Alkaloid E.—The combined fractions 601–639 (150 mg) were rechromatographed on 500 g of neutral grade IV alumina; elution with benzene (200 ml) afforded 50 mg of a readily crystallizable alkaloid, mp 136–137°, $[\alpha]^{25}\text{D}$ −150° (c 0.8, $CHCl_3$). *Anal.* Calcd for $C_{18}H_{21}NO_4$: C, 68.5; H, 6.72; N, 4.44. Found: C, 68.46; H, 6.49; N, 4.60. This alkaloid is identical in every respect (infrared, pmr, tlc) with the minor reduction product, epicephalotaxine, obtained from the reduction of cephalotaxinone.

Epicephalotaxine.—In a 50-ml flask of a micro Soxhlet extractor was placed 150 mg of cephalotaxinone and 40 ml of dry tetrahydrofuran. The solution was refluxed for 4 hr, and the condensing vapors were passed over 500 mg of lithium aluminum hydride contained in the extraction cup of the apparatus. The excess lithium aluminum hydride was then decomposed with saturated aqueous Na_2SO_4. The mixture was filtered and to the filtrate was added 200 ml of ether. The organic layer was then collected, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The remaining amorphous material (120 mg) was chromatographed on 200 g of neutral grade IV alumina. Slow chromatographic elution with benzene (75 ml) afforded 15 mg of epicephalotaxine, mp 135–137°. *Anal.* Calcd for $C_{18}H_{21}NO_4$: C, 68.5; H, 6.72; N, 4.44. Found: C, 68.38; H, 6.90; N, 4.60.

Further elution with benzene (300 ml) afforded a mixture (105 mg) of mainly cephalotaxine with only a trace of epicephalotaxine, as determined by tlc [R_f (epicephalotaxine)/R_f (cephalotaxine) 1.0–1.35, tlc silica gel plates, benzene].

Registry No.—1, 24316-19-6; 2, 38750-57-1; 3, 39707-71-6; 4, 39707-72-7; acetylcephalotaxine, 24274-60-0; benzophenone, 119-61-9; tetrahydrofuran, 109-99-9.

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Thermal Decomposition of a Phenanthroxyl Quinol Ether. A Kinetic Study Using Laser Raman Spectroscopy

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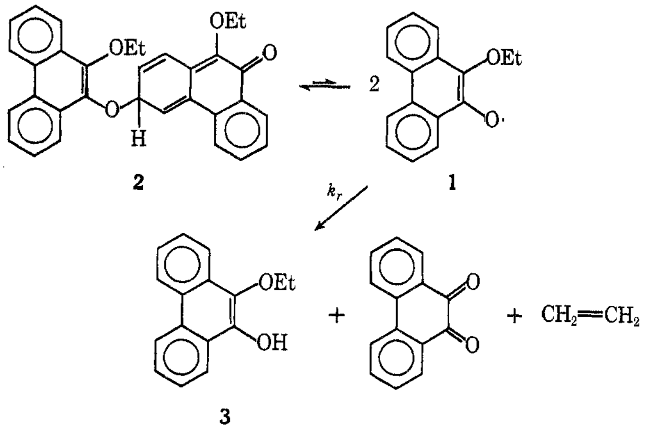
We have recently shown that the 10-ethoxy-9-phenanthroxyl radical **1** exists in equilibrium with its dimer **2** both in solution[2] and in the solid state,[3] and that the thermolysis of degassed samples of **2**, either in solution or as neat melts, leads to the slow formation of equimolar amounts of 10-ethoxy-9-phenanthrol (**3**), phenanthrenequinone, and ethylene.[2,3] This is thought to occur *via* disproportionation of **1**, as indicated in Scheme I, although unimolecular decomposition of **2** cannot be rigorously excluded. It is characteristic of this system and of other quinol ethers[4,5] that the ir, uv, and nmr spectra of the dimers and of the decomposition products are sufficiently complex and overlapped as to be useless for kinetic analysis of the decomposition; the usual recourse has been to monitor the concentration of radicals by esr.[2,5] We now wish to report that the thermolysis of **2** in degassed solution may be conveniently followed by laser Raman spectroscopy, which makes possible the direct monitoring of both **2** and **3**.

SCHEME I



In the course of routine laser Raman studies, it was noticed that spectra of *ca.* 0.1 *M* solutions of **2** in CCl_4 contained a peak at 1354 cm^{-1} attributable to **3** in addition to a peak at 1292 cm^{-1} characteristic of **2** (Figure 1). The frequency of the peak at 1292 cm^{-1} suggests that it is associated with the aryl ether C–O linkage in **2**; since the peak at 1354 cm^{-1} is also present in spectra of 10-chloro-9-phenanthrol, we infer that it is associated with the phenanthrol C–O bond. It should be noted that the positions of both peaks are insensitive to concentration and are, in fact, the same in solution as in the solid phase.

Since the amplitudes of the two peaks are proportional to the concentrations of **2** and **3**, it should in principle be possible to use the measured amplitudes directly for kinetic analysis. That turned out not to be true in this case; the high concentration of **2** required for the laser Raman spectra resulted in gradual precipitation of phenanthrenequinone as the decomposition progressed, causing excessive noise and base-line drift at reaction times longer than about 55 hr. As Table I shows, the observed amplitudes were unsuitable for direct analysis because of light scatter and base-line drift induced by the precipitate. However, since both peaks appear to arise from a vibrational mode of the aryl C–O group, it is not unreasonable to assume that the molar intensities of the two peaks are similar, if not equal. Given the known[2] 1:1 re-

TABLE I

NORMALIZATION OF LASER RAMAN KINETIC DATA[a]

Time, hr	Observed amplitudes, mm 1292 cm^{-1}	Observed amplitudes, mm 1354 cm^{-1}	Sum	N^b	Normalized amplitudes, mm 1292 cm^{-1}	Normalized amplitudes, mm 1354 cm^{-1}
0.0	47	24	71	1.41	66	34
5.0	48	43	91	1.10	53	47
18.0	40	47	87	1.15	46	54
30.0	38	58	96	1.04	40	60
42.3	25	47	72	1.39	35	65
54.5	19	44	63	1.59	30	70

[a] Degassed 0.10 *M* solution in CCl_4 at 67°. [b] Normalization factor = 100/sum.

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[1] Syva Research Institute, 3221 Porter Drive, Palo Alto, Calif. 94304.

[2] R. E. Schwerzel and J. E. Leffler, *J. Org. Chem.*, **37**, 3096 (1972).

[3] R. E. Schwerzel, Ph.D. Dissertation, Florida State University, 1970.

[4] D. J. Williams and R. Kreilick, *J. Amer. Chem. Soc.*, **90**, 2775 (1968).

[5] S. A. Weiner and L. R. Mahoney, *ibid.*, **94**, 5029 (1972).

lationship between the concentrations of **2** and **3**, one may conclude that the *sum* of the observed amplitudes should ideally remain constant.[6] To correct the observed amplitudes, therefore, the sum at each time was normalized to a constant value (arbitrarily set at 100 mm); multiplying the observed amplitudes by the normalization factor $N = 100/\text{sum}$ at each time gave a set of normalized amplitudes which produced acceptable kinetic plots (Table I).[7,8]

As indicated in Table II, the values of the first-order rate constant k so obtained compare quite well with that previously obtained by esr measurements,[2,3,11] considering the differences in concentration and in method. We therefore feel that, in many cases, laser Raman spectroscopy will prove to be a useful adjunct to the more conventional techniques of kinetic analysis. This should apply particularly to those systems in which, as in the present case, the large number of ir-active vibrational modes renders the infrared spectrum useless as a kinetic tool.

TABLE II

SUMMARY OF THERMOLYSIS RATE DATA[a]

Analytical method	$[\mathbf{2}]_0$,[b] M	10^6k,[c] sec^{-1}, ± 1.0
Laser Raman		
1292-cm^{-1} peak	0.10	3.2
1354-cm^{-1} peak	0.10	2.2
Esr[d]	0.02	1.3

[a] Degassed CCl_4 solutions at 67°. [b] Initial concentration of dimer. [c] First-order rate constant for the decomposition; see ref 11. [d] Reference 2.

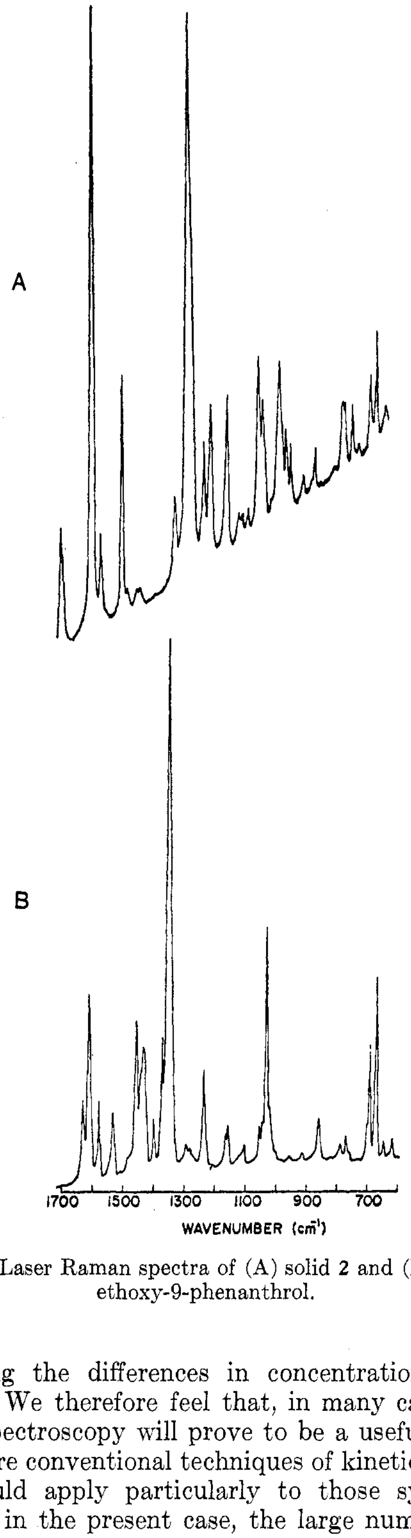

Figure 1.—Laser Raman spectra of (A) solid **2** and (B) solid 10-ethoxy-9-phenanthrol.

Experimental Section[12]

Materials.—10-Chloro-9-phenanthrol, 10-ethoxy-9-phenanthrol, and the ethoxy dimer **2** were prepared as described previously.[2,3] Commercial spectroscopic grade CCl_4 was used as solvent for all runs.

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(6) This is true even if the molar intensities of the two peaks are not precisely equal. The amplitude of the peak at 1292 cm^{-1} at any time t may be expressed as $A_2(t) = \alpha_2[\mathbf{2}]$, where α_2 is the molar intensity of the peak. Similarly, the amplitude of the peak at 1354 cm^{-1} is given by $A_3(t) = \alpha_3[\mathbf{3}]$. Since the stoichiometry of the reaction demands that $[\mathbf{2}] + [\mathbf{3}] = [\mathbf{2}]_0$, where $[\mathbf{2}]_0$ is the initial concentration of **2**, it is easily shown that

$$A_2(t) + A_3(t) = (\alpha_2 - \alpha_3)[\mathbf{2}] + \alpha_3[\mathbf{2}]_0$$

As long as α_2 and α_3 are of roughly the same magnitude it will be true that $(\alpha_2 - \alpha_3)[\mathbf{2}] \ll \alpha_3[\mathbf{2}]_0$, and to a good approximation the sum of the amplitudes will be constant: $A_2(t) + A_3(t) \cong \alpha_3[\mathbf{2}]_0$.

(7) It is important to recognize that this procedure in no way affects the value of the first-order rate constant, k, which is obtained from the plots. For instance, the normalized amplitude of the 1292-cm^{-1} peak at each time is given by

$$A_2' = NA_2 = A_2\left(\frac{100}{A_2 + A_3}\right) \cong [\mathbf{2}]\left(\frac{100\alpha_2}{\alpha_3[\mathbf{2}]_0}\right)$$

so that

$$\ln A_2' \cong \ln\,[\mathbf{2}] + \ln\left(\frac{100\alpha_2}{\alpha_3[\mathbf{2}]_0}\right)$$

Since the first-order decay of **2** is expressed by

$$\ln\,[\mathbf{2}] = \ln\,[\mathbf{2}]_0 - kt$$

it can be seen that a plot of $\ln A_2'$ *vs.* t is linear, with the same slope that would be obtained from a plot of $\ln\,[\mathbf{2}]$.

(8) A referee has objected to the fact that the points at $t = 0$ deviate considerably from the linear plot obtained for the remainder of the reaction. This troublesome behavior was also observed for esr kinetic runs carried out in commercial spectroscopic grade CCl_4, but *not* for esr runs carried out in benzene purified by the photochlorination technique of Saltiel.[9] The clear implication is that an impurity in the CCl_4 scavenges the radicals **1** during the early stages of the reaction. This is further supported by the observation that solutions of **2** in CCl_4, no matter how carefully prepared, always contained significant amounts of **3** as evidenced by the presence of a peak at 1354 cm^{-1}; this behavior made it impossible to accurately determine the molar intensity of the 1292-cm^{-1} peak. We consider that these observations are fully consistent with the recent report by Schuster and Weil[10] that commercial spectroscopic grade CCl_4, obtained from a variety of sources, contains varying amounts of 1,1-dichloropropene. This olefin should be an efficient scavenger for phenanthroxyl radicals such as **1**, with the decomposition proceeding normally once the supply of scavenger has been exhausted. Since the deviation of the point at $t = 0$ for a plot of the appearance of the peak at 1354 cm^{-1} (due to **3**) is roughly twice the deviation of the $t = 0$ point for a plot of the disappearance of the 1292-cm^{-1} peak, we infer that the scavenger serves as a hydrogen donor, giving two molecules of **3** per molecule of **2**.

(9) (a) J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, **2**, 331 (1970); (b) J. Saltiel, private communication.

(10) D. I. Schuster and T. M. Weil, *Mol. Photochem.*, **4**, 447 (1972).

(11) The rate constant k for the disappearance of **2** (or the appearance of 10-ethoxy-9-phenanthrol) is related to k_r by $k = k_rK_{eq}$, where K_{eq} is the dissociation equilibrium constant. Assuming the process depicted in Scheme I, the rate law for disappearance of **1** is

$$\frac{-\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = \frac{k_rK_{eq}}{2}[\mathbf{1}]$$

so the value of k is easily extracted from esr data.[2,5]

(12) Laser Raman spectra were recorded on a Cary 81 Raman spectrophotometer, using a Spectra-Physics Model 125 He–Ne gas laser which produced an 80-mW beam at 632.8 nm. High-resolution mass spectra and mass measurements were obtained using an A. E. I. MS-902 double-focusing mass spectrometer equipped with a MSDS-II data reduction system.

Laser Raman Kinetics.—Routine laser Raman spectra of solutions were measured with the sample contained in a melting point capillary aligned coaxially with the laser beam. While **2** absorbed no light at the laser frequency, prolonged exposure to the beam (20–30 min) inevitably resulted in some deterioration of the sample. To minimize this problem in the kinetic study, the sample was contained in a 3-mm-o.d. Pyrex tube having one end flat; the other end was sealed after degassing the sample *in vacuo*. The larger diameter of this tube permitted thermal mixing of the solution in the vicinity of the laser beam, reducing the amount of laser-induced decomposition. The sample was kept in a thermostatted oil bath at 67.0 ± 0.1° and removed only long enough to record the two peaks for each point.

Registry No.—**1**, 38512-16-2; **2**, 35099-79-7; **3**, 35099-80-0.

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Communications

See Editorial, *J. Org. Chem.*, **37**, No. 19, 4A (1972).

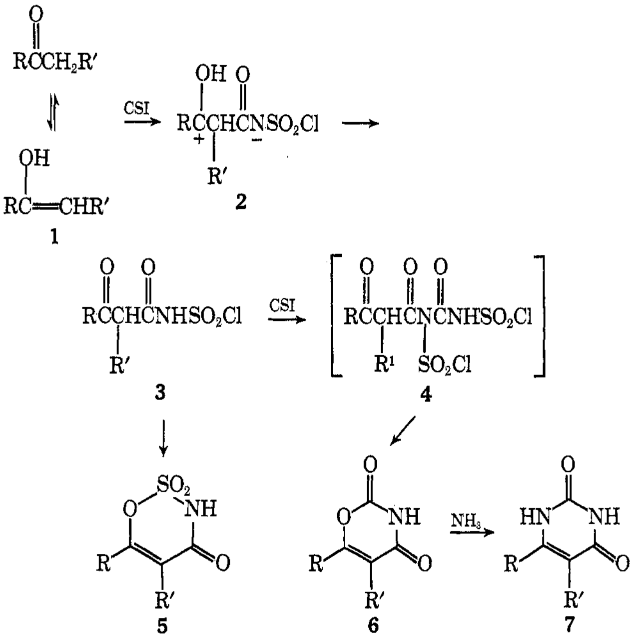
The Electrophilic Addition of Chlorosulfonyl Isocyanate to Ketones. A Convenient Synthesis of Oxazines, Oxathiazines, and Uracils[1]

Summary: CSI is found to react with ketones **1** in ether solution to produce 1,2,3-oxathiazines **5** and 1,3-oxazines **6** but, in CH_2Cl_2 solution, only **6** is formed; oxazines **6** are readily converted into uracils **7**.

Sir: Chlorosulfonyl isocyanate (CSI) has received considerable attention recently owing to its reactivity in various cycloadditions and its use in heterocyclic syntheses.[2] This remarkable electrophile reacts with a variety of compounds, including olefins,[2b] acetylenes,[2c] strained bicyclic hydrocarbons,[2d] and ketene thioacetals.[2e] Recent evidence[3a] has been interpreted mechanistically as involving $[_{\pi}2_s + {}_{\pi}2_a]$ cycloaddition of CSI to olefins; heterolytic ring opening of the initially formed β-lactam to a 1,4 dipole may then lead to rearranged products. However, 1,4 dipoles may still be the primary intermediates, giving 1,2 addition under kinetic control and rearranged products under thermodynamic control.[3b]

We wish to report the first examples of the electrophilic addition of CSI to simple ketones **1**,[4] a reaction which provides a facile entry into the 3,4-dihydro-4-oxo-1,2,3-oxathiazine 2,2-dioxide (**5**) and the 3,4-dihydro-2*H*-2,4-dioxo-1,3-oxazine (**6**) systems (Scheme I). The former represents a new heterocyclic system,[5] the novel reactions of which are currently under study.

Scheme I



The latter are readily converted into uracil derivatives **7**.[6]

Treatment of **1**[7] with 2.3 equiv of CSI in ether or dichloromethane solution under nitrogen at room temperature for up to 7 days, followed by reductive hydrolysis with aqueous sodium sulfite solution,[8] provided **5** and **6** as the major isolated products (Table I).

As depicted in Scheme I, electrophilic addition of CSI to the enol form of **1** would produce the 1,4 dipole **2**,[9] which yields amide **3** by a proton shift. We have succeeded in trapping intermediate **3** by the isolation of various derivatives. These results will be described in our full paper. Reaction of **3** with a second equiva-

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(1) Cycloadditions. XII. For paper XI, see A. Hassner and D. J. Anderson, *J. Amer. Chem. Soc.*, **94**, 8255 (1972).

(2) (a) For a recent review, see R. Graf, *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968); (b) E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968); E. J. Moriconi and W. C. Meyer, *ibid.*, **36**, 2841 (1971); L. A. Paquette, T. Kakihana, J. R. Hansen, and J. C. Phillips, *J. Amer. Chem. Soc.*, **93**, 152 (1971); L. A. Paquette, S. Kirschner, and J. R. Malpass, *ibid.*, **92**, 4330 (1970); (c) E. J. Moriconi and Y. Shimakawa, *J. Org. Chem.*, **37**, 196 (1972); (d) E. J. Moriconi and C. P. Dutta, *ibid.*, **35**, 2443 (1970); L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **93**, 4503 (1971); (e) F. A. Carey and J. R. Neergaard, *J. Org. Chem.*, **36**, 2731 (1971).

(3) (a) T. J. Barton and R. J. Rogido, *J. Chem. Soc., Chem. Commun.*, 878 (1972); T. J. Barton and R. J. Rogido, *Tetrahedron Lett.*, 3901 (1972); (b) J. R. Malpass and N. J. Tweddle, *J. Chem. Soc., Chem. Commun.*, 1244, 1247 (1972); J. R. Malpass, *ibid.*, 1246 (1972).

(4) CSI has been reported to react with a few β diketones such as dimedone and acetylacetone, leading to β-ketoamides. See ref 2a, p 180.

(5) The only previously reported examples appear to be the 5,6-dimethyl compound [K. Clauss and H. Jensen, *Tetrahedron Lett.*, 119 (1970)] and the 6-phenyl compound [K.-D. Kampe, *ibid.*, 123 (1970)].

(6) Satisfactory elemental analyses (+0.3%) were obtained for all new compounds, and the nmr, ir, and mass spectral data were in complete agreement with the structural assignments.

(7) Ketones in which neither R nor R′ is aryl appear to react in an entirely different manner. For example, 4-heptanone reacts with CSI in CH_2Cl_2 to yield butyric acid in 75% yield following work-up. Further investigation of this novel reaction is in progress.

(8) T. Durst and M. J. O'Sullivan, *J. Org. Chem.*, **35**, 2043 (1970).

(9) None of our experimental results, however, would preclude initial β-lactam formation followed by rapid ring opening to **2**.