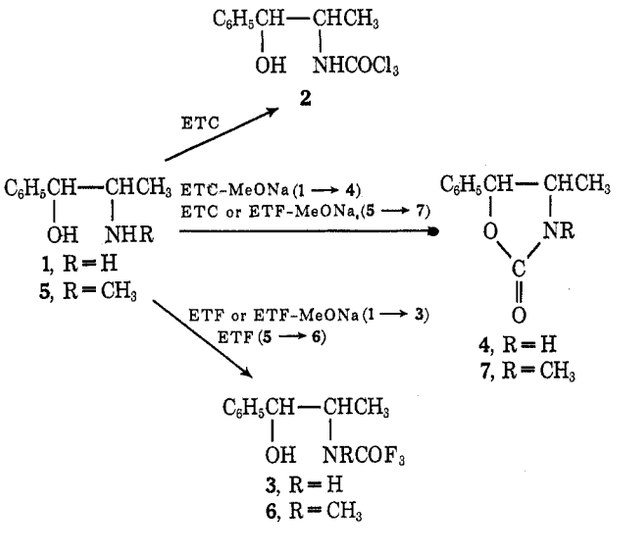

in the presence of sodium methoxide.[3] The same oxazolidinone **7** was obtained by treatment of **5** with ETC also in absence of sodium methoxide.

The isolation of **6** and the tlc identification of **2** during the base-catalyzed reaction of **5** with ETF and **1** with ETC, respectively, indicates that the formation of the 2-oxazolidinones proceeds through the corresponding trihaloacetamides.[4]

The conversion of *N*-benzylethanolamines to oxazolidinones has been suggested to occur either through an initial O-acylation, followed by splitting of chloroform, or through an initial haloform-type cleavage to a *N*-carboethoxy derivative, followed by an intramolecular alcoholysis.[1] Our results do not support these hypotheses, but suggest a reaction pattern involving an initial aminolysis of the halo ester, followed by a nucleophilic intramolecular attack by the alkoxide ion on the carbonyl group and loss of haloform.

Deprotonation at nitrogen may compete with cyclization in the case of the secondary trihaloacetamides[5] and this may account for their reduced ability to afford 2-oxazolidinones. A stronger inductive effect favors the N deprotonation of trifluoro- more than trichloroacetamides. This may contribute to the failure of **3** to cyclize, although the greater reactivity of trichloro- *vs.* trifluoroacetamides can be more generally determined by the superior leaving group ability of the trichloromethyl moiety.[6]

Experimental Section

Melting points were taken in a capillary apparatus and are uncorrected. Optical rotations were determined in dioxane at 24° unless otherwise stated. Ir spectra were measured in Nujol mull on a Perkin-Elmer 457 instrument. Tlc was run with 9:1 benzene–acetone on 250-μ-thick layers of silica gel (C. Erba, Milan, Italy), containing 1% fluorescence indicator (S5 grün/1, Leuchstoffwerk GmbH and Co., Heidelberg, West Germany) and spots were visualized under short-wave uv light (254 mμ). Microanalyses were performed by Ilse Beetz Microanalytisches Laboratorium, Kronach, West Germany.

DL-**Trifluoro-*N*-(2-hydroxy-1-methyl-2-phenylethyl)acetamide** (**3**).—A solution of **1** (1 g) in ETF (5 ml) and EtOH (2 ml) was kept at room temperature for 60 min. Evaporation of the solvent under reduced pressure afforded **3** (1.5 g, 91.7%): mp 131–132° (benzene); ν_{max} 3460, 3230, 3100, 1700 cm^{-1}.

Anal. Calcd for $C_{11}H_{12}F_3NO_2$: C, 53.44; H, 4.78; N, 5.66. Found: C, 53.37; H, 4.81; N, 5.64.

Following the same procedure but using ETC, trichloroacetamide **2** was obtained (60%): mp 72–76° (hexane); ν_{max} 3420, 3300, 1680 cm^{-1}. This compound was fully characterized as the *O*-benzoate: mp 148–150° (MeOH); ν_{max} 3460, 1710, 1690 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}Cl_3NO_3$: C, 53.96; H, 4.02; Cl, 26.55; N, 3.49. Found: C, 53.79; H, 4.06; Cl, 26.73; N, 3.35.

L-**Trifluoro-*N*-(2-hydroxy-1-methyl-2-phenylethyl)-*N*-methylacetamide** (**6**).—A solution of **5** (7 g) in ETF (10 ml) was kept at room temperature for 150 min and then processed as above to give **6** (10 g, 90.3%): mp 63–65° (hexane); ν_{max} 3440, 1680 cm^{-1}; $[\alpha]_D$ −8° (*c* 4).

Anal. Calcd for $C_{12}H_{14}F_3NO_2$: C, 55.17; H, 5.40; N, 5.36. Found: C, 54.92; H, 5.64; N, 5.26.

The *O*-benzoate had mp 111–113° (MeOH); ν_{max} 1728, 1685 cm^{-1}; $[\alpha]_D$ +36° (*c* 1).

Anal. Calcd for $C_{19}H_{18}F_3NO_3$: C, 62.47; H, 4.96; N, 3.38. Found: C, 62.42; H, 4.90; N, 3.80

DL-**4-Methyl-5-phenyloxazolidin-2-one** (**4**).—A solution of **1** (3.02 g) in ETC (2.1 ml) was treated with 1 *M* MeONa (2 ml) and kept at room temperature for 150 min. Concentration under reduced pressure and dilution with water afforded **4** (2.9 g, 82%): mp 147–149° (benzene) (lit.[7] mp 145–147°); ν_{max} 3380, 1745, 1720 cm^{-1}. Tlc at 30-min intervals revealed the presence of amide **2**, which disappeared at the end of the reaction.

L-**3,4-Dimethyl-5-phenyloxazolidin-2-one** (**7**).—A solution of **5** (4 g) in ETF (6 ml) was treated with 1 *M* MeONa (3 ml), kept under stirring at room temperature for 150 min, and worked up as above to give **7** (4.3 g, 93%): mp 91–92° (EtOH); $[\alpha]_D$ −125° (*c* 1, $CHCl_3$); ν_{max} 1735 cm^{-1} [lit.[8] mp 91–92°; $[\alpha]^{20}D$ −110.6° ($CHCl_3$)].

When the reaction was allowed to proceed for only 5 min, the trifluoroacetamide **6** was isolated.

B.—A solution of **5** (3 g) in ETC (2.1 ml) was kept at room temperature for 180 min and worked up as above to yield **7** (2.6 g, 75%), mp 90–92°.

Registry No.—**1**, 14838-15-4; **2**, 39663-72-4; **2** *O*-benzoate, 39663-73-5; **3**, 39663-74-6; **4**, 39663-75-7; **5**, 299-42-3; **6**, 39663-77-9; **6** *O*-benzoate, 39663-78-0; **7**, 16251-46-0; ETF, 383-63-1; ETC, 575-84-4.

(3) *N*-Benzylethanolamine has been reported to afford the corresponding salt by reaction with ETF.[1]

(4) Evidence for the formation of an intermediate showing tlc behavior reasonable for the trichloroacetamido derivative was obtained also in the reaction of **5** with ETC.

(5) *Cf.* S. S. Biechler and R. W. Jaft, Jr., *J. Amer. Chem. Soc.*, **79**, 4927 (1957).

(6) *Cf.* C. A. Panetta and T. G. Casanova, *J. Org. Chem.*, **35**, 4275 (1970).

(7) A. H. Homeyer, U. S. Patent 2,399,118 (1946); *Chem. Abstr.*, **40**, 4084 (1946).

(8) J. B. Hyne, *J. Amer. Chem. Soc.*, **81**, 6058 (1959).

Cyclohexadienyl Cations. V. Concerning the Acidity Dependence of the Dienone–Phenol Rearrangement

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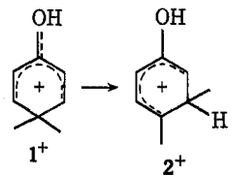
In the previous papers[1,2] in this series we have suggested that the kinetic acidity dependence in concentrated acid solutions of the acid-catalyzed dienone–phenol rearrangement can be understood in terms of two factors: (a) the equilibrium protonation acidity

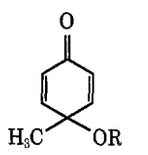
(1) V. P. Vitullo and E. A. Logue, *J. Org. Chem.*, **37**, 3339 (1972).

(2) V. P. Vitullo and N. Grossman, *J. Amer. Chem. Soc.*, **94**, 3844 (1972).

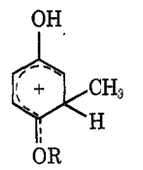
dependence of cyclohexadienones[3-6] and (b) a kinetically inverse dependence on the water activity of the medium. Since the rate-determining step[7] in the dienone–phenol rearrangement involves alkyl migration from C-4 to C-3 in the protonated dienone (eq 1) we suggested[1,2] that the inverse dependence on



(1)



3-OCH_3, R = CH_3
3-OH, R = H



3-OCH_3^+, R = CH_3
3-OH^+, R = H

water activity resulted from the desolvation of the hydroxy group in the protonated dienone whose acidity is substantially reduced in the transition state. Although solvation through acidic OH groups has been shown[8] to be an important factor in determining the acidity dependence of reactions occurring in moderately concentrated acid solutions, we wished to obtain more direct information regarding the importance of this effect in determining the acidity dependence of the dienone–phenol rearrangement.

In an earlier paper[1] we have reported our studies of the dienone–phenol rearrangement of 4-methoxy-4-methylcyclohexadienone (3-OCH_3). This substrate rearranges in acid solution with exclusive methyl migration. Although this dienone is substantially less basic than 4,4-dimethylcyclohexadienone,[4] the kinetic acidity dependence for its rearrangement could be understood in terms of the two factors discussed above. In this note we report kinetic data for a structurally similar system, 4-hydroxy-4-methylcyclohexadienone (3-OH), which bears directly on the problem of interpreting the acidity dependence of the dienone–phenol rearrangement.

The intrinsic basicities of 3-OCH_3 and 3-OH are expected to be similar, and, since the 4-OH group in 3-OH is insulated from the positive charge in the protonated species, there should be little difference in the equilibrium protonation acidity dependence for 3-OCH_3 and 3-OH. Thus, any differences in the kinetic acidity dependence for these substrates should reflect differences in transition state solvation. The kinetic data for the rearrangement of 3-OH are recorded in Table I.

In the acidity range 37.9–59.7 wt % $HClO_4$ plots of log k_{obsd} against $-H_0$ (the Hammett acidity function) are linear and less than 20% of either substrate

(3) V. P. Vitullo, *J. Org. Chem.*, **34**, 224 (1969).
(4) V. P. Vitullo, *J. Org. Chem.*, **35**, 3976 (1970).
(5) K. L. Cook and A. J. Waring, *Tetrahedron Lett.*, 1675 (1971).
(6) K. L. Cook and A. J. Waring, *Tetrahedron Lett.*, 3359 (1971).
(7) V. P. Vitullo and N. Grossman, *Tetrahedron Lett.*, 1559 (1970).
(8) A. J. Kresge, H. J. Chen, L. E. Hakka, and J. E. Kouba, *J. Amer. Chem. Soc.*, **93**, 6174 (1971); A. J. Kresge, S. Mylonakis, Y. Sato, and V. P. Vitullo, *ibid.*, **93**, 6181 (1971), and references cited therein.

TABLE I
RATES OF REARRANGEMENT OF 4-HYDROXY-4-METHYL-CYCLOHEXADIENONE IN PERCHLORIC ACID AT 25.1 ± 0.1°

$10^4 k_{obsd}$, sec^{-1}	Wt % $HClO_4$	$-H_0$[a]
0.576	37.93	2.18
1.07	41.68	2.54
1.94	44.82	2.84
4.01	47.84	3.20
12.0	52.53	3.92
30.2	55.01	4.28
120.0	59.53	5.16
343.0	62.70	5.86

[a] K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

is protonated. A summary of the kinetic acidity dependence data for both 3-OCH_3[9] and 3-OH is given below (eq 2 and 3).

$$\text{3-}OCH_3 \log k_{obsd} = (-7.17 \pm 0.14) - (0.92 \pm 0.04)H_0 \quad (2)$$

$$\text{3-OH, } \log k_{obsd} = (-5.94 \pm 0.05) - (0.78 \pm 0.02)H_0 \quad (3)$$

The acidity dependence is considerably less steep for the rearrangement of 3-OH, suggesting that the transition state of 3-OH is more extensively solvated[8] than the transition state for 3-OCH_3. Migration of the methyl group in protonated 3-OH and 3-OCH_3 yields the isomeric ions 3-OH^+ and 3-OCH_3^+. Interestingly, both ions are stabilized by the delocalization of the nonbonded electrons of the oxygen of C-4. Thus, for 3-OH methyl migration reduces the acidity of the C-1 hydroxy group but increases the acidity of the hydroxy group at C-4. This additional mechanism for the solvation of the transition state for 3-OH will result in a shallower acidity dependence for 3-OH compared to substrates for which this additional mode of solvation is not possible. In 3-OCH_3 solvation through hydrogen bonding with the partially positively charged methoxy group at C-4 formed in the transition state is not possible and the acidity dependence for the rearrangement of 3-OCH_3 is correspondingly steeper.

It is interesting to note that even in 3-OH *some* net desolvation attends the formation of the transition state from protonated 3-OH. If this were not the case, the kinetic acidity dependence would be the same as the protonation equilibrium acidity dependence (*i.e.*, the plot of log k_{obsd} *vs.* $-H_0$ would have a slope of *ca.* 0.6[3-6]).

These results clearly implicate solvation as one of the most dominant factors governing the acidity dependence of this A-1 reaction.

Experimental Section

4-Hydroxy-4-methylcyclohexadienone.—This material was prepared according to Goodwin and Witkop.[10] Our product had mp 74–77° after sublimation and recrystallization from CCl_4 (lit. mp 76–78°,[10] 75–76°[11]): ir ($CDCl_3$) 3580, 3400 (broad), 1665, 1630 cm^{-1}.

Kinetics.—The kinetics were followed by monitoring the loss of dienone spectrophotometrically (Gilford Model 2400) as described in a previous publication.[2] In most cases results reported in Table I are the average of three determinations.

(9) Data from ref 1.
(10) S. Goodwin and B. Witkop, *J. Amer. Chem. Soc.*, **79**, 179 (1957).
(11) F. Wessley and F. Sinwell, *Monatsh. Chem.*, **81**, 1055 (1950).

Registry No.—4-Hydroxy-4-methylcyclohexadienone, 23438-23-5.

Acknowledgment.—We wish to thank the National Science Foundation for support of this work (Grant No. GP-29738X).

A Simple Procedure for the Epoxidation of Acid-Sensitive Olefinic Compounds with *m*-Chloroperbenzoic Acid in an Alkaline Biphasic Solvent System[1]

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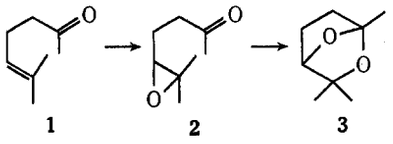
Received March 7, 1973

The epoxidation of acid-sensitive olefins or the epoxidation of olefins yielding acid-sensitive epoxides are typically conducted in the presence of a buffer such as solid sodium carbonate, sodium bicarbonate, or disodium hydrogen phosphate.[2] During the course of our research we found the solid buffer–single solvent procedure to be unsuited for certain acid-sensitive compounds. We wish to report a mild and simple epoxidation procedure using a two-phase system which proved superior to the single solvent method for the epoxidation of acid-sensitive compounds.

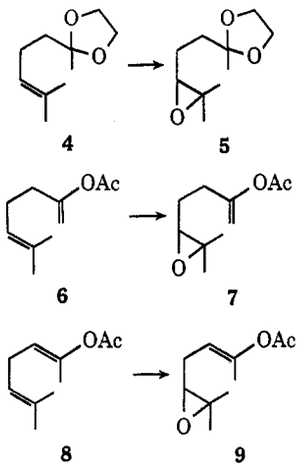
The epoxide **2**, derived from 6-methylhept-5-en-2-one (**1**), is known to undergo very facile rearrangement to 1,3,3-trimethyl-2,7-dioxabicyclo[2.2.1]heptane (**3**).[3] This rearrangement occurs thermally and is acid catalyzed. The preparation of the unstable epoxide, **2**, has previously been accomplished by careful epoxidation of **1** in methylene chloride using peracetic acid–sodium acetate.[3a] When we attempted to prepare **2** using *m*-chloroperbenzoic acid–sodium bicarbonate we obtained a mixture of **2** and **3** in approximately



1 **2** **3**

equal proportion (as estimated by nmr[4]). Epoxidation of **1** with *m*-chloroperbenzoic acid in a dichloromethane–aqueous sodium bicarbonate biphasic system led to the formation of **2** in high yield (83–85%) with no detectable amounts of the rearranged product, **3**.[4]

Similar biphase epoxidation of the ketal **4** and enol acetates **6** and **8** proceeded smoothly to give **5**, **7**, and **9**, respectively, in 80–85% yields.[5,6]



4 **5**

6 **7**

8 **9**

In a study of the scope of this reaction we examined the biphasic epoxidation of simple mono-, di-, and trisubstituted olefins.[7] Table I[8] gives the results

TABLE I

TWO-PHASE EPOXIDATION OF OLEFINS WITH *m*-CHLOROPERBENZOIC ACID

Compd	Olefin–peracid ratio, *M*	Reaction time, hr	Product[a]	Yield, %[b]
Cyclohexene	1:1	4	Cyclohexene oxide[c,e]	71
1-Hexene	1:1	9	1,2-Epoxyhexane[d]	56
Limonene	1:1	2	1,2-Epoxy-*p*-menth-8-ene[e]	85
Limonene	1:2	4	1,2,8,9-Diepoxy-*p*-menthane[e]	66
Limonene	1:3	4	1,2,8,9-Diepoxy-*p*-menthane[e]	68

[a] Products were characterized by nmr, ir, glc, and mass spectrometry. [b] Yields were calculated by glc. [c] Reference 8a. [d] Reference 8b. [e] Reference 8c.

of this study and it is evident that the two-phase epoxidation procedure can be extended to mono- and disubstituted olefins. Furthermore, the yields of epoxides were comparable to those obtained by a single solvent procedure.[8]

In the case of limonene (*p*-mentha-1,8-diene) the two-phase epoxidation procedure was compared with the epoxidation using *m*-chloroperbenzoic acid in dichloromethane. With 1 equiv of peracid both procedures gave selective epoxidation of the trisubstituted double bond in identical yields (a slightly longer reaction time was required in the two-phase system).

(1) This research was supported by Grant 1 R01 CA11880 from the National Cancer Institute, National Institutes of Health.

(2) D. Swern in "Organic Peroxides," Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, pp 355–533.

(3) (a) E. Klein and W. Rojahn, *Dragoco Rep. Engl. Ed.*, **14**, 155 (1967); (b) Y. Gaoni, *J. Chem. Soc. C*, 2925 (1968).

(4) 5,6-Epoxy-6-methylhepten-2-one (**2**) quantitatively rearranged to **3** during attempted glc analysis; so the crude reaction mixture, following work-up, was analyzed by nmr. In the nmr spectrum of **2** (CCl_4) the C-1 methyl appeared at τ 7.87 and in the spectrum of **3** the C-1 methyl appeared at τ 8.52.

(5) **4** was prepared from **1** by *p*-toluenesulfonic acid catalyzed ketalization; **6** and **8** were prepared from **1** by BF_3-catalyzed enol acetylation (the two isomers could be separated by spinning band distillation and preparative glc). All compounds were characterized by mass spectrometry, ir, and nmr (including spin-decoupling studies).

(6) For an example of epoxidation of an isolated double bond in the presence of an enol acetate, see R. B. Moffet and G. Slomp, Jr., *J. Amer. Chem. Soc.*, **76**, 3678 (1954).

(7) Water is known to decrease the rate of peracid epoxidation of olefins and the presence of aqueous sodium bicarbonate would be expected to increase the rate of peracid decomposition.[2]

(8) (a) G. B. Payne, P. H. Deming, and P. H. Williams, *J. Org. Chem.*, **26**, 659 (1961); (b) D. J. Pasto and C. C. Cumbo, *ibid.*, **30**, 1271 (1965); (c) B. A. Arbuzov and B. M. Mikhailow, *J. Prakt. Chem.*, **127**, 92 (1932) [*cf. Chem. Abstr.*, **24**, 4285 (1932)].