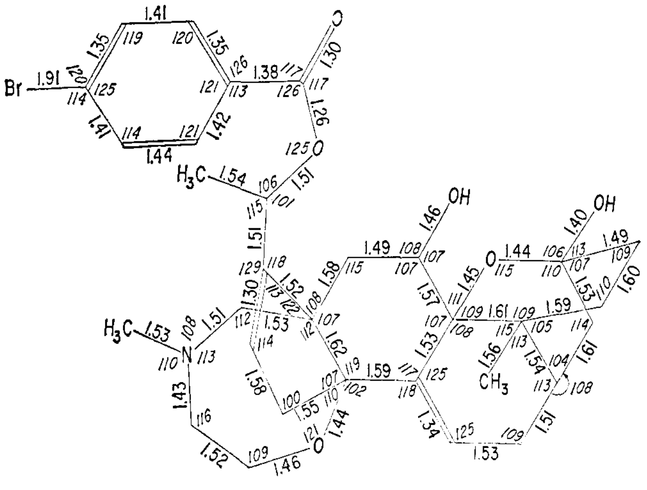
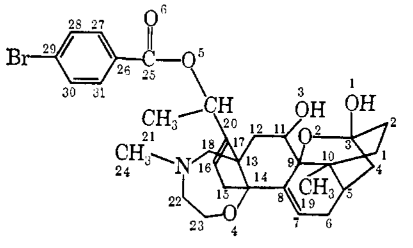


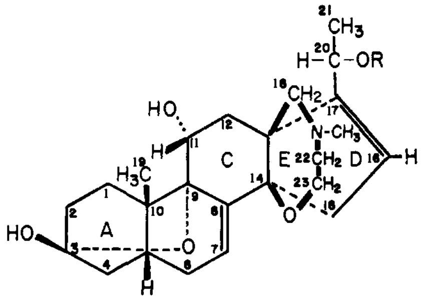
Figure 1. Bond lengths and angles of batrachotoxinin A *p*-bromobenzoate (I).

obtain additional phases. Further atoms were found in the resulting E maps. In several cycles all 39 atoms were located. E maps computed from phases obtained in this manner are much better resolved than those obtained by the heavy atom method. In this particular case, the fact that the heavy atom was specially placed and the data were severely limited made the direct application of the heavy atom method quite unsuitable.

The identification of the six oxygen atoms was obvious from the weights of the peaks in the E maps. The identification of the nitrogen atom was based on the size of the thermal factors in the least-squares refinement, difference maps, and bond lengths. A least-squares refinement of the coordinates for each atom, isotropic thermal factors for all atoms except for the Br atom, and anisotropic thermal factors for the Br atom resulted in an agreement factor of 9.7%. In this way structure I was obtained with the bond lengths and angles shown in Figure 1.



I



II, R=H; BrC$_6$H$_4$CO-

Structure I, when expressed as a steroid derivative, becomes 3α,9α-epoxy-14β,18β-[epoxyethano-N-methylimino]-5β-pregna-7,16-diene-3β,11α,20α-triol (II) which is the structure of batrachotoxinin A. The three-dimensional picture of this novel steroid is presented in the stereodrawing, Figure 2. The structural relationship and the pharmacology of batrachotoxin, isobatrachotoxin, pseudobatrachotoxin, and batrachotoxinin A will be the subject of future papers.

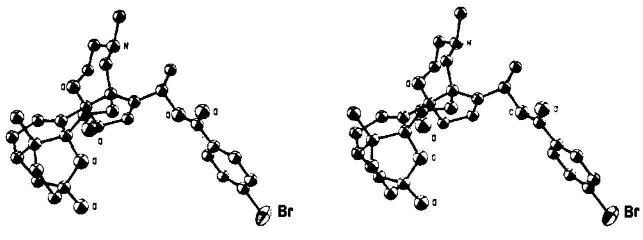


Figure 2. Stereodrawing of the configuration of batrachotoxinin A as determined by X-ray analysis. The drawing was made by a computer from a program prepared by C. Johnson, Oak Ridge National Laboratory. The picture should be seen with a three-dimensional viewer for printed stereophotographs (commercially available, *e.g.*, from Stereo-Magniscope, Inc., Elmhurst, N. Y.).

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Ultraviolet Spectrum of the ClOO Radical

Sir:

The ClOO radical was first proposed by Porter and Wright[1] as an intermediate in the flash photolysis of chlorine–oxygen mixtures.

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$
$$Cl + O_2 + M \rightleftarrows ClOO + M$$
$$Cl + ClOO \longrightarrow ClO + ClO$$
$$Cl + ClOO \longrightarrow Cl_2 + O_2$$
$$ClO + ClO \longrightarrow Cl_2 + O_2$$

From absorption spectroscopy in the ultraviolet (2600–3000 Å), they observed the intermediate diatomic radical ClO. Although not observed, the peroxy radical was postulated to be a short-lived precursor to ClO in their system. Since then, the ultraviolet absorption spectrum of ClO has been observed repeatedly;[2] however, until very recently no spectrographic evidence existed for the presence of ClOO. Rochkind and Pimentel[3a] detected a new infrared absorption in a matrix-isolation study, and Arkell and Schwager[3b] have shown this to be one band in the infrared spectrum of ClOO.

The molecular modulation apparatus described elsewhere[4] has been adapted for work in the ultraviolet.

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[1] G. Porter and F. J. Wright, *Discussions Faraday Soc.*, **14**, 23 (1953).

[2] M. A. A. Clyne and J. A. Coxon, *Trans. Faraday Soc.*, **62**, 1175 (1966).

[3] (a) M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.*, **46**, 4481 (1967); (b) A. Arkell and I. Schwager, *J. Am. Chem. Soc.*, **89**, 5999 (1967).

[4] H. S. Johnston, G. E. McGraw, T. T. Paukert, L. W. Richards, and J. Van den Bogaerde, *Proc. Natl. Acad. Sci. U. S.*, **57**, 1146 (1967).

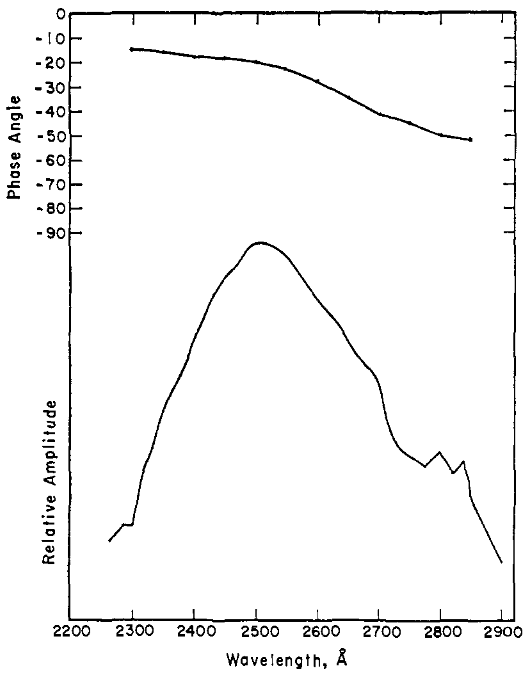

Figure 1. Modulation spectrum taken at 1 cps.

The region 2100–3000 Å has been reinvestigated and found to contain not only ClO but a weaker band with a much shorter lifetime. This has been assigned to ClOO.

Chlorine at 1.8 torr in the presence of 1 atm of oxygen was photolyzed by fluorescent lamps flashing in a square-wave mode at 1 cps. The rate of light absorption by Cl_2 was 1.1 × 10^{14} photons/(cc sec). A modulation spectrum was observed between 2250 and 2900 Å (Figure 1). The phase spectrum lies in the quadrant for simple intermediates (0 to −90°), but the angle varies with wavelength, indicating a mixture of two or more species. The small negative phase angle around 2300–2400 Å represents a fast intermediate, that is, one whose lifetime is short compared to the flashing frequency. The large negative angle around 2800 Å indicates a slow intermediate. Observation of the 2771.6-Å band head[5] of ClO shows that it is the slow intermediate in this system.

It was desired to obtain a spectrum of the fast intermediate with a minimum interference from ClO. Since ClO is the slow intermediate, its modulation amplitude can be suppressed by increasing the flashing frequency of the photolyzing radiation. The amplitude falls off sharply when the driving frequency is greater than the time constant of the chemical system. If the flashing frequency is chosen approximately equal to the time constant of the fast intermediate, this frequency is much faster than the ClO time constant. A spectrum taken at 40 cps is given in Figure 2. The modulation spectrum extends from 2250 to 2700 Å. The phase angle is almost constant (−60 to −65°) over this range, indicating ClO was effectively suppressed. This is the first of two independent methods of separating the spectrum of the fast intermediate from that of ClO.

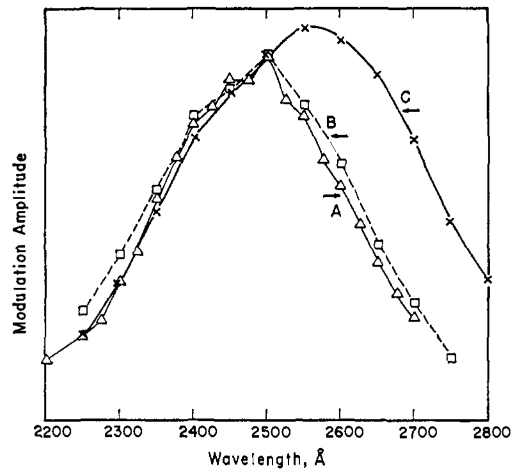

Figure 2. (A) Spectrum of ClOO obtained directly at 40 cps. (B) Spectrum of ClOO obtained by decomposing 0.25-cps spectrum. (C) Modulation spectrum of ozone obtained by photolyzing NO_2 in oxygen.

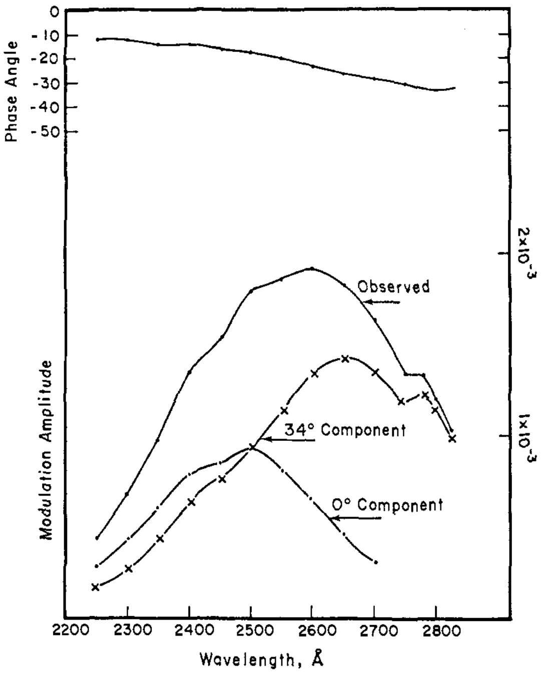

Figure 3. Spectrum taken at 0.25 cps; decomposition into two species with constant phase.

From the appropriate differential equations, it can be shown that if an intermediate has a phase of −60° at 40 cps, it would have essentially zero phase angle at 0.25 cps. If the complex spectrum consists of only two species and if the phase of each is known, then the modulation amplitude can be factored into two separate spectra by vector addition. At 0.25 cps, four runs were carried out and averaged point by point (Figure 3). The observed modulation shows a maximum at 2600 Å, and the phase varies from −12° at 2300 Å to −34° at 2800 Å.

The fast intermediate has zero phase, and the measurement at 2800 Å as well as the 2772-Å band at high resolution indicate ClO has a phase of −34°. With these assumptions, the observed amplitude is decomposed into two separated spectra, one for ClO and the other for the fast intermediate. The results from the two methods are in good agreement with each other as can be seen in Figure 2.

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(5) G. Porter, *Discussions Faraday Soc.*, **9**, 60 (1950).

The amplitude spectrum of the new intermediate does not resemble published spectra for OClO or ClOCl, nor does it match a modulation spectrum of ozone obtained by photolyzing NO_2 in oxygen done on this instrument with the same slit widths. An infrared modulation experiment showed no ozone although the ultraviolet and infrared absorption cross sections are comparable. (In the matrix work some ozone was seen.[3b])

The modulation of each species was shown to depend on both oxygen and chlorine concentrations. No modulation can be detected if either reactant is absent. From the Porter and Wright mechanism the effect on the modulation amplitude of halving the oxygen or doubling the chlorine concentrations can be calculated. The experimental results are in satisfactory agreement with these calculations.

A rate constant for the complex reaction

$$\mathrm{Cl} + \mathrm{Cl} + \mathrm{O_2} \longrightarrow$$

can be estimated by combining two literature values. Porter and Wright say this rate is 46 times faster in oxygen than in nitrogen. Combining this with a recent measurement of chlorine atom recombination[6] in argon gives the approximation

$$d[\mathrm{Cl}]/dt = -2[\mathrm{Cl}]^2[\mathrm{O_2}]k$$

$$k = 5.3 \times 10^{-31}\ \mathrm{cm^6/(molecule^2\ sec)}$$

The phase shift of the fast intermediate (regarded as ClOO) and the value for the light absorbed by chlorine give a rate constant approximately 1.5 times that predicted. However, one would expect nitrogen to be a better gas than argon in catalyzing the recombination of chlorine atoms.

Since the fast intermediate does not match the spectra of known molecules which could be in the system, and since it behaves as ClOO would be expected to, the fast intermediate is assigned as the radical ClOO.

Work is now proceeding to gather kinetic data on this system.

Acknowledgment. This work was supported by a National Science Foundation traineeship to E. D. M. and by the Division of Air Pollution, Bureau of State Services, U. S. Public Health Service, Washington, D. C., under Grant AP-104.

(6) E. Hutton and M. Wright, *Trans. Faraday Soc.*, **61**, 78 (1965).

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Alternate Electrocyclic Pathways. A Quantitative Energy Evaluation

Sir:

We wish to report the rate constants and activation parameters for the gas-phase, unimolecular valence isomerization[1,2] of bicyclo[2.1.0]pent-2-ene to cyclopentadiene: $\log k\,(\mathrm{sec}^{-1}) = (14.2 \pm 0.2) - (26{,}900 \pm 300)/2.303RT$ $(299 \leqslant T(^\circ\mathrm{K}) \leqslant 381)$. The activation energy allows us to make a quantitative evaluation of the energy difference between alternate electrocyclic pathways in cyclobutene isomerizations.

Since the definition and characterization by Woodward and Hoffmann[3] of electrocyclic reactions, a considerable amount of research has been directed toward exploring the validity and extent of applicability of the "Woodward–Hoffmann rules." Thus far, within the limitations of the hypotheses no counterexamples have been observed; the stereochemical products have been only those predicted. It is of considerable importance to evaluate quantitatively the energy difference between allowed and nonallowed processes. The "rules" follow directly from orbital symmetry considerations, and although calculations can be carried out, there is *a priori* no good way of evaluating the added stability of the preferred pathway. The stereochemical results might allow an estimate to be made experimentally. However, since a difference of $\Delta E_a \cong 2 \times 2.303RT$ yields 99% of the favored product, this test is not nearly sensitive enough. Thus, while it is certain that at least 4 kcal/mol separate the possible pathways, the difference may be much greater.

The "rules" do not exclude the possibility of less favored reactions "under very energetic conditions." This might be taken to suggest that the unfavored process will occur only with high activation energies or at high temperatures in situations where the favored process is impossible due to, say, steric constraints.[3] On the basis of such criteria, the disrotatory reaction which we have studied constitutes a counterexample to the "rules" since it has a lower activation energy (and proceeds at a lower temperature)[4] than its allowed, conrotatory, monocyclic analog, cyclobutene → butadiene.[5]

Since there are good reasons to believe that formulation of electrocyclic reactions into allowed and nonallowed processes is valid, it is clear that the hypothesis should be refined to account for the case of bicyclo[2.1.0]pent-2-ene. In doing this, we will, in addition, define a useful quantitative measure of the difference in energy for the alternate pathways.

We propose that the transferable quantity with which the Woodward–Hoffmann rules deal is the *unstrained* bond dissociation energy of the bond between the termini of the π system in the transition state.[6a] Defining strain energy (SE) in a cyclic compound in the usual way,[7] as the difference between the observed and

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(1) Equation 2, $n = 1$.

(2) Reactions were carried out in a 500-cc quartz vessel (situated in an aluminum block oven) which is part of the sampling optical system of a modified Cary 15 spectrometer: D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965).

(3) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965), and succeeding papers. Also, see H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(4) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *ibid.*, **88**, 846 (1966). The half-life at room temperature reported in this reference (2 hr) is shorter than the "true" unimolecular half-life reported here (40 hr) presumably due to dimerization reactions in solution.

(5) An article by H. M. Frey, B. M. Pope, and R F. Skinner, *Trans. Faraday Soc.*, **63**, 1166 (1967), contains a review covering this and similar compounds.

(6) (a) In this proposal we make use of *formal* definitions based on a *model*. Other, similar descriptions will work equally well, and use of the *model* is not meant to imply its existence *per se*. This type of formulation is precisely analogous to the definition of empirical resonance energy. (b) This bond dissociation energy ($\mathrm{UBE}^{\ddagger}$) is the sum of several interactions including σ, π, and delocalized π components. It is the empirically derived quantity most closely related to the calculated Woodward–Hoffmann values. With this definiton, $\mathrm{UBE}^{\mathrm{gs}}$ is the BE of the corresponding saturated system.

(7) G. J. Janz, "Thermodynamic Properties of Organic Compounds," revised ed, Academic Press Inc., New York, N. Y., 1967, p 107.