curred. However, since the time required for bromination was very short, the effect of evaporation was negligible.

All brominations requiring the absence of light were carried out in a dark room with a photographic safelight.

Procedure for Analyses of Products.—The vpc analysis of the dibromides was accomplished with an Aerograph 90 P-3 chromatograph under the following conditions: flow rate (He) 300 cc/min; column length and diameter, 6 ft × 0.25 in.; column temperature, 50°; column composition, 2.5% SE-30 on 60–80 mesh DMCS Chromosorb W. Under these conditions the retention times of **1**, **2**, and **3** are, respectively, 108, 297, and 247 sec. The retention time of α-bromoethylbenzene was 372 sec.

None of the dibromides rearranged under the conditions of analysis. This was determined by collecting the dibromide mixture after it had passed through the chromatograph and observing that no change in composition had occurred on reinjection.

The percentages of the dibromides were based on their adjusted areas in the chromatograms. The adjustments were based on the following determination: the ratio of A_1/A_2 divided by W_1/W_2 is equal to 0.85. The area/weight ratio for dibromides **2** and **3** was assumed to be unity on the basis of their similar molecular structures.

The relative reactivities of butadiene and ethylbenzene were determined from the following expression where C_8H_9Br refers

$$\left[\frac{2(1+2+3)}{(C_8H_9Br)}\right]\left[\frac{(C_8H_{10})_0}{(C_4H_6)_0}\right]$$

to the quantity of α-bromoethylbenzene formed in the reaction, and $(C_8H_{10})_0$ and $(C_4H_6)_0$ refer to the initial concentrations of ethylbenzene and butadiene, respectively.

The Authentic Dibromide Isomers.—Dibromides **1** and **2** were prepared according to the methods described by Hatch, *et al.*[2] Dibromide **3** was prepared as described by Valette.[8] The peaks assigned to dibromides **1** and **2** were confirmed by comparison of their retention times with those of authentic samples, and by collecting the compounds as they emerged from the vpc and comparing the absorption bands in their infrared spectra with the reported absorption bands.[2] The peak assigned to dibromide **3** was done so on the basis of a comparison of its retention with that of authentic **3**.

Registry No.—Butadiene, 106-99-0; **1**, 10463-48-6; **2**, 821-06-7; **3**, 18866-73-4.

Acknowledgment.—Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, and to Union Oil Co., Bea, Calif., for the support of this research.

(8) A. Valette, *Ann. Chim.*, **3**, 644 (1948).

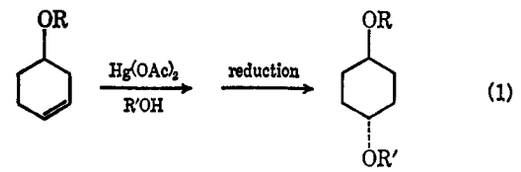
Solvent Effects in the Oxymercuration of 2-Cyclohexenol and Related Allylic Derivatives

M. Ross Johnson[1] and Bruce Rickborn[2]

Department of Chemistry, University of California, Santa Barbara, California 93106

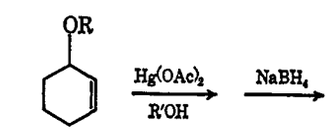
Received December 3, 1968

Stereoselective reactions are of great importance in the design of synthetic procedures. A number of simple olefin addition reactions exhibit this feature, which increases by a large factor the degree of synthetic utility. A related phenomenon, stereoselective addition controlled by a substituent in the vicinity of the double bond, has been explored in several reactions. Examples for which high selectivity has been reported include the epoxidation of 2-cyclohexeneol[3] (*cis*), the Simmons–Smith reaction of both allylic and homoallylic alcohols (*cis*),[4] and the hydroxymercuration of 3-cyclohexenol[5] (eq 1).

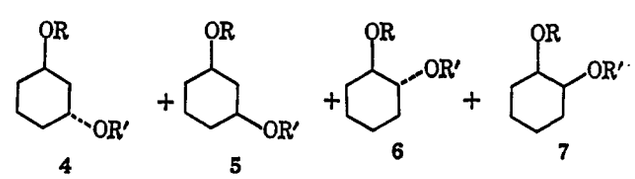


(1)

We have recently reported preliminary results on the hydroxymercuration of 2-cyclohexenol (**1**), its methyl ether (**2**), and acetate (**3**) derivatives.[6] The reaction proved to be only moderately stereoselective as normally carried out (THF–water), but appeared, in the limited range examined, to be somewhat solvent dependent. We report here the results of an expanded study of solvent effects with these systems. The products in each case were reduced by borohydride to the corresponding diols (or derivatives), which in turn were analyzed by vpc. The results are shown in Table I.



1, R = H
2, R = CH_3
3, R = $COCH_3$



R' = H, CH_3, or $COCH_3$ (2)

The most significant aspect to be noted is the high selectivity associated with the use of acetonitrile (5% water) as solvent. Thus all three substrates (**1**–**3**) give nearly pure (>94%) *trans*-3-hydroxy product in this medium. This feature should prove of synthetic utility.

All three starting materials show approximately the same responses to solvent changes, suggesting that nearly identical directive influences are exerted by the different substituents. The observed product distributions do not vary in any easily predictable manner with solvent change; the formation of 1,2 product appears to be associated with the less *trans*-3-selective reaction of **1**, but similar behavior is not found with the allylic acetate **3**.[7] In general, the preferred for-

(1) NDEA Title IV Predoctoral Fellow.

(2) Alfred P. Sloan Fellow, 1967–1969.

(3) (a) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957). (b) For a recent example of solvent effect on epoxidation of a homoallylic alcohol, see R. Zurflüh, E. N. Wall, J. B. Siddall, and J. A. Edwards, *J. Amer. Chem. Soc.*, **90**, 6224 (1968).

(4) J. H. Chan and B. Rickborn, *ibid.*, **90**, 6406 (1968); references to earlier work are given here.

(5) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959).

(6) M. R. Johnson and B. Rickborn, *Chem. Commun.*, 1073 (1968).

(7) Two early runs with **3** in aqueous THF gave only product **4** in moderate yield;[6] numerous subsequent attempts to repeat this observation have all resulted in the distribution shown in Table I.

TABLE I
PRODUCT DISTRIBUTION FROM OXYMERCURATION-REDUCTION (eq 2)

Solvent	R	R'	Yield, %	% 4	5	6	7
8% H_2O in THF	H	H	37[a]	73.5	24.6	0.9	1.0
50% H_2O in THF	H	H	86	78.2	19.6	0.9	0.8
H_2O	H	H	84	83.6	15.1	0.7	0.6
20% H_2O in glyme	H	H	78	86.4	12.6	0.6	0.4
5% H_2O in DMSO	H	H	[b]	90.5	1.6	3.3	4.6
20% H_2O in CH_3CN	H	H	78	94.0	6.0	0	0
5% H_2O in CH_3CN	H	H	83	96.3	3.7	0	0
CH_3OH	H	CH_3	92	84.4	15.6	0	0
AcOH	H	Ac	95	82.0	6.8	4.4	6.8
40% H_2O in THF	CH_3	H	85	86.8	13.2	0	0
50% H_2O in THF	CH_3	H	92	89.0	11.0	0	0
5% H_2O in DMSO	CH_3	H	[b]	88.8	11.2	0	0
5% H_2O in CH_3CN	CH_3	H	93	94.0	6.0	0	0
AcOH	CH_3	Ac	87	93.6	6.4	0	0
25% H_2O in THF	Ac	H	95	70.0	30.0	0	0
75% H_2O in THF	Ac	H	95	70.5	29.5	0	0
5% H_2O in DMSO	Ac	H	[b]	85.6	3.3	8.6	2.5
5% H_2O in CH_3CN	Ac	H	95	96.0	4.0	0	0
CH_3OH	Ac	CH_3	90	74.5	25.5	0	0
AcOH	Ac	Ac	95	92	8	0	0

[a] The reaction is quite slow under these conditions; 58% of starting material recovered after 33 hr. [b] Yields were not determined owing to difficulty in separating solvent from products.

mation of 1,3 derivative can be ascribed to the inductive effect of the ring substituent. Halpern and Tinker[8] have demonstrated that oxymercuration of **1** occurs at about one-tenth the rate for cyclohexene, and there is thus no kinetic basis for anticipating stereospecific reaction of this system.[4]

Experimental Section

Oxymercuration and Reduction.—The olefin was added in one portion to a stirred solution of solvent and mercuric acetate. The reactions were run at 25°, and in general for 0.5 hr after the disappearance of the colloidal yellow mercuric oxide (not formed in nonaqueous solvents or pure water). The reactions for the most part were rapid, requiring only a few minutes to become colorless. The reactions in acetonitrile (5% H_2O) were fast (4 min to decolorize). DMSO, glyme, and THF containing small amounts of water required longer times for reaction.

Reduction was accomplished by using the sodium borohydride procedure of Brown and Geoghegan.[9] The aqueous base used in this method causes rapid hydrolysis of the acetate esters; this can be avoided by omitting the base and using excess borohydride.

The mercury was removed by filtration through Celite, the aqueous solution saturated with salt and extracted several times with ether. The combined ether extracts were dried with magnesium sulfate and evaporated. The diols thus obtained were taken up in pyridine and treated with excess acetic anhydride. The diacetates were analyzed using a 9 m × 3.2 mm 15% Carbowax 20M column at 152°. Retention times (RT) in minutes for these derivatives follow: **4**, 86; **5**, 100; **6**, 66; **7**, 62. The methoxy alcohols formed by hydroxymercuration of **2** or methoxymercuration of **1** were analyzed directly using the same column at 132°: **4**, 50.5; **5**, 45.6; **6**, 25; **7**, 19. The starting materials 2-cyclohexenol (**1**),[4,10] 3-methoxycyclohexene (**2**),[4] and 2-cyclohexenyl acetate (**3**)[11] have been described previously.

Product Assignments.—Commercial samples of *cis,trans*-1,2-cyclohexanediol and *cis,trans*-1,3-cyclohexanediol were converted into the diacetate derivatives. Literature procedures were used to prepare *trans*-1,2-diol,[12] *trans*-1,3-diol,[13] and *trans*-2-methoxycyclohexanol.[14] Jones oxidation of the latter gave 2-methoxycyclohexanone (96%), which in turn was reduced by $LiAlH_4$ in ether to give a mixture (nearly equal amounts) of the *cis* and *trans* alcohols. *trans*-3-Methoxycyclohexanol was obtained by the procedure of Eliel and Brett.[15] All compounds exhibited the anticipated nmr and ir spectral properties.

Registry No.—2-Cyclohexenol, 822-67-3.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation (GP 6043).

(8) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).
(9) H. C. Brown and P. Geoghegan, Jr., *ibid.*, **89**, 1522 (1967).
(10) R. Willstätter and E. Sonnenfeld, *Chem. Ber.*, **46**, 2952 (1913).
(11) H. J. Shine and J. R. Slagle, *J. Amer. Chem. Soc.*, **81**, 6309 (1959).
(12) A. C. Cope, H. E. Johnson, and J. S. Stephenson, *ibid.*, **78**, 5599 (1956).
(13) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2103 (1959).
(14) S. Winstein and R. B. Henderson, *J. Amer. Chem. Soc.*, **65**, 2196 (1943).
(15) E. L. Eliel and T. J. Brett, *J. Org. Chem.*, **28**, 1923 (1963).

Convenient Synthesis of 2,2-Dimethylcyclobutanone

WILLIAM C. AGOSTA AND DAVID K. HERRON

Laboratories of the Rockefeller University, New York, New York 10021

Received February 13, 1969

In connection with another investigation we required a convenient source of 2,2-dimethylcyclobutanone (**1**). There are two previously recorded preparations of this substance, the first[1] being the reaction of dimethylketene with ethylene at 200 atm pressure, and the second[2] involving addition of 2 equiv of diazomethane to dimethylketene. Neither of these seemed suitable for our purposes; the first requires pressure equipment not conveniently available, while the second gives largely the isomeric 3,3-dimethylcyclobutanone, from which the desired minor product **1** is difficultly separable. We describe below a useful preparative route to **1** from *t*-butyl acrylate and the dimethylenamine of isobutyraldehyde. Although four steps are involved from commercially available

(1) H. Bestian and D. Guenter, *Angew. Chem.*, **75**, 841 (1963).
(2) J.-M. Conia and J. Salaün, *Bull. Soc. Chim. Fr.*, 1957 (1964).