduced and the x axis is chosen perpendicular to this saturated bond. Under these conditions, the band of lower energy is y polarized.[22a,25] Many absorption components are actually observed in the Q region; they are assigned to vibrations of the electronic states and are referred as $0 \rightarrow 0$, $0 \rightarrow 1$ bands (*e.g.*, $Q_0{}^y$, $Q_1{}^y$). The bands located on the blue side of the Soret band have not yet been completely described[26]

---

(8) A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, **17**, 399 (1966).

(9) D. A. Schooley, E. Bunnenberg, and C. Djerassi, *Proc. Natl. Acad. Sci. U. S.*, **53**, 519 (1965).

(10) (a) B. Briat, *Compt. Rend.*, **259**, 2408 (1964); **260**, 853, 3355 (1965); (b) B. Briat, Ph.D. Thesis, University of Paris, 1966.

(11) (a) P. J. Stephens, W. Suëtaka, and P. N. Schatz, *J. Chem. Phys.*, **44**, 4592 (1966); (b) P. N. Schatz, A. J. McCaffery, W. Suëtaka, G. N. Henning, A. B. Ritchie, and P. J. Stephens, *ibid.*, **45**, 722 (1966).

(12) Y. R. Shen and N. Bloembergen, *Phys. Rev.*, **133**, A515 (1964); Y. R. Shen, *ibid.*, **134**, A661 (1964).

(13) R. G. Denning, *J. Chem. Phys.*, **45**, 1307 (1966).

(14) J. Margerie, Proceedings of the Zeeman Centennial Conference, Amsterdam, Sept 1965; *Physica*, **33**, 238 (1967).

(15) B. Briat, M. Billardon, J. Badoz, and J. Loriers, *Anal. Chim. Acta*, **34**, 465 (1966).

(16) (a) V. E. Shashoua, *J. Am. Chem. Soc.*, **87**, 4044 (1965); (b) *Arch. Biochem. Biophys.*, **111**, 550 (1965).

(17) (a) J. G. Foss and M. E. McCarville, *J. Chem. Phys.*, **44**, 4350 (1966); (b) *J. Am. Chem. Soc.*, **89**, 30 (1967).

(18) J. M. Thorne, Ph.D. Thesis, University of California, Berkeley, 1966.

(19) E. A. Dratz, Ph.D. Thesis, University of California, Berkeley, 1966.

(20) G. P. Gurinovitch, A. N. Sevchenko, and K. N. Solovev, *Soviet Phys. Usp.*, **6**, 67 (1963).

(21) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(22) See, for example, (a) M. Gouterman, *J. Mol. Spectry.*, **6**, 138 (1961); (b) C. Weiss, H. Kobayashi, and M. Gouterman, *ibid.*, **16**, 415 (1965); (c) M. Gouterman and G. H. Wagniere, *ibid.*, **11**, 108 (1963).

(23) G. R. Seely, *J. Chem. Phys.*, **27**, 125 (1957).

(24) J. R. Platt, "Radiation Biology," Vol. 3, A. Hollaender, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 2.

(25) B. G. Anex and R. S. Umans, *J. Am. Chem. Soc.*, **86**, 5026 (1964).

(26) W. S. Caughley, R. M. Deal, C. Weiss, and M. Gouterman, *J. Mol. Spectry.*, **16**, 451 (1965).

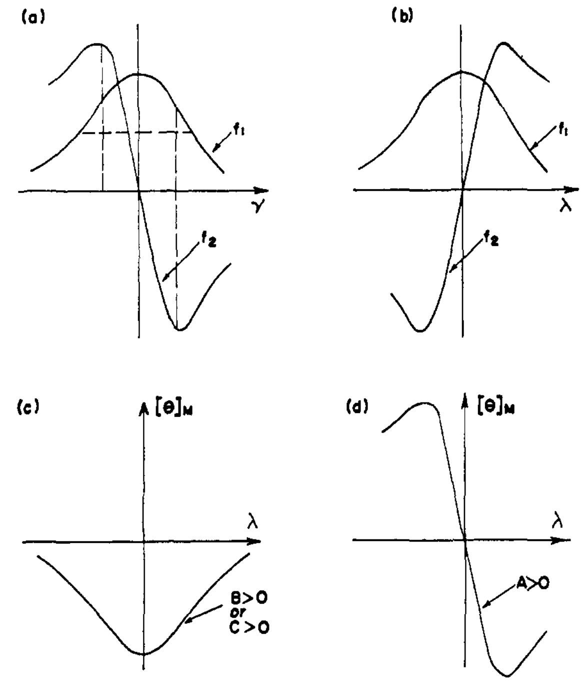


Figure 2. Nomenclature used in the present MCD work: (a and b) dispersion of f_1 and f_2 functions *vs.* the frequency ν or the wavelength λ, respectively; (c) dispersion term corresponding to a positive B or C value; (d) dispersion term for a positive A value.

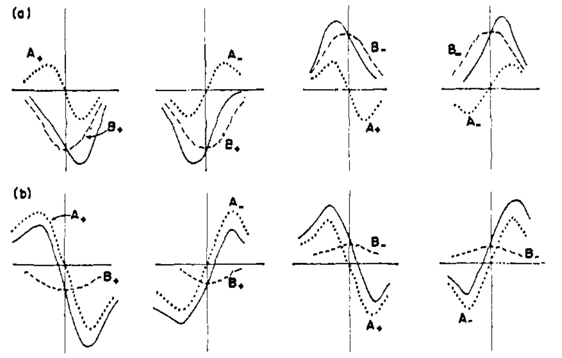


Figure 3. Shift in the position of maxima or zero ellipticity value for $[\theta]_M = f(\lambda)$. The wavelength axis is horizontal (λ increasing to the right): (a) B term dominant ($A/B < \Gamma/4$); (b) A term dominant ($A/B > \Gamma/4$). The solid curve represents the summation of the A (· · · ·) and B (– – – –) dispersion terms.

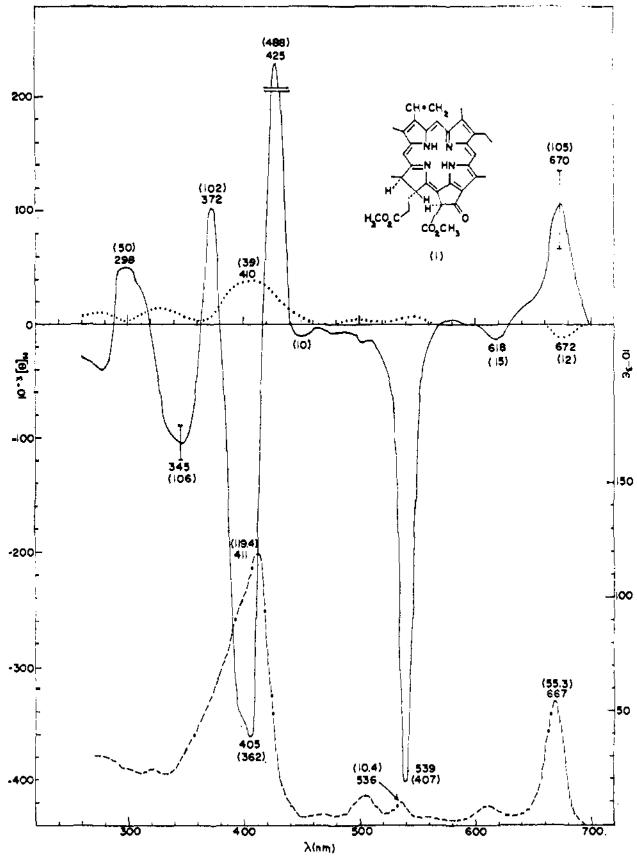


Figure 4. Absorption (– – – –), circular dichroism (· · · ·), and magnetic circular dichroism (———) of methylpheophorbide a (**1**). MCD $[\theta]_M$ is reported for a 41.7-kgauss magnetic field.

and they will therefore not be included in our discussion.

Nomenclature of MCD Spectra. A certain misunderstanding may result in using different sets of conventions to describe the observed phenomena; consequently we describe briefly the nomenclature used throughout our work.

The externally applied magnetic field is directed parallel and in the sense of the direction of propagation of the light; the ellipticity θ of the previously linearly polarized light is then measured with the same sign convention as natural optical circular dichroism (this convention is unfortunately different from that used in early Faraday effect work).

Following Stephens, *et al.*,[11b] the molar ellipticity ($[\theta]_M$ in deg gauss^{-1} cm^2 mole^{-1} if not expressly specified) may be expressed as $[\theta]_M = -21.3458\{f_1A + f_2(B + C/kT)\}$, where f_1 and f_2 are functions of the frequency ν of the incident light. Assuming now a damped oscillator model for the absorption band shape, one has

$$f_1 = \frac{\nu^3\Gamma}{[\nu_0^2 - \nu^2]^2 + \nu^2\Gamma^2}$$

$$f_2 = \frac{4\nu_0\nu^3(\nu_0^2 - \nu^2)\Gamma}{h[(\nu_0^2 - \nu^2)^2 + \nu^2\Gamma^2]^2}$$

where ν stands for the frequency of the light, ν_0 for the frequency of maximum absorption, and Γ for the width at half-maximum absorption; ν_0, ν, and Γ are expressed in cm^{-1} and h is the Planck constant.

Qualitative pictures are given in Figure 2 for the frequency and wavelength dependence of functions f_1 and f_2, respectively. It then follows from the definition of molar magnetic ellipticity that a *positive A value* will give the experimental curve shown in Figure 2d, whereas a *positive B or C value* will lead to the dispersion curve reported in Figure 2c. Negative values, of course, give rise to mirror image curves with respect to the wavelength axis. It should be noted, therefore, that a *positive A value* leads to a so-called *negative* Cotton effect if we retain the conventions used in natural optical activity (ORD or CD).

As shown elsewhere,[11a] experimental curves result in the more general case from a mixing of two dispersion terms; therefore, they have a different shape or shift to longer or shorter wavelengths according to the relative signs and values of A, B, C/kT, and Γ.[10b] This is illustrated in Figure 3 where the subscript sign on the right of the capital letters refers to the sign of the corresponding A and B values; the C term has been ignored

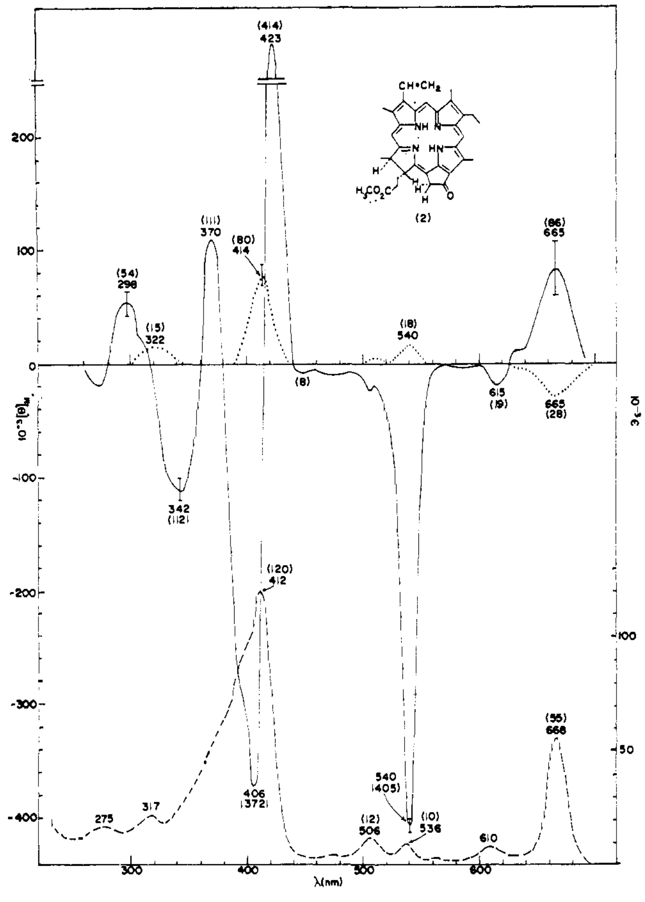


Figure 5. Absorption (– – – –), circular dichroism (· · · ·), and magnetic circular dichroism (———) of pyromethylpheophorbide a (**2**).

in this instance, since it is absent in the compounds under consideration.

Experimental Section

The instrumentation involved in our MCD measurements has already been described[1] and will only be discussed briefly here. Throughout this work we used a Japan Spectroscopic Co. spectropolarimeter (Durrum-JASCO Model ORD-UV-5) modified to allow CD measurements. The magnetic field was provided by a superconducting magnet built by Lockheed Palo Alto Research Laboratories (Model SSCM 102). Absorption spectra were measured on a Cary Model 14 spectrophotometer and all spectra (absorption, CD, and MCD) were run in dioxane solution at concentrations such that the optical density was less than 2.

Although the maximum field obtainable is 50 kgauss, all the experiments reported here were performed with a 41.7-kgauss field. In Figures 4–9 are reported absorption, CD, and MCD dispersion curves of the various chlorins. MCD was determined by the difference in the recorded specific signal in the presence or absence of the magnetic field. The error in the ellipticity values depends upon the concentration used, the spectral range, and a number of features of the instrumentation (*e.g.*, spectral source, sensitivity of the phototube, and geometric factors). This error has been estimated in different regions of the spectra and reported with a vertical line. From a general point of view, owing to possible shifts in the baseline position or to inaccuracy in the recorded wavelengths, the peak to peak values of MCD are much more reliable than the absolute positive and negative values. Moreover, results for the band at higher wavelength (*ca.* 660 nm) are less accurate and they provide an order of magnitude only, which however is of interest for our purpose.

Since the relative merit of CD and MCD measurements for this series of chlorins will be compared, all molar ellipticities (for both CD and MCD) have been expressed with the same units, *i.e.*, deg mole^{-1} cm^3. In other words, the *MCD values are reported for a 41.7-kgauss field* contrary to our previous standardization of

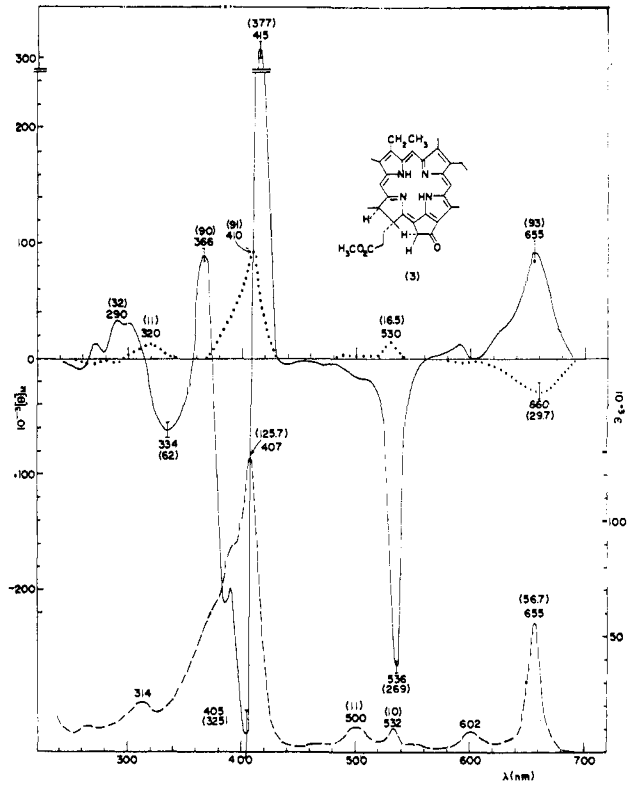


Figure 6. Absorption (– – – –), circular dichroism (· · · ·), and magnetic circular dichroism (———) of *meso*-pyromethylpheophorbide a (**3**).

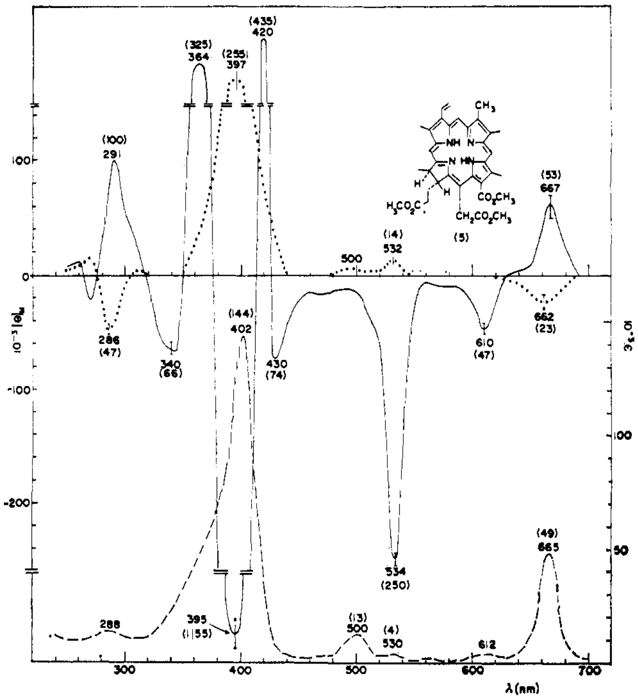


Figure 7. Absorption (– – – –), circular dichroism (· · · ·), and magnetic circular dichroism (———) of chlorin-e$_6$ trimethyl ester (**5**).

values for 10 kgauss.[1,19] The synthetic samples were kindly supplied by Professor H. H. Inhoffen, in whose laboratory their optical rotatory dispersion and some circular dichroism spectra had recently been measured.[27]

---

[27] H. Wolf, *Ann.*, **695**, 98 (1966).

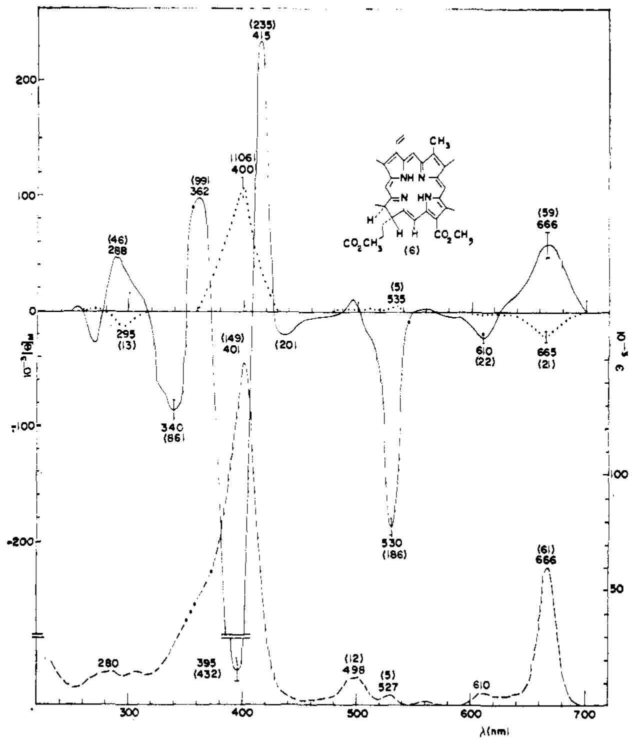


Figure 8. Absorption (– – – –), circular dichroism (· · · ·), and magnetic circular dichroism (———) of rhodochlorin dimethyl ester (**6**).

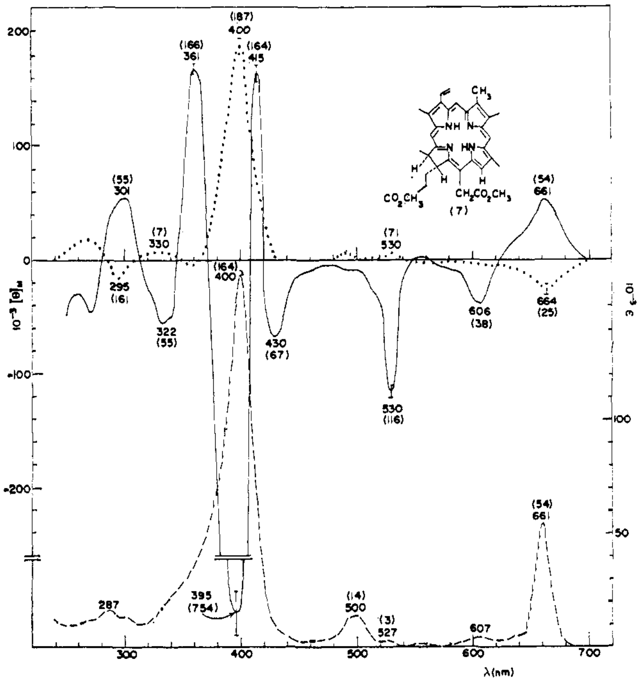
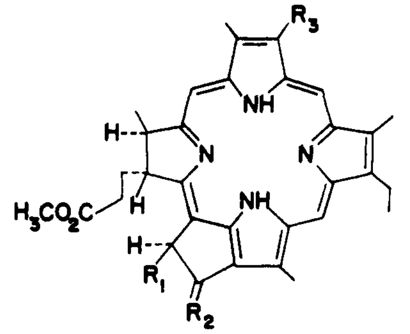
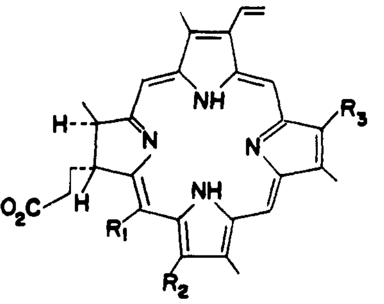


Figure 9. Absorption (– – – –), circular dichroism (· · · ·), and magnetic circular dichroism (———) of isochlorin-e_5 dimethyl ester (**7**).

Analytical Results

The structure of the compounds, the corresponding number (identical with that used in Wolf's paper[27]), and the nature of the substituents are shown in Table I; all but **4** were examined by MCD. In terms of their basic framework, they may be classified into two series, according to the presence (in **1**, **2**, **3**) or absence (in **5**, **6**, **7**) of a fifth additional ring; this leads to important spectral consequences as will be seen later.

Table I. Structure of Chlorins

No.	R_1	R_2	R_3	Compound
				
1	CO_2CH_3	O	$CH{=}CH_2$	Methylpheophorbide a
2	H	O	$CH{=}CH_2$	Pyromethylpheophorbide a
3	H	O	CH_2CH_3	*meso*-Pyromethylpheophorbide a
4	H	H_2	CH_2CH_3	9-Desoxo-*meso*-pyromethylpheophorbide a
				
5	$CH_2CO_2CH_3$	CO_2CH_3	CH_3	Chlorin-e_6 trimethyl ester
6	H	CO_2CH_3	CH_3	Rhodochlorin dimethyl ester
7	$CH_2CO_2CH_3$	H	CH_3	Isochlorin-e_5 dimethyl ester

A. **Absorption.** Before dealing in more detail with CD and MCD, it is first necessary to consider the measured absorption spectra of these compounds. They all exhibit the characteristic pattern shown in Figure 1: $Q_0{}^y$ around 660 nm, $Q_0{}^x$ around 530 nm, and B or Soret band in the 400-nm range; the maximum molar extinction coefficient values are reported in Table II. As already reported,[28] the two B components have a tendency to split, this becoming more obvious when there is a considerable lowering of the symmetry, as in samples **1**, **2**, **3** (Figures 4–6), as compared to samples **5**, **6**, **7** (Figures 7–9). Moreover, the Q bands are widely split and the $Q_0{}^y$ band has a large intensity.[22a] On the other hand, a comparison of the data for the $Q_0{}^x$ and $Q_1{}^x$ shows that the intensity of the forbidden $Q_0{}^x$ band depends much more on the nature of substituents (and therefore symmetry considerations) than that of the allowed $Q_1{}^x$ band. Both bands are of about the same intensity for compounds **1**, **2**, **3** (larger perturbation due to the additional ring) whereas the $Q_1{}^x$ band is more intense than $Q_0{}^x$ for compounds **5**, **6**, **7**.

---

(28) M. Gouterman and G. H. Wagnière, *J. Mol. Spectry.*, **11**, 108 (1963).

Table II. Absorption, Circular Dichroism, and Magnetic Circular Dichroism Data[a]

	Substituents			Absorption, $10^{-3}\epsilon_m$				MCD, $10^{-3}[\theta]_M$			CD, $10^{-3}[\theta]_M$		
Compd	R_1	R_2	R_3	Q_0^y	Q_0^x	Q_1^x	B	Q_0^y	Q_0^x	B	Q_0^y	Q_0^x	B
1	CO_2CH_3	O	$CH{=}CH_2$	55.3	10.4	13	118.4	+105	−407	+488 850 −362	−13 (−8)	+6.2 (+4)	39 (+41.5)
2	H	O	$CH{=}CH_2$	55	10	12	120	+86	−405	+414 785 −372	−28 (−28)	+18 (+18)	+80 (+80)
3	H	O	CH_2CH_3	56.7	10	11	125.7	+93	−269	+377 702 −325	−30 (−26)	+16.5 (+18)	+9 (+93)
4	H	H_2	CH_2CH_3								(−44)		(107.5)
5	$CH_2CO_2CH_3$	CO_2CH_3	CH_3	49	4	13	144	+53	−250	+435 1590 −1115	−23 (−30)	+13.5 (+14)	+255 (+220)
6	H	CO_2CH_3	CH_3	61	5	12	148.8	+59	−186	+235 667 −432	−21 (−30)	+4.7 (+4)	+106 (74.6)
7	$CH_2CO_2CH_3$	H_2	CH_3	54	3	14	164.2	+54	−116	+164 918 −754	−25 (−44)	+7 (+6)	+187 (+191)

[a] The actual positions (in nm) of the various absorption, MCD, and CD bands are marked in Figures 4–9 and hence are not repeated in this table. MCD $[\theta]_M$ values are related to a 41.7-kgauss magnetic field and are expressed in deg mole^{-1} cm^3.

In addition, the intensity of the Soret band is increased by about 30% from one group to the other.

However, despite these few correlations between structure and spectral properties, it appears that absorption spectroscopy, at least in this particular series, is not a very sensitive tool for differentiating the effects of substituents on an empirical basis. No satisfactory theoretical explanation has been offered for this lack of sensitivity, which should be contrasted with the very interesting results obtained in treating the same problem in porphyrins.[29]

B. Circular Dichroism. Natural circular dichroism provides better results in that respect, as already emphasized by Wolf.[27] Our maximum $[\theta]_M$ values are reported in Table II for the two Q_0 and the B bands. We have also included the published[27] ORD Cotton effect amplitude values of the corresponding bands by citing them in parentheses in the last three columns. The agreement between the two series of measurements is good if one considers that the two values should be approximately equal (the natural rotation and the corresponding ellipticity are here expressed in terms of the same units). The following conclusions can be reached. (1) Cotton effects are of opposite signs for the Q_0^y and Q_0^x bands (negative and positive, respectively). (2) *Maximum values for the B band are particularly sensitive to the nature of the substituent on the ring and differ greatly from the first to the second group of compounds* ($10^{-3}[\theta]_M$ is 39 for compound **1** and 255 for compound **5**). (3) The larger Cotton effect is always observed for the forbidden absorption transition (see, for example, the maximum values $[\theta]_M$ in Figure 7 for the Q_0^x (532 nm) and Q_1^x (500 nm) components). (4) When present (compare, for example, Figure 5 with Figure 4), the Cotton effect corresponding to the Q_1^y vibrational band (*ca.* 595 nm in Figure 5) only appears as a shoulder.

With the exception of compound **3** (Figure 5) it is not obvious whether the partly resolved absorption and ORD[27] for the B band (400-nm region) in the first group leads to a dissymmetric CD curve. It should be said, however, that this expected dissymetry is beyond the limit of the experimental error.

Of particular interest is compound **5** which gives rise to the greatest CD $[\theta]_M$ value through the Soret (B) band probably due to interaction of the bulky substituents R_1 and R_2. This is likely to be explained in terms of an important perturbation of the wave functions of the electronic states involved in the transitions considered.

C. Magnetic Circular Dichroism. Considering now the MCD curves, the situation for attempting correlations between the magnitude of the magnetic Cotton effects and the nature or position of the substituents on the chlorin skeleton is by far more favorable than in CD. The main reason arises from the *much larger experimental signals when the field is induced* in the superconducting magnet, as compared to the situation without the magnetic field.

Once again, the general features of all the spectra are the same: a positive $[\theta]_M$ maximum value corresponding to the Q_0^y band, a very large negative $[\theta]_M$ minimum for Q_0^x, and a more complicated curve in the region of the B band. The relevant data are summarized in Table II in terms of maximum $[\theta]_M$ values for the Q bands, as well as the ellipticity for the positive maximum (on the red side), and the next negative minimum (*e.g.*, at 425 and 405 nm in Figure 4) together with their absolute difference $\Delta[\theta]_M$ for the B band. It is worth noticing that this latter S-shaped Cotton effect, although almost symmetrical in the first group of samples (Figures 4–6), is very dissymetrical in the second group (Figures 7–9), the negative value being much greater than the positive one.

The data collected in Table II allow comparisons to be made between MCD and CD results. Disregarding the relative inaccuracy of the Q_0^y band values, the ratio (MCD:CD) of the absolute maximum values for the Q_0^x band is in most cases of the order of 20–30. Considering now the B band, the ratio of $\Delta[\theta]_M$ to the corresponding CD maximum value is about 8–20 for compounds **1**, **2**, **3** and 5–6 for **5**, **6**, **7**. This *much greater sensitivity of MCD as compared to CD* is also shown in Figures 4–9, where the curves are plotted with the same ordinate scale as pointed out earlier. It also

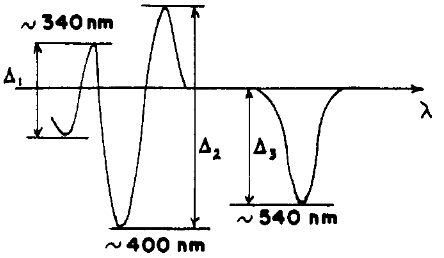
---

(29) M. Gouterman, *J. Chem. Phys.*, 30, 1139 (1959).

follows that, as the noise level is the same for both kinds of measurements, MCD values are much more reliable than CD ones and are therefore to be preferred in that case from a purely analytical point of view.

Not only does MCD give rise to larger Cotton effects but the magnitude of these effects is *closely related and very sensitive to the nature of external substituents.* As already pointed out, peak-to-peak molar ellipticity values are more reliable than absolute positive or negative values. Δ_1, Δ_2, and Δ_3 *empirical values* have consequently been extracted from the data (and Table II) and are reported in Table III. The corresponding Cotton effects are easily found from the experimental results in Figures 4–9. It should be emphasized that differences between the various Δ figures are much larger than the experimental error. It is not yet clear how these data may be supported by theoretical arguments. However, of interest is the fact that Δ_2 is about twice as large for compound **5** than for all the others (with the exception of 7) and this is also what is observed in CD measurements for the same band. Moreover, Δ_2 and Δ_3 values decrease from compounds **1** to **3** and this may tentatively be interpreted in terms of the additional π electrons made available by the acetyl and vinyl groups. On the other hand, the $CH_2CO_2CH_3$ group in compounds **5** and **7** increases Δ_1 and Δ_2, whereas the relative order of the magnitudes is different for Δ_3.

Table III. MCD Data Showing Empirically the Influence of Substituents[a]



Compd	Δ_1	Δ_2	Δ_3
1	208	850	407
2	223	795	405
3	152	700	269
4			
5	391	1590	250
6	185	670	186
7	221	920	116

[a] Units are the same as in Table II.

All these results are of great analytical value to characterize the influence of substituents. It should be kept in mind, however, that a larger number of additional measurements would be necessary to lead to more comprehensive correlations.

Discussion of MCD Results

If we assume an idealized D_{2h} symmetry for the chlorin skeleton, all states are nondegenerate and theory predicts[8,11a] that only *B* terms should appear in MCD spectra. The simplified treatment of Pershan, *et al.*,[30] allows only two nondegenerate excited states to be coupled by the magnetic field and leads to two equal and opposite *B* terms for the Q_0^x and Q_0^y bands if pure *x* and *y* polarization is assumed. The *B* value may be extracted from MCD data by evaluating the area under the curve; however, it is seen from Figures 4–9 that the *B* terms are not of equal magnitude in the case of the chlorins. A number of reasons can be invoked to explain this lack of equality. First, as in ref 11a, the mixing of Q_0^x and Q_0^y states with B^y and B^x, respectively, should be considered. Second, the assumed pure *x* or *y* polarization is likely to be only a rough estimate in molecules containing so many substituents on their framework. This argument seems to be supported by the fact that the difference between the area of the positive and negative lobes of the MCD curve decreases considerably when passing from Figure 4 to Figure 9, *i.e.*, when the symmetry of the molecule is increased. It is also noteworthy that the *B* value corresponding to the maximum at longer wavelengths (Q_0^y) is negative here (see our sign convention in Figure 2), in contrast to the result obtained for the free base phthalocyanin[11a] which possesses no reduced bond. In order to avoid a possible confusion in signs, this point has been checked carefully by rerunning the phthalocyanin and potassium ferricyanide spectra under the same conditions as for our reported curves. Further theoretical work is needed to explain this different behavior.

The magnetic Cotton effects corresponding to the Q_1 bands (*i.e.*, at 506 and 610 nm in Figure 5) are quite small in contrast to those observed in the case of metal-free protoporphyrin.[19] Moreover, if the band at 610 nm were purely *y* polarized, a positive $[\theta]_M$ value would be expected as in the case of the Q_0^y band. Actually, it is known[19,31] that only totally symmetric A_g vibrations (which leave the polarizations unaltered) and B_{1g} vibrations (which converts *x* polarization into *y* polarization) are allowed in the 0–1 bands for the D_{2h} point group. Our results for the range between the two Q_0 bands in Figure 5 seem to indicate that the component of B_{1g} symmetry is dominant, the positive shoulder occurring between 615 and 665 nm being tentatively assigned to the A_g vibrational component. Our results on the blue side of the Q_0^x band seem to indicate either that the B_{1g} part is zero (the A_g part being small) or that the B_{1g} part reduces the A_{1g} vibrational component to a large extent.

The MCD spectra through the B bands seem more complex, a double S-shaped curve being observed in all cases (actually the second negative nimimum is well resolved around 380 nm in Figure 5). The positive $[\theta]_M$ value (at 415 nm in Figure 6) observed on the red side of the Soret band leads us to assign this dispersion term to the B_0^y component of the absorption curve[19] (the sign of $[\theta]_M$ being the same for this band and for the Q_0^y band), the negative minimum occurring at 405 nm corresponding to the B_0^x component. It should be pointed out also that the fact that the wavelength of the positive maximum (at 415 nm in Figure 6) is well removed from that of the absorption maximum (407 nm) is not an argument against the above interpretation. Two explanations can be advanced. First, if the splitting between the B_0 component is relatively small, the separation in wavelengths between the positive maximum and the negative minimum in the MCD spectrum

---

(30) P. S. Pershan, M. Gouterman, and R. L. Fulton, *Mol. Phys.*, 10, 397 (1966).

(31) K. N. Solovév, *Opt. Spectry. USSR*, 10, 389 (1961).

can be considerably larger.[8] Second, as in the case of CD measurements,[32] it may well be that the recorded absorption maximum at room temperature does not correspond to the actual one of a B component. We have confirmed this hypothesis by measuring the absorption spectrum of compound **3** at liquid nitrogen temperature in EPA (five parts of ether, five parts of isopentane, and two parts of ethanol). As expected, the spectrum is resolved into three components with maxima occurring at *409*, 393, and 375 nm (as compared to *405* nm with shoulders at about 394 and 375 nm at room temperature). The S-shaped magnetic Cotton effect observed on the blue side of the Soret band can be tentatively assigned either to the B_1 components (mostly x and y polarized around 380 and 366 nm, respectively) or to other transitions. In particular, it is possible that the additional π orbitals arising from the external double bonds of the vinyl and carbonyl groups lie in the same energy range as the B states.

Finally, in view of the great dependence of MCD on the polarization of the absorption components (and therefore on the substituents on the framework), it is hoped that these studies may provide a useful basis for a new approach to the problem of the role of substituents on the spectroscopic properties of chlorophyll-like molecules. Our experimental results complement the important earlier work on porphyrins.[11a,16,19]

However, although the *relative* sign of B values seems to be well understood, it is not yet clear to us why the *absolute* sign (corresponding to the Q_0^y band, for example) is different here from that observed in porphyrins. Additional theoretical studies are therefore required, as well as new data about the polarization of various transitions.

Acknowledgments. We are grateful to Professor A. Moscowitz (University of Minnesota) and Dr. E. A. Dratz (University of California) for stimulating discussions. We are also indebted to Mr. Gordon H. Scott for technical assistance and Mr. Lonnie Scott for help in the plotting of the spectra.

---

(32) C. Djerassi, H. Wolf, and E. Bunnenberg, *J. Am. Chem. Soc.*, **85**, 324 (1963).

The Coupling of 4-Chloro-4-methyl-2-pentyne and Similar Propargyl Chlorides with Organometallic Compounds[1]

Thomas L. Jacobs and Pairoje Prempree

Contribution No. 1855 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received May 18, 1967*

Abstract: Coupling of 4-chloro-4-methyl-2-pentyne (I) and similar substituted propargyl chlorides with Grignard reagents yields mixtures of acetylenic and allenic hydrocarbons; some enyne is also produced by an elimination reaction. Conjugated dienes reported earlier[2] as major products have been shown to arise by a facile, acid-catalyzed rearrangement of the allenes. The proportion of allenic product is increased by decrease in Grignard reagent concentration or decrease in temperature. Very different products are obtained from the radical reaction which occurs in the presence of cobaltous chloride. Organolithium compounds give high proportions of allenic products in improved yields; this reaction is an excellent method for the synthesis of tetrasubstituted allenes. 4-Methyl-1,2,3-pentatriene was synthesized; methyllithium and methylmagnesium bromide do not undergo addition reactions with this cumulene.

Recently it was reported[2] that the coupling of 4-chloro-4-methyl-2-pentyne (I) with methylmagnesium bromide gave a 77% yield of a hydrocarbon mixture which contained 65–72% of 4,4-dimethyl-2-pentyne (II, R = CH_3; the normal coupling product), 7–24% of 2,4-dimethyl-1,3-pentadiene (III, R = CH_3), and 11–21% of 2-methyl-1-penten-3-yne (IV), the elimination product. Phenylmagnesium bromide gave a similar mixture which in addition to IV contained 4-methyl-4-phenyl-2-pentyne (II, R = C_6H_5, 56%), 4-methyl-2-phenyl-1,3-pentadiene (VI, 41%), and 2-methyl-4-phenyl-1,3-pentadiene (III, R = C_6H_5, 3%). Earlier reports, summarized in ref 2, were conflicting but Zakharova[3] reported that tetrasubstituted allenes were the principal products in these reactions. Her results were confirmed in a very recent communication.[4]

Formation of conjugated dienes[2] rather than allenes seemed particularly surprising and several suggestions were made to explain their formation. It was shown[2] that they did not arise by coupling of the Grignard reagents with rearranged chlorides (allenic or conjugated dienic). Experiments were carried out[2] to show that III was not formed by rearrangement of 2,4-dimethyl-2,3-pentadiene (V, R = CH_3; the expected allene) in the reaction mixture or on the glpc column used to analyze the reaction mixture. These experiments have now been found to be in error and the

---

(1) This paper is taken from the Ph.D. thesis of P. Prempree, University of California, Los Angeles, Calif., 1966. A summary of the work was presented before the Organic Chemistry Division at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract 66S. This research was supported by grants from the National Science Foundation and from the U. S. Army Research Office (Durham).

(2) T. L. Jacobs and R. A. Meyers, *J. Am. Chem. Soc.*, **86**, 5244 (1964).

(3) A. I. Zakharova, *Zh. Obshch. Khim.*, **17**, 1277 (1947); **19**, 1297 (1949); A. I. Zakharova and R. A. Sapozhnikova, *ibid.*, **22**, 1804 (1952); *Chem. Abstr.*, **42**, 3722 (1948); **44**, 100 (1950); **47**, 6857 (1953).

(4) J. Bianchini and A. Guillemonat, *Compt. Rend.*, **C264**, 600 (1967).