Peak 1 was *trans,syn*-Δ^2-octalol-1 (**40**): ir (CCl_4) 3633 (s, free OH) and 3500 cm^{-1} (m, b, bonded OH); nmr δ 5.88 (m, 2, CH=CH), 3.88 (broad singlet, 1, CHOH), 1.33 (s, 1, OH), and 0.50–2.40 (broad band, 13, all other protons). It was hydrogenated over Adams catalyst in methanol to *trans,syn*-1-decalol (**38**) whose ir was identical with that of authentic **38**.[21]

Anal. Calcd for $C_{10}H_{16}O$ (152.23): C, 78.89; H, 10.59. Found: C, 78.62; H, 10.49.

Peak 2 was *trans,anti*-Δ^2-octalol-1 (**41**): ir (CCl_4) 3625 and 3650 (s, free OH), and 3500 cm^{-1} (s, b, bonded OH); nmr δ 5.60 (m, 2, CH=CH), 3.80 (broad singlet, 1, CHOH), 1.67 (s, 1, OH), and 0.50–2.40 (broad band, 13, all other protons). Its ir absorption in dilute carbon tetrachloride solution in the intermolecular O–H stretching region was more intense than in the corresponding spectrum of **40**. It was hydrogenated over Adams catalyst in methanol to *trans,anti*-1-decalol (**39**) whose ir was identical with that of authentic **39**.[21] Jones oxidation of fraction 2 produced the enone **42** which was collected by preparative glpc (column A) and subsequently reduced by lithium aluminum hydride to a mixture which contained *ca.* 95% **41**.

Anal. Calcd for $C_{10}H_{16}O$ (152.23): C, 78.89; H, 10.59. Found: C, 78.61; H, 10.39.

Peak 3 was not identified.

Registry No.—Selenium dioxide, 7446-08-4; **4**, 23758-22-7; **7**, 23758-23-8; **7** (2,4-dinitrophenylhydrazone), 23758-24-9; **7** (semicarbazone), 23829-43-8; **8**, 23758-25-0; **9**, 23758-26-1; **13**, 23713-60-2; **15**, 23758-27-2; **16**, 23713-61-3; **20**, 23713-62-4; **22**, 23746-53-4; **23**, 23713-63-5; **24**, 23713-64-6; **26**, 23713-65-7; **31**, 23713-66-8; **32**, 23713-67-9; **33**, 23713-68-0; **34**, 23713-69-1; **40**, 23713-70-4; **41**, 23713-71-5.

Acknowledgment.—Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this research.

Mechanism of Selenium Dioxide Oxidation of Olefins[1]

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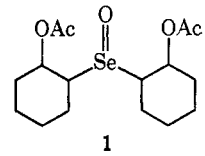
The mechanism of allylic oxidation of olefins by selenium dioxide is discussed. Evidence is presented in favor of an initial oxaselenocyclobutane intermediate forming an allylic selenite ester, which then solvolyzes.

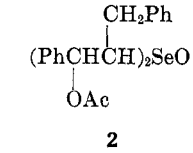
The mechanism of allylic oxidation of olefins by selenium dioxide has been the subject of several studies over the past 30 years.[4] The first hypothesis, that of Guillemonat,[5] invoked the intermediacy of tetraalkyl and dialkyl selenides in which the selenium is bonded to an allylic carbon. The gross inadequacy of this proposal has already been commented upon adequately,[4,6] but it should be recognized that Guillemonat's comprehensive studies of the behavior of selenium dioxide in acetic acid–acetic anhydride led to the formulation of many useful and still valid generalizations with respect to the site of attack in unsymmetrical alicyclic and acyclic olefins.

Another early suggestion put forth by Waters without any experimental support was that the reaction involves neutral radical species.[7] This was based on analogy to the allylic oxidation observed with benzene diazonium acetate, lead tetraacetate, or air catalyzed by osmium and on the fact that many oxidations involve radical-chain mechanisms. Although Wiberg and Nielsen[8] credit Waters with suggesting that the reaction proceeds "*via* a hydrogen atom abstraction from the alkene," Waters did recognize that the 2-cyclohexenol acetate produced by selenium dioxide oxidation of cyclohexene could also be formed by addition of two acetoxy radicals followed by elimination of acetic acid. No support has, however, been forthcoming for a free-radical process. Quite the contrary, Schaefer, Horvath, and Klein[9] have shown that the reaction is unaffected by inhibitors and, therefore, cannot be radical chain. We wish to report that the reaction does not involve free radicals at all. Thus, we find that an oxidizing system is incapable of initiating polymerization of acrylonitrile under conditions of temperature and concentration where acrylonitrile is rapidly polymerized if a source of free radicals is present.

There is now evidence that the oxidation proceeds by two different mechanisms, a low energy solvolytic pathway and a pyrolytic one. Guillemonat[5] had early observed that the organoselenium intermediates which he postulated as selenides thermally decompose to regenerate olefin and to produce allylic oxidation products. Wiberg[8] established that these compounds are selenoxides, rather than selenides, by isolating **1** from the oxidation of cyclohexene in acetic acid–acetic anhydride. Schaefer, Horvath, and Klein,[9] however, showed that the analogous compound **2** isolated from



1



2

the oxidation of 1,3-diphenylpropene (**3**) decomposes to 1,3-diphenyl-2-propen-1-ol acetate (**4**) at too slow a rate to account for the main course of the oxidation.

The main pathway must involve the solvolysis of an allylic selenite ester, although the structure of the latter has not been rigorously established. Schaefer[9]

(1) A preliminary report of some of this work was made at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, Abstract, p 78Q.

(2) Extracted in part from the Ph.D. dissertation submitted by C. H. N. to Clark University in 1964. A National Science Foundation Cooperative Graduate Fellowship for 1961–1962 is gratefully acknowledged.

(3) Extracted in part from the Ph.D. dissertation submitted by J. R. C. to Clark University in 1969.

(4) For a review of the scope and limitations of this reaction, see (a) E. N. Trachtenberg in "Oxidation," Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, pp 119–187; (b) N. Rabjohn, *Org. React.*, **5**, 331 (1949); (c) G. R. Waitkins and C. W. Clark, *Chem. Rev.*, **36**, 235 (1945).

(5) A. Guillemonat, *Ann. Chim.* (Paris), **11**, 143 (1939).

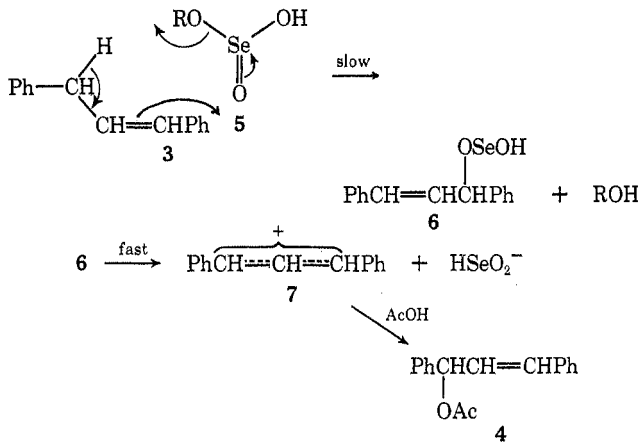
(6) T. W. Campbell, H. G. Walker, and C. M. Coppinger, *Chem. Rev.*, **50**, 279 (1952).

(7) W. A. Waters, *J. Chem. Soc.*, 1805 (1939).

(8) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, **29**, 3353 (1964).

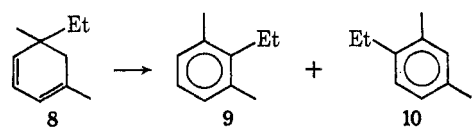
(9) J. P. Schaefer, B. Horvath, and H. P. Klein, *ibid.*, **33**, 2647 (1968).

SCHEME I

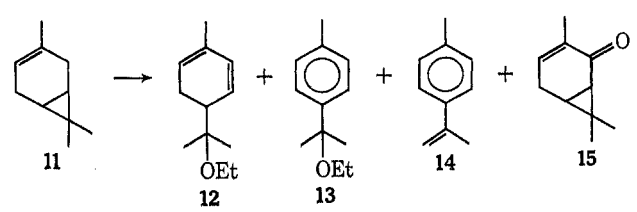


has suggested the mechanism shown in Scheme I. The rapid SN1 of **6** is in agreement with the observation that **3** deuterium labeled at C-3 shows equilibration of C-1 and C-3. Furthermore, the presence of a final solvolytic step is in agreement with observations on many systems. Thus, one obtains alcohols, acetates, and ethers when the selenium dioxide oxidation is performed in water, acetic acid (or acetic acid–acetic anhydride), or alcohol, respectively.[4] Since alcohols formed under the mildly acidic reaction conditions would not be converted into ethers, it follows that the latter must be formed directly in a solvolytic step; by analogy, the same should also be true for acetate formation. In further support of a solvolytic mechanism, at least part of which must be SN1 in character, is our observation that, whereas D-(+)-1-*p*-menthene in wet dioxane yields optically active, albeit partially racemized, *cis*- and *trans*-carvotanacetols and carvotanacetone, the acetates produced in the better ionizing solvent, acetic acid–acetic anhydride, are completely racemic. This accords with a competition between uni- and bimolecular solvolysis.

The observation of rearranged products in a system such as **8** agrees with the formation of an allylic cation at C-6 which then undergoes Wagner–Meerwein rearrangement followed by proton loss to generate the



aromatic system **9**.[10] The formation of **10** is similarly explicable. Another example involves the oxidation of 3-carene (**11**) in ethanol to give **12–15**.[11] Finally, the



(10) M. Zaidlewicz, A. Uzarewicz, and W. Zacharewicz, *Rocz. Chem.*, **40**, 437 (1966) (English summary).

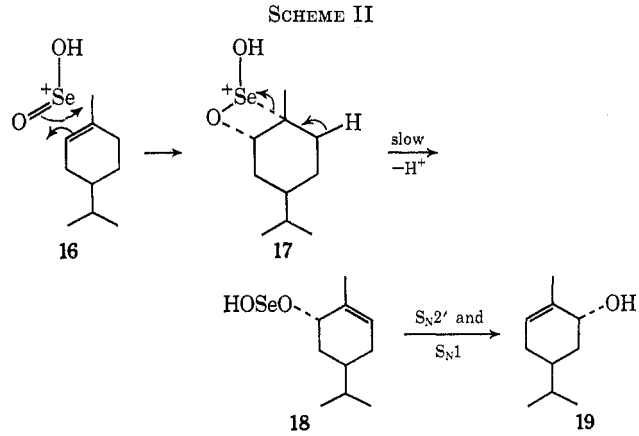
(11) Z. G. Isaeva, B. A. Arbuzov, and V. V. Ratner, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 475 (1965); *Bull. Acad. Sci. USSR, Ser. Chem.* (Engl. Transl.), 458 (1965).

observed formation of dienes in systems in which the preferred site of oxidation is tertiary is in accord with the expectation of E1 competing with SN1 in such systems.[5,12]

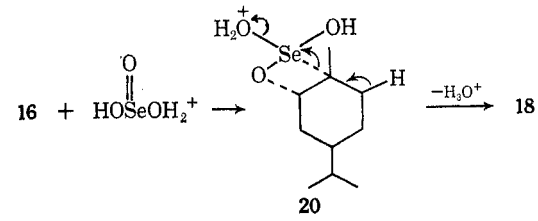
The first step of the Schaefer mechanism (Scheme I) is harder to justify. If what is implied is a synchronous electrocyclic reaction, one cannot explain the large kinetic deuterium isotope effect of 3.1 for reaction of PhCHDCH=CHPh in refluxing acetic acid. This effect clearly implies that, in the cleavage of the allylic C–H bond, bond breaking markedly leads over bond making. If this is so, and the proposed mechanism is to be generally true, one is faced with the dilemma of explaining why the C-6 and not the C-3 position is oxidized in 1-alkyl-, 1-halo-, and, above all, 1-arylcyclohexenes. Irrespective of whether the hydrogen is removed as proton, atom, or hydride ion, the extra resonance stability available to a C-3 anion, radical, or cation over that available in the cross-conjugated C-6 position should favor its oxidation. Finally, the Schaefer mechanism does not explain the stereochemical results which are reported in this and the accompanying paper[13] (*vide infra*).

We wish to propose a different mechanism which appears to accommodate our stereochemical findings as well as all other information in the literature. It is shown in Scheme II with D-(+)-1-*p*-menthene (**16**) as substrate. Although the oxidant is here written as

SCHEME II



protonated selenium dioxide, it may instead well be some hydrated (or solvated) form of this, in which case the first two steps of the mechanism would be altered as shown below. Evidence in favor of a protonated



oxidant has previously been presented.[9] It should be noted that the first step does not imply a concerted 2 + 2 cycloaddition but rather a typical Markovnikov-type electrophilic addition with attack occurring through oxygen to generate positive character at the

(12) R. K. Callow, *J. Chem. Soc.*, 462 (1936).

(13) E. N. Trachtenberg and J. R. Carver, *J. Org. Chem.*, **35**, 1646 (1970).

tertiary carbon, followed by cyclization. In agreement with electrophilic attack are the observations that dienes are more reactive than olefins, olefin reactivity increases with alkyl substitution,[4] and electron-feeding groups slightly accelerate the rate of oxidation of **3**.[9] It is essential to the mechanism shown in Scheme II that the closure of the four-membered ring occur either before full carbonium-ion character develops at C-1 or more rapidly than a Wagner–Meerwein rearrangement can occur if carbonium-ion character does develop. If this were not the case, one would anticipate Wagner–Meerwein rearrangement in the oxidation of systems such as α- and β-pinene and typical camphene–isobornyl rearrangement in the oxidation of camphene. The latter is not observed, and only a small amount of rearranged product is formed in the pinene case.[14]

The postulated slow conversion of **17** (or **20**) into **18** is in agreement with the primary deuterium isotope effect reported by Schaefer.[9] It seems reasonable that this process should be slow for, although the breaking of the four-membered ring might provide some steric acceleration, the carbon–selenium bond which must be cleaved is very similar to that present in an alkylseleninic acid, and even benzylseleninic acid proves unreactive toward solvolysis.[15] It should be noted that, if the deprotonation step is slow in an acyclic system such as **3**, this will be accentuated in a cyclic system such as in the conversion of **17** (or **20**) into **18**. The carbon–hydrogen bond undergoing cleavage cannot become *trans* diaxial to the carbon–selenium bond in the preferred conformation for the transition state for elimination unless the isopropyl group also becomes axial. Thus, the molecule either is forced into this unfavorable conformation or else must undergo elimination through a less favorable conformational arrangement of departing groups. The latter might well happen if the necessary chair–chair interconversion introduces 1,3-*syn*-diaxial interactions or is otherwise prevented from occurring in *trans*-decalin or other conformationally frozen systems.

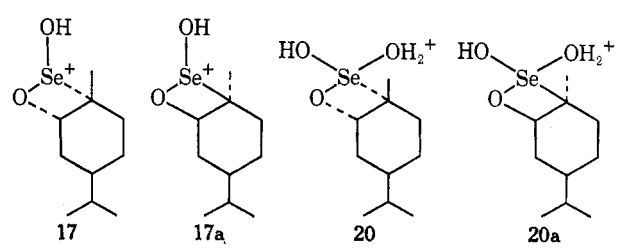
Finally, the postulated combined SN2′–SNi solvolysis of **18**, similar to a suggestion made by Schaefer, Horvath, and Klein,[9] is required by our observation that the major product from D-(+)-1-*p*-menthene is partially racemized D-(+)-*trans*-carvotanacetol when the reaction is carried out in wet dioxane. Since there is overall retention of configuration with respect to C-4, it follows that either zero or an even number of allylic rearrangements is occurring. Wiberg, who did a similar study, has nicely explained why it must be the latter.[8] It should be emphasized that the well-established stereochemistry of the SN2′ [16] requires that **18** have *trans* stereochemistry if the observed major product is *trans*-carvotanacetol. We cannot at this point eliminate another alternative for the last step of Scheme II in which SN2′ is replaced by SNi′; the stereochemical result is, however, the same.

The main reason for favoring the mechanism shown in Scheme II is that it permits us to explain the stereochemistry of the products observed in the oxidation of a number of cyclohexenyl systems. The results are shown in Table I; the details on **16** are given in the Experimental Section; and those on the other compounds are given in the accompanying paper.[13]

TABLE I

Olefin oxidized	Allylic alcohols produced and yields
21	**22**, 41%; **23**, 18%
16	**19**, 48%; **24**, 20%; **25**, 23%
26	**27**, 39%; **28**, 12%; **29**, 7%
30	**31**, 20%; **32**, 4.3%; **33**, 5.2%
34	**35**, 19%; **36**, 7%; **37**, 7%; **38**, 5%
39	**40**, 35%; **41**, 3%; **42**, 4.5%; **43**, 0.6%
44	**45**, 42%; **46**, 24%

If one makes the reasonable assumption that the steric requirements of selenium are greater than those of oxygen in intermediates such as **17** or **20** and that oxygen must attack the less substituted end of a trisubstituted double bond to get to the observed product with allylic substitution at C-6 and not C-3, there are two stereochemical possibilities, **17** and **17a** (or **20** and **20a**). Since **17** (or **20**) involves 1,3-diaxial interaction between oxygen at C-2 and hydrogen at C-4 and C-6,



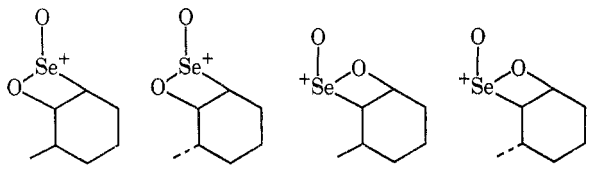
17 **17a** **20** **20a**

whereas **17a** (or **20a**) necessitates more serious interaction of selenium at C-1 with the C-3 and C-5 hydrogens, one predicts and finds that the preferred intermediate is that leading eventually to *trans*-carvotanacetol. The same argument applies to other 1,4-disubstituted cyclohexenes such as **21** and **26**, and again the results agree with the predictions based on the proposed intermediacy of an oxaselenocyclobutane. The 2.4-fold preference for **19** over **24** observed in the oxidation of **16** in wet dioxane is in substantial agreement with the ratio of 1.5 reported by Wiberg[8] who carried out the reaction in acetic acid–acetic anhydride. Under the

(14) See ref 4a, 4b, and 4c and references cited therein.
(15) C. L. Jackson, *Ann.*, **179**, 13 (1875).
(16) G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4609 (1956).

latter conditions, in contrast to ours, there is no further oxidation to carvotanacetone. Since we have observed that *cis*-carvotanacetol **24** is oxidized more rapidly than its epimer, the ratio when adjusted for selective further oxidation of **24** agrees exactly with Wiberg's result.

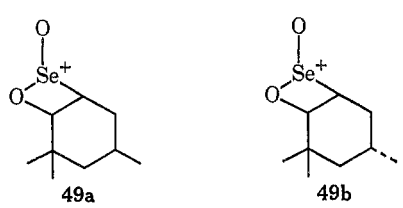
The situation becomes more complex with **30** since it is now possible, on electronic grounds, to add across the double bond in either direction as well as from either side. If one considers the preferred conformations for the four stereochemical possibilities (shown only for intermediates of the type **17** since the stereochemical arguments are the same for those of the type **20**), **47a** introduces a skew interaction between methyl and oxygen and two 1,3-diaxial interactions between oxygen



47a **47b** **48a** **48b**

and hydrogen, whereas epimer **47b** suffers from 1,3-diaxial interactions between selenium and hydrogen. Apparently, these about balance for the yields of **32** and **33**, derived from **47a** and **47b**, respectively, show almost no stereoselectivity. Of the two possible intermediates derived from addition in the opposite sense, **48a** has little to recommend it, but **48b** only involves 1,3-diaxial interactions between oxygen and hydrogen. In agreement with this, the yield of **31** is over twice the combined yields of **32** and **33**. It should be noted that it is not possible in this system to demonstrate that **48b**, rather than **48a**, is the precursor of **31**, but such distinction becomes possible in a study of *cis*-3,5-dimethylcyclohexene (**34**). Here again, there is almost no stereoselectivity observed in the secondary carbinol products **37** and **38**, and the tertiary products **35** and **36** are favored by over twofold. What is interesting is that the axial tertiary carbinol **35** derived from the analog of **48b** is favored over its epimer by almost threefold.

Equally interesting are the results with 3,3,5-trimethylcyclohexene (**39**). For steric reasons, the direction of addition is again fixed so that only the intermediates **49a** and **49b** are possible. Since **49a** introduces two 1,3-diaxial interactions between oxygen and hydrogen, whereas **49b** in one conformation introduces

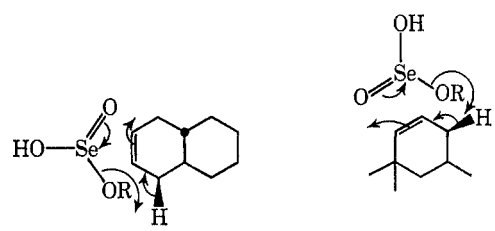


49a **49b**

1,3-diaxial interactions between methyls and in the other between methyl and selenium, the preference for **49a** should be more emphatic than in the other cases studied. Indeed, **40** is favored over **41** by over tenfold.

The case of *trans*-Δ^2-octalin (**44**) is instructive because symmetry makes the two directions of addition equivalent, conformation is fixed, and one can therefore get a measure of the difference between 1,3-diaxial interactions involving hydrogen with either selenium or oxygen. The preference for oxygen is such that the stereoselectivity is almost twofold.

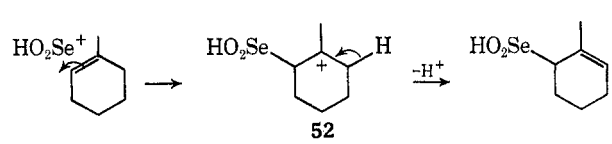
The characteristic feature of the mechanism which we are proposing is that it involves both ends of the double bond unsymmetrically. The intermediacy of an oxaselenocyclobutane had previously been considered by Schaefer and Horvath[17] but was rejected solely on the grounds that the evidence then available could be explained by a less complex intermediate. It is now useful to enquire whether other types of intermediates can accommodate our stereochemical findings as well as fit other literature evidence. We have already discussed some of the difficulties with Scheme I. As mentioned previously, this mechanism also breaks down on stereochemical grounds. If one assumes, as Schaefer did, that the attack must be axial for stereoelectronic reasons, one is unable to explain why a conformationally fixed system such as **44** shows only a twofold preference for axial product, whereas **39** gives over tenfold stereoselectivity. In the transition states for the two, **50** and **51**, respectively, axial attack would be from the top of the molecules as drawn.



50 **51**

Exactly the same types of 1,3-diaxial interactions between oxygen and hydrogen are introduced in both, but **51** additionally involves a skew interaction between oxygen and methyl. One is also unable to explain why the slightly preferred mode of attack in the case of **30** is equatorial.

Another mechanism which has previously been proposed involves attack by protonated selenium dioxide at the less substituted end of a trisubstituted double bond leading to an intermediate of the type **52**.[8]

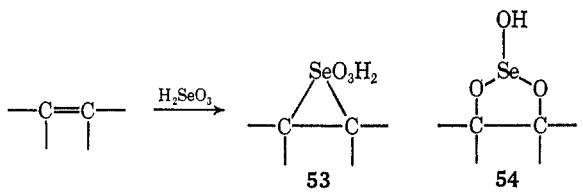


52

Some of the difficulties with this suggestion have already been pointed out elsewhere.[9] Additionally, this mechanism is unable to explain the stereochemical results whether one assumes that the group must preferentially come in axially or assumes no such preference. The same criticism applies to a similar sequence of reactions with attack through oxygen instead of selenium.[18]

Other types of mechanism which are excluded by our stereochemical findings are those involving symmetrical

(17) J. P. Schaefer and B. Horvath, *Tetrahedron Lett.*, 2023 (1964).
(18) E. N. Trachtenberg and C. H. Nelson, ref 1.



intermediates such as **53**[8] or **54**. As indicated above, stereoselectivity derives from differential steric demands of groups attached to the original olefinic carbons.

In conclusion, we find that intermediates which either involve both of the olefinic carbons symmetrically or alternately only involve one are incapable of explaining the observed stereoselectivity. We recognize that the energy factors involved must be relatively small, but all are in the right direction and relative magnitude. We also wish to reiterate that this discussion applies only to the low energy solvolytic mechanism and that we do not rule out the operation of a pyrolytic pathway leading through organoselenium compounds and also producing allylic oxidation products.

Experimental Section

Infrared spectra were obtained on thin liquid films with a Perkin-Elmer Infracord. Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Nuclear magnetic resonance spectra were determined with a Varian HA-60 or a Jeolco JNM C-60H on samples dissolved in deuteriochloroform containing tetramethylsilane (TMS) as internal standard. Optical rotations were determined on benzene solutions (unless otherwise noted) with a Rudolph Model 80 CSPI photoelectric polarimeter, and refractive indices were measured on a Bausch and Lomb Abbe 3L refractometer. Melting points were determined in soft glass capillaries on a Thomas–Hoover apparatus and are corrected. Microanalyses were performed by the Alfred Bernhardt Microanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany.

Gas chromatographic analyses and separations were performed on a Wilkens–Varian Model A-700 Autoprep packed with the Wilkens–Varian materials specified below and equipped with a thermal conductivity detector with helium gas as carrier. Peak areas were determined by cutting out the peaks and weighing them or, in the case of sharp symmetrical peaks, by measuring peak height. Calibration curves for each compound in the appropriate solution were prepared to determine the proportionality between peak area and concentration in the concentration range encountered in these experiments. The preparative column used was $^3/_8$ inch by 10 ft stainless steel containing 20% FFAP (free fatty acid phase of Carbowax) on 60–80 mesh Chromosorb W, acid washed and treated with DMCS (dimethyldichlorosilane). The analytical column used was $^1/_4$ inch by 10 ft aluminum containing 15% FFAP on 60–80 mesh Chromosorb W.

D-(+)-1-*p*-Menthene (16).—Redistilled D-(+)-limonene (**26**, Eastman White Label) was selectively catalytically reduced by the method of Newhall[19] with the uptake of 1 mol of hydrogen. The product was vacuum fractionated through a 100-mm Vigreux column to give **16** (91%) as a colorless liquid, bp 66–67° (1 mm), $n^{20}D$ 1.4566 (lit.[20] $n^{20}D$ 1.4570), $[\alpha]^{24}D$ +100.2° (*c* 9) (lit.[19,20] $[\alpha]^{23}D$ +95.8°, $[\alpha]^{25}D$ +109°).

Selenium Dioxide Oxidation of D-(+)-1-*p*-Menthene (16) in Wet Dioxane.—A solution of selenious acid made by warming 0.740 g (6.6 mmol) of Fairmount selenium dioxide in 0.5 ml of water and 10.0 ml of dioxane, purified by the method of Vogel,[21] was added dropwise over a 3-hr period to a magnetically stirred, refluxing solution of 7.4 g (53 mmol) of **16** in 10.0 ml of purified dioxane. It was determined in separate experiments that Fairmount selenium dioxide could be used without further purification as it gave identical results with those obtained with freshly sublimed material prepared by the oxidation of selenium metal with hot concentrated nitric acid by the method of Baker and Maxson.[22] On addition of the selenious acid, the solution rapidly yellowed and the color then intensified to orange and then red as selenium precipitated during the subsequent 12–20-hr period of refluxing. Glpc analysis showed 83.7 ± 1.1% of recovered **16** in addition to four oxidation products (*t* 142°), peak 1 (1.5%, R_t 9.0 min), peak 2 (7.7%, R_t 10.5 min), peak 3 (3.3%, R_t 13.2 min), and peak 4 (3.8%, R_t 21.9 min). The crude product was vacuum distilled through a 100-mm Claisen column to yield fraction 1, bp <25° (1–2 mm), consisting of dioxane, water, and some unreacted **16**, fraction 2, bp 37–88° (1 mm), consisting of unreacted **16** and its volatile oxidation products, and a residue consisting of selenium and organoselenium compounds. It was necessary to do this crude distillation to avoid contamination of the preparative glpc column by noneluting organoselenium by-products. The glpc peak ratios on both crude and distilled products agreed, indicating lack of decomposition or isomerization during distillation.

Peak 1 was D-(+)-carvotanacetone (**55**), identified by glpc peak enhancement and ir comparison with an authentic sample prepared by selective hydrogenation of Aldrich glpc unipeak D-(+)-carvone (**56**) over 5% Pt on carbon and having physical and spectral properties in agreement with those of **55** reported by Hallsworth.[23] If the oxidation was carried out at increasingly higher selenium dioxide/olefin ratios, peak 1 became correspondingly larger with concomitant disappearance of both peaks 2 and 3. Thus, at an olefin/selenium dioxide ratio of 3:2, peaks 2 and 3 were absent; peak 1 from a reaction with this stoichiometry was glpc collected and showed $[\alpha]^{24}D$ +37.6° (*c* 1.6) (lit.[23,24] $[\alpha]^{25}D$ +55.2°, $[\alpha]^{25}D$ +49.5°). Its physical and spectral properties were identical with those of authentic **55**.

Peak 2 was D-(+)-*trans*-carvotanacetol (**19**), $n^{20}D$ 1.4779 (lit.[20] $n^{20}D$ 1.4777), $[\alpha]^{25}D$ +97.8° (*c* 2) (lit.[25] $[\alpha]^{20}D$ +169.1°). Its ir[26] and nmr[27] spectra agreed with literature reports and its α-naphthylurethan had mp 129–130° which was not depressed upon admixture of a sample with that prepared from authentic **19** made by the method of Schroeter.[25]

Peak 3 was D-(+)-*cis*-carvotanacetol (**24**), $n^{20}D$ 1.4805 (lit.[25] $n^{20}D$ 1.4817), $[\alpha]^{25}D$ +32.2° (*c* 5) (lit.[23] $[\alpha]D$ +56.5°). Its ir[26] and nmr[27] spectra agreed with reported spectra and its α-naphthylurethan had mp 122.5–123.5° which was not depressed upon admixture of a sample with that prepared from authentic **24** made by the method of Schroeter.[25]

Peak 4 was D-(+)-phellandrol (**25**), $n^{20}D$ 1.4810 (lit.[28] $n^{20}D$ 1.4826), $[\alpha]^{25}D$ +76.8° (*c* 5) {lit.[29] $[\alpha]^{20}D$ +102.8° (neat)}. Its ir spectrum agreed with that reported by Mitzner;[26] its nmr ($CDCl_3$) spectrum consisted of δ 5.53 (broad s, 1, C=CH), 3.80 (s, 2, CH_2OH), 3.07 (s, 1, OH), 1.17–2.40 (broad band, 8, CH, CH_2), and 0.85 [d, 6, $CH(CH_3)_2$]. Its phenylurethan had mp 76–77° (lit.[28] mp 79°) and its α-naphthylurethan had mp 65–67° (lit.[28] mp 69.5°).

Selenium Dioxide Oxidation of D-(+)-*trans*-Carvotanacetol (19) and of D-(+)-*cis*-Carvotanacetol (24).—A solution of 0.2 g (1.8 mmol) of selenium dioxide in 0.2 ml of water and 10.0 ml of dioxane was added to a solution of 1.0 g (6.7 mmol) of an equimolar mixture of **19** and **24** in 5.0 ml of dioxane. The solution rapidly yellowed and the color intensified to orange and then red as selenium precipitated during the 1-hr period of refluxing. Glpc analysis of the crude product (*t* 142°) showed the presence of D-(+)-carvotanacetone (**55**) and of **19** but of very little **24** as determined by peak enhancement with authentic samples.

Selenium Dioxide Oxidation of D-(+)-1-*p*-Menthene (16) in Acetic Acid–Acetic Anhydride.—A solution of 23 g (0.17 mol) of **16** in 50:50 (v/v) acetic acid–acetic anhydride was oxidized with 13.9 g (0.125 mol) of selenium dioxide at room temperature for 10 hr. The reaction was quite exothermic and required cooling in an ice bath. The crude product was filtered several times

(19) W. Newhall, *J. Org. Chem.*, **23**, 1274 (1958).
(20) R. L. Kenney and G. S. Fisher, *ibid.*, **28**, 3509 (1963).
(21) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1956, p 177.
(22) R. H. Baker and R. N. Maxson, *Inorg. Syn.*, **1**, 119 (1939).
(23) A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *J. Chem. Soc.*, 1969 (1957).
(24) C. Harries, *Chem. Ber.*, **34**, 1924 (1901).
(25) S. Schroeter, *Ann.*, **674**, 118 (1964).
(26) B. M. Mitzner, V. J. Mancini, S. Lemberg, and E. T. Theimer, *Appl. Spectrosc.*, **22**, 34 (1968).
(27) S. H. Schroeter and E. L. Eliel, *J. Org. Chem.*, **30**, 1 (1965).
(28) J. P. E. Human, A. K. Macbeth, and H. J. Rodda, *J. Chem. Soc.*, 350 (1949).
(29) F. Porsch, *Dragoco Report*, 59 (1964); *Chem. Abstr.*, **61**, 16099*d* (1964).

through Celite until clear and the filtrate, diluted with ether, was washed with water until the washings were neutral. The ethereal solution was then dried (sodium sulfate), filtered, and rotary evaporated to an oil which was vacuum fractionated to afford 3.65 g (15%) of a mixture of carvotanacetol acetates, bp 79–81° (5 mm), $[\alpha]^{25}D$ 0.0°.

Selenium Dioxide Oxidation of D-(+)-1-*p*-Menthene (16) in Wet Dioxane in the Presence of Acrylonitrile.—To a solution of 10 g (0.070 mol) of **16** in 80 ml of purified dioxane maintained under an atmosphere of nitrogen was added 2.0 ml (0.03 mol) of acrylonitrile [Eastman practical grade freshly distilled (bp 75–76°) just prior to use to remove inhibitor]. Both the dioxane and **16** were peroxide free as determined by negative test with acidified potassium iodide. To the solution of **16** was added dropwise a solution of 8.0 g (0.07 mol) of selenium dioxide in 200 ml of purified dioxane containing 5.0 ml of distilled water. The reaction was maintained under nitrogen at ambient temperature for several days. Under these conditions, **16** was oxidized to a mixture of *cis*- and *trans*-carvotanacetols, phellandrol, and carvotanacetone (*vide supra*) but no polyacrylonitrile precipitated. It was determined in control experiments that polyacrylonitrile is highly insoluble in this medium and would have been readily discernible had initiation of polymerization occurred. It was further established that acrylonitrile polymerizes rapidly under the same reaction conditions if a source of free radicals in introduced. Indeed, a solution of 2.0 ml of freshly distilled acrylonitrile in 280 ml of purified dioxane maintained under a nitrogen atmosphere at 40° gave an immediate precipitate when successively treated with 0.3 g of potassium persulfate in 10 ml of aqueous dioxane and 0.15 g of sodium bisulfite in 10 ml of aqueous dioxane.

Registry No.—Selenium dioxide, 7446-08-4; **16**, 1195-31-9; **21**, 23713-54-4; **26**, 23713-55-5; **30**, 23713-56-6; **34**, 23713-57-7; **39**, 23713-58-8; **44**, 2001-50-5.

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Micellar Effects on the Hydrolysis of 2,4-Dinitrophenyl Sulfate[1]

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Hexadecyltrimethylammonium bromide (CTAB) and poly(oxyethylene)(24)dinonylphenol (DNPE) enhance the rate of neutral hydrolysis of 2,4-dinitrophenyl sulfate by factors of 3.2 and 2.6, respectively, but sodium dodecyl sulfate (NaLS) has no effect on the rate. The rate enhancement arises from a decrease in both the enthalpy and entropy of activation. From the kinetic data at 25.00°, the binding constant between CTAB and 2,4-dinitrophenyl sulfate is calculated to be 1.9×10^5 l. mol^{-1}. The effects of these surfactants on the acid- and base-catalyzed hydrolysis of 2,4-dinitrophenyl sulfate are less specific; both charged and uncharged micelles enhance the rate of the acid-catalyzed reaction, while the base-catalyzed rate is only affected by DNPE. The retardation of the base-catalyzed hydrolysis by DNPE is a manifestation of an increase in both the enthalpy and entropy of activation with respect to the base-catalyzed hydrolysis in the absence of surfactant. Micellar effects on the hydrolyses of sulfate esters are compared with those on aryl phosphates and are discussed in terms of electrostatic and hydrophobic interactions.

The recent vigorous interest in micellar effects on reaction rates has been stimulated by the recognized analogies between protein and micelle structures and between enzymatic and micellar catalysis.[2] The influence of surfactants on the hydrolysis of aryl phosphates has been shown to be specific. Hexadecyltrimethylammonium bromide (CTAB) increases the rate constants for the dianion hydrolysis of 2,4- and 2,6-dinitrophenyl phosphate by a factor of 25 but does not affect the hydroxide ion catalyzed reaction of the dianion or the hydrolysis of the monoanion of *p*-nitrophenyl phosphate, whereas sodium dodecyl sulfate (NaLS) and poly(oxyethylene)(24)dinonylphenol (Igepal DM-730), a nonionic amphiphile, do not significantly alter the rates of hydrolysis of dinitrophenyl phosphate dianions.[3] Since a number of analogies can be made between the mechanisms for the hydrolyses of sulfate[4] and phosphate esters and since both reactions are of vital importance in biochemical processes, we have undertaken a study of micellar effects on the neutral, acid-catalyzed, and base-catalyzed hydrolysis of 2,4-dinitrophenyl sulfate in order to compare these two systems and to elucidate the nature of micellar catalysis.

Experimental Section

The preparation and purification of 2,4-dinitrophenyl sulfate has been described.[4] Hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (NaLS) were purified by the method of Duynstee and Grunwald.[5] Poly(oxyethylene)-(24)dinonylphenol (Igepal DM-730, General Aniline and Film Corp.) was used without further purification[6] and is denoted as DNPE in the text. Deionized distilled water was used for the preparation of the buffer, the surfactant, and the standard acid and alkali solutions. The pH of the buffer solutions was adjusted by the addition of hydrochloric acid or sodium hydroxide at 25.0° using an Orion Model 801 pH meter. The concentrations of the acid solutions were determined by titration with standard 0.100 or 1.00 *M* NaOH (BDH) using Lacmoid as the indicator. The alkali solutions were prepared from the 1.00 *M* NaOH standard by dilution.

The hydrolysis was followed spectrophotometrically on a Beckman DU-2 by measuring the absorbance of the phenoxide ion (360 nm) or the phenol (320 nm).[4] The temperature of the thermostated baths and the cell compartment was maintained within ±0.05°, as monitored by NBS thermometers. Good first-order plots were obtained in all cases for at least 75% reaction. The pseudo-first-order rate constants, k_ψ, for the hydrolysis of 2,4-dinitrophenyl sulfate have been calculated by the Guggenheim method.[7]

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(2) For a comprehensive review of micellar effects on reaction rates, see E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

(3) C. A. Bunton, E. J. Fendler, L. Sepulveda, and K.-U. Yang, *J. Amer. Chem. Soc.*, **90**, 5512 (1968).

(4) E. J. Fendler and J. H. Fendler, *J. Org. Chem.*, **32**, 3852 (1968).

(5) E. F. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, **81**, 4540 (1959).

(6) We are greatly indebted to Dr. L. W. Burnette of the General Aniline and Film Corp. for providing us with samples of nonionic surfactants.

(7) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).