with mercury cathodes were the one previously described[20] and also a scaled-down version cathode area 38.4 cm², catholyte volume ~75 ml. The vpc analyses were performed on a Varian Series 1200, Hi-Fi III gas chromatograph (single column, single flame ionization detector). The two columns used were both 6-ft, 1/8 in. diameter stainless steel packed respectively with 10% Carbowax 20M on 80–100 mesh Chromosorb W (NAW) and 3% SE-30 on 100–200 mesh Varaport 30.

The esr spectra were obtained using a Varian V-4502 spectrometer equipped with a 12 in. magnet. The modulation frequency was 100 kHz. The Varian rapid scan cavity was used in conjunction with the Varian rapid scan unit and the C-1024 time averaging computer. The microwave frequency under experimental conditions was measured with a Hewlett-Packard X350A wavemeter and was 9.544 GHz. The sweeps were calibrated using a basic aqueous solution of potassium peroxylamine disulfonate (g = 2.0055, a = 13 G) and were found to be satisfactorily linear.

Procedures.—The macroelectrolyses were carried out under the conditions summarized in Tables II and III. The mercury was then separated from the catholyte and the latter diluted with water and thoroughly extracted with methylene chloride. The extracts were washed and dried over anhydrous magnesium sulfate. The analyses were performed as follows. The excess methylene chloride was carefully removed from the products using a rotary evaporator and a vacuum pump (10 mm), keeping the water bath at room temperature. When most of the CH_2Cl_2 had been removed, the temperature of the water bath was increased to 50° and the vacuum increased to 5 mm. The low boiling products were collected in two Dry Ice–acetone traps in series.

The above distillate typically contained the ketones and methylene chloride. These products were analyzed neat at 70° using 10% Carbowax 20M.

The residue from the above stripping, which contained the bulk of the products, was analyzed (20% in acetone) using 10% Carbowax 20M, programmed from 120 to 220° at 10° min⁻¹. Relative retention times and relative response factors were calculated using diethyl malonate as an internal standard. Components were qualitatively determined by subsequent injection of authentic samples prepared independently.

For determining the esr spectra, separate solutions of 1.65 g of **1** (with R = C_6H_5) in 5 ml of ethanol (with 0.025 g of sodium) and of 2.25 g of **2** in 20 ml of ethanol were mixed under exclusion of oxygen. The sample tubes were sealed under nitrogen and heated for a few minutes at 50–70° before they were transferred to the esr cavity at room temperature. A well-resolved five-line spectrum was detected under the proper modulation conditions (optimum conditions about 0.75 peak to peak modulation). The spectra were very weak and required many hours of data accumulation. Typically, accumulation of 900 scans over 8 hr gave a signal to noise ratio of about 12. The intensity ratios of the peaks varied with the modulation amplitude, pointing to the fact that the peaks were of different widths and shapes and contained unresolved features; at 0.75 G peak to peak modulation the ratio was 1:1.6:2.6:1. Because of the weakness of the signals it was not possible to resolve additional structure by lowering the modulation amplitude. The same five-line spectrum (although much weaker) was also obtained when **2** was excluded, but oxygen was allowed to come into contact with the solution. This observation, together with the explanations that follow, lead us to attribute the spectrum to the phenylmercaptyl radical. The g factor was found to be 2.030. This value is close to the isotropic g value of 2.040 attributed by Zandstra and Michaelsen[21] to phenylmercaptyl radical produced during the pyrolysis of diphenyldisulfide. This assignment has been criticized by Schmidt[22] who found a much smaller g factor (isotropic g = 2.007) for the supposed phenylmercaptyl radical produced by uv irradiation of diphenyl disulfide. It should be noticed that in both references the radicals were observed in a frozen matrix, and that therefore no hyperfine structure was detected that could support the assignments. On the other hand, the hyperfine structure of phenoxyl radical has been resolved by Stone and Waters[23] who reported the following hyperfine constants: $a_{2,6}$ = 6.65 G, a_4 = 10.1 G, $a_{3,5}$ = 1.8 G. Our spectrum can be interpreted in terms of hyperfine constants $a_{2,6}$ = 2.7 G, a_4 = 5.4 G, $a_{3,5}$ = 1.0 G. The splitting with the 3,5 hydrogens was too small to be resolved, but from the observed linewidth an upper limit of about 1 G was estimated for $a_{3,5}$. Compared to the phenoxy radical, the much smaller hyperfine constants observed in our case are consistent with the fact that in mercaptyl radicals the spin density is concentrated on the sulfur atom most of the time.[21]

(20) M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).
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Registry No.—**2**, 17407-28-2; **4**, 25528-05-6; **5**, 25528-06-7.

The Cyclization of Epoxy Olefins. VIII. Attempted π Routes to Bridged Bicyclic Systems[1]

DAVID J. GOLDSMITH AND R. C. JOINES[2]

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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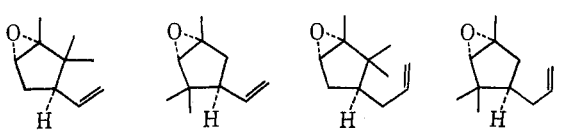
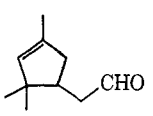
In a previous report[3] on work in the area of epoxide cyclizations we described attempts to form the bornane skeleton by closure of **1**. These experiments led only to noncyclic rearrangement products. As suggested previously,[3,4] the transition state for cyclization of compounds like **1** appears to allow for little overlap between the orbitals of the double bond and the ring carbon atom. In addition, one of the rearrangement reactions of **1** has as a strong driving force the relief of the crowding of groups on three adjacent positions of a cyclopentane ring. In order to investigate these factors we chose to examine the reactivities of three related epoxy olefins **2**, **3**, and **4**.



1 **2** **3** **4**

In structure **2** the propensity of the α-campholene system for rearrangement[5] has been eliminated since this compound no longer features 1, 2, 3 ring substitution. In addition, opening of the epoxide ring of **2** in either a cyclization or a ketone forming reaction should occur at the tertiary center which in this case is insulated from the *gem*-dimethyl group. With **3** the steric difficulties encountered with **1** in bringing an olefinic carbon and a ring carbon within bonding distance should be diminished. Compound **4** in turn embodies both structural variations discussed for **2** and **3**.



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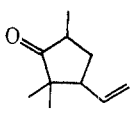
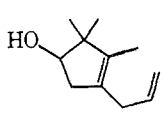
(1) This work was supported in part by the National Institutes of Health, Grant No. GM 11728. (b) The previous paper in this series is D. J. Goldsmith and C. F. Phillips, *J. Amer. Chem. Soc.*, **91**, 5862 (1969).
(2) Coca Cola Research Fellow, 1963–1965.
(3) D. J. Goldsmith and C. J. Cheer, *J. Org. Chem.*, **30**, 2264 (1965).
(4) L. J. Dolby and R. H. Iwamoto, *ibid.*, **30**, 2420 (1965).
(5) (a) F. Tieman, *Chem. Ber.*, **29**, 3006 (1896); (b) E. R. Buchman and H. Sargent, *J. Org. Chem.*, **7**, 140 (1942).

Compounds **2** and **4** were prepared from iso-α-campholenealdehyde[6] (**5**); the former by the method previously described[1] for **1**, and the latter by addition of methylene triphenylphosphorane to the aldehyde and subsequent epoxidation of the more highly substituted double bond. Epoxy olefin **3** was prepared from α-campholenealdehyde by the same Wittig reaction, epoxidation sequence. The stereochemistry of these compounds follows from the previously described[1,7] results for epoxidation of cyclopentenyl systems.

When **2** was subjected to cyclizing conditions[8] with anhydrous stannic chloride in benzene a single product, ketone **6**, was obtained. Thus no cyclization had occurred with **2** as well as with **1** and rearrangement of the



6



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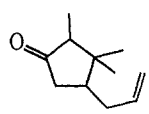
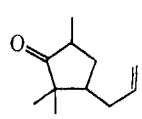


8

appended groups on adjacent positions of the cyclopentane ring could not be solely responsible for the indisposition of the 4-vinylcyclopentene oxide system to form bicyclic products.

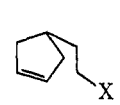
A molecular model of the second epoxy olefin **3** indicates that little or no angle strain is required to make the potential bonding orbitals of the olefinic carbon and the epoxide carbon assume a parallel relationship. Despite this consideration, however, when **3** was treated with stannic chloride in benzene solution no cyclization product was obtained. The products of the reaction were analogous in structure to those obtained from **1**.[3] Thus preparative glpc of the crude reaction mixture yielded 54% (relative yield) of alcohol **7** which displayed in its nmr spectrum multiplets at 4.78, 4.97, and 5.50 ppm corresponding to three vinyl hydrogens plus a signal at 1.52 ppm for a vinyl methyl group. The second product obtained in 42% relative yield was a ketone. Both the nmr spectrum and the infrared spectrum indicated that the terminal vinyl group was present in this product also and by analogy with the ketonic product from **1**[3] the structure **8** was assigned.

The final epoxy olefin in this series, **4**, also yielded no bicyclic products from treatment of the epoxide with acid. The only product from the reaction of **4** with stannic chloride in benzene was the ketone **9**.



9

The "π route" to bicyclic systems has been the subject of considerable investigation.[9] Most of the reported cases, however, are of the cyclopentenyl ethyl type; that is the cationic center is exocyclic to the ring and the cyclization reaction proceeds through a bicycloheptyl cation as in i to ii.

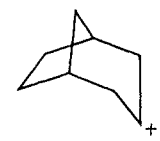


i

ii

The system exemplified by epoxy olefins **5** and **6** in which the participating π bond is exocyclic was expected to cyclize *via* a cation which can be represented in a general way by either the bridged structure iv or the classical structure v.

iii



iv

The fact that no cyclization of either **5** or **6** occurs suggests that either these ions lack the stability associated with bridged ions of the type exemplified by ii or that steric factors continue to play a larger role in these reactions than assumed. In support of this it is interesting to note that rearrangement of 2-*exo*-norbornylcarbinyl amine by nitrous acid deamination affords only 18% of **18** while the corresponding *endo* derivative yields none of this type of product.[10,11] This rearrangement when it does occur must proceed *via* an ion related to iv or v. The failure of the *endo* case to yield **18** was ascribed by Benson and Willner[11] to the necessity for a "boat conformation in the rearrangement of this isomer. They also noted, however, that the predominant rearrangement pathway of the *exo* compound also involves boatlike conformations. Thus, factors other than this simple conformational one must be important in production of bridged cations like iv.[11]

Experimental Section[12]

1,3,3-Trimethyl-4(2′-hydroxyethyl)cyclopentene.—Reduction of iso-α-campholenealdehyde, **5**[6] (45.0 g, 0.29 mol), with sodium borohydride (30.0 g, 0.78 mol) in 600 ml of ethanol by standard methods afforded 42.5 g (93%) of the alcohol: bp 63.5–64.5° (0.56 mm); n^{23}D 1.4689; ir (neat) 3300, 1750, 1058, and 828 Cm^{-1}; nmr (CCl_4) δ 0.80 (s, 3), 1.00 (s, 3) 1.52 (s, 3), 3.52 (t, 2, J = 6 Hz), 4.38 (s, 1), 5.03 (m, 1).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 1176. Found: C, 77.61; H, 11.70.

1,3,3-Trimethyl-4-(2′-acetoxyethyl)cyclopentene.—The alcohol from above (39 g, 0.25 mol) was converted to the corresponding acetate with acetic anhydride (200 ml) and sodium acetate (20.0 g, 0.25 mol) employing standard methods: bp 63° (0.3 mm); n^{23}D 1.4540; ir (neat) 1730, 1650, 1238, 1043, and 829 cm^{-1}.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.42; H, 10.27. Found: C, 73.53; H, 10.43.

1,3,3-Trimethyl-4-vinylcyclopentene.—The preceeding acetate was pyrolyzed as described previously[3] using a modified Johnson pyrolysis column.[13] In a typical run 20 g of acetate was pyrolyzed under the following conditions: oil bath, 180–185°; pyrolysis column, 465–475°; fractionating column, 70–80° (155–160 mm). The yield after redistillation of the product was 10.0 g of diene: bp 91.5–94.5° (163 mm); n^{22}D 1.4513; ir (neat) 3060, 1640, 1650, 1370, 1000, 914, and 828 cm^{-1}; nmr (CCl_4) δ 0.78 (s, 3), 0.98 (s, 3), 1.63 (s, 3), 2.23 (m, 3), 5.0 (m, 2), 5.75 (m, 2).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.42; H, 11.76.

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(12) Boiling points are uncorrected. Nmr spectra were obtained at 60 MHz, with tetramethylsilane as an internal reference.
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1,3,3-Trimethyl-4-vinylcyclopentene 1,2-Oxide (2).—To a cold stirred solution of 4 g (0.029 mol) of the diene from above there was added in a dropwise manner 55.2 ml of a solution of monoperphthalic acid in ether (0.029 mol). After an additional 3 hr of reaction at room temperature the mixture was worked up in the usual way[8] to yield 3.2 g of oxide **2** which eluted as a single substance on Carbowax 20M and Apiezon L glpc columns: $n^{22}D$ 1.4502; ir (neat) 3050, 1635, 998, 910, and 838 cm^{-1}; nmr (CCl_4) δ 0.72 (s, 3), 0.99 (s, 3), 1.35 (s, 3), 1.80 (m, 3), 2.71 (s, 1), 4.73 (m, 1), 4.97 (m, 1), 5.41 (m, 1).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 79.12; H, 10.55.

Reaction of Epoxide 2 with Stannic Chloride.—Stannic chloride (0.20 ml) was added to a solution of 2 (1.0 g, 0.0065 mol) in 25 ml of benzene and the mixture stirred for 10 hr at room temperature. The reddish reaction mixture was then poured into ice water, shaken vigorously, and extracted with ether. Removal of the solvent after drying over sodium sulfate afforded 0.8 g of material which showed only a single glpc peak on Apiezon L and Carbowax 20M columns. Purification by preparative glpc yielded **6**: $n^{24}D$ 1.4522; ir (CCl_4) 3050, 1730, 1683, and 920 cm^{-1}; nmr (CCl_4) δ 0.83 (s, 3), 0.98 (s, 3), 1.12 (d, 3, J = 7 Hz), 2.22 (m, 4), 4.88 (m, 1), 5.11 (m, 1), 5.58 (m, 1).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.93; H, 10.56.

2,3,3-Trimethyl-4-allylcyclopentene.—α-Campholenealdehyde (10.0 g, 0.065 mol) in 50 ml of ether was added rapidly to 225 ml of a solution of methylene triphenylphosphorane (prepared from 16.6 g, 0.049 mol of triphenylmethyl phosphonium bromide and 35 ml, approx 0.05 mol, of n-butyllithium) maintained at 0–5°. After 10 min 150 ml of water was added to the creamy suspension. Removal of the solvent after extraction of the aqueous layer with ether and drying afforded 8.6 g of crude product. Distillation through an 18-in. spinning-band column yielded 3.6 g (36%) of pure diene: bp 68–71 (21 mm); $n^{23}D$ 1.4581; ir (neat) 3050, 3000, 1640, 1355, 911, and 800 cm^{-1}; nmr (CCl_4) δ 0.77 (s, 3), 0.97 (s, 3), 1.57 (m, 3), 4.88 (m, 1), 5.00 (m, 1), 5.12 (m, 2), 5.52 (m, 1).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 87.99; H, 12.16.

2,2,2-Trimethyl-4-allylcyclopentene 1,2-Oxide (3).—The epoxidation of the allylcyclopentene from above was carried out as described for **2** to yield **3** (97%): $n^{23}D$ 1.4556; ir (neat) 3050, 1635, 1358, 910, and 846 cm^{-1}; nmr (CCl_4) δ 0.72 (s, 3), 0.95 (s, 3), 1.22 (s, 3), 3.02 (m, 1), 4.73 (m, 1), 4.96 (m, 1), 5.42 (m, 1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.73; H, 11.01.

Reaction of 3 with Stannic Chloride.—Treatment of **3** (1.0 g) with stannic chloride in benzene in the manner described above for **2** afforded 0.95 g of dark oil. Analytical glpc on Apiezon L at 160° showed two major components and one minor one with retention times of 8.5, 11.0, and 9.5 min, and in the proportions 54%, 42%, and 4% respectively. The minor component could not be isolated.

Preparative glpc on Apiezon L afforded the 54% component, 2,3,3-trimethyl-4-allylcyclopentanone, **8**, as an oil: $n^{22}D$ 1.4651; ir (CCl_4) 3080, 1740, 1638, and 920 cm^{-1}; nmr (CCl_4) δ 0.70 (s, 3), 0.95 (s, 3), 0.96 (d, 3), 4.87 (m, 1), 5.10 (m, 1) 5.65 (m, 1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.29; H, 10.85.

Isolation of the 42% component by preparative glpc afforded 2,3,3-trimethyl-1-allylcyclopenten-4-ol, **7**: $n^{22}D$ 1.4816; ir (CCl_4) 3600, 3050, 1630, 1057, 992, and 915 cm^{-1}; nmr (CCl_4) δ 0.90 (s, 3), 0.96 (s, 3), 1.52 (m, 3), 3.72 (m, 1), 4.78 (m, 1), 4.97 (m, 1), 5.50 (m, 1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.63; H, 10.69.

1,3,3-Trimethyl-4-allylcyclopentene.—Application of the previously described procedure for addition of methylene triphenylphosphorane to campholenealdehyde to **5** afforded the title compound: bp 60–61° (17 mm); $n^{24}D$ 1.4521; ir (neat) 3050, 1635, 1645, 995, 911, and 825 cm^{-1}; nmr (CCl_4), 0.80 (s, 3), 1.0 (s, 3), 1.62 (m, 3), 4.78 (m, 1), 5.02 (m, 1), 5.45 (m, 1).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 87.94; H, 12.11.

1,3,3-Trimethyl-4-allylcyclopentene 1,2-Oxide (4).—Epoxidation of the diene from above by the previously described procedure[8] afforded **4**, purified by preparative glpc: $n^{23}D$ 1.4500; ir (neat) 3030, 1635, 1359, 996, 913, and 840 cm^{-1}; nmr (CCl_4) δ 0.72 (s, 3), 0.98 (s, 3), 1.30 (s, 3), 4.72 (m, 1), 4.97 (m, 1), 5.42 (m, 1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.43; H, 11.01.

Reaction of 6 with Stannic Chloride.—Treatment of **4** (0.5 g) with stannic chloride in benzene by the previously described procedure afforded 0.45 g of **9**. The material was purified by preparative glpc on Apiezon L at 160°: $n^{22}D$ 1.4536; ir (CCl_4) 3050, 1725, 1635, 1242, 920, and 865 cm^{-1}; nmr (CCl_4) δ 0.80 (s, 3), 0.96 (s, 3), 1.06 (d, 3, J = 7 Hz), 4.87 (m, 1), 5.10 (m, 1), 5.60 (m, 1).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.35; H, 10.68.

Registry No.—1,3,3-Trimethyl-4-(2′-hydroxyethyl)-cyclopentene, 4605-50-9; 1,3,3-trimethyl-4-(2′-acetoxyethyl)cyclopentene, 25527-89-3; 1,3,3-trimethyl-4-vinylcyclopentene, 25527-90-6; **2**, 25515-35-9; **3**, 25515-36-0; **4**, 25515-37-1; 1,3,3-trimethyl-4-allylcyclopentene, 25527-91-7; **6**, 25527-92-8; 2,3,3-trimethyl-4-allylcyclopentene, 25527-93-9; **7**, 25527-94-0; **8**, 25527-95-1; **9**, 25527-96-2.

Reduction of Cyclic Anhydrides with $NaBH_4$. Versatile Lactone Synthesis

DENIS M. BAILEY AND ROBERT E. JOHNSON

Sterling-Winthrop Research Institute, Rensselaer, New York 12144

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Over 20 years ago Chaikin and Brown[1] reported that, with $NaBH_4$, acid anhydrides show only slight reduction on prolonged heating. Since then, only two isolated examples of the $NaBH_4$ reduction of cyclic anhydrides have appeared in the literature.[2,3] More recently, the $NaBH_4$ reduction of mixed carboxylic-carbonic anhydrides[4] and thiophthalic anhydride[5] have been recorded. We have examined the reduction of a number of cyclic anhydrides with this reagent and have found that δ and γ lactones can be isolated in good to excellent yields (51–97%). This procedure is more convenient and more versatile than the previoulsy reported methods using $LiAlH_4$[6] or $LiAlH(O\text{-}t\text{-}Bu)_3$.[6a] The steric course of the $NaBH_4$ reduction of 5-membered unsymmetrical cyclic anhydrides is identical with that observed with $LiAlH_4$[6a] or Na–EtOH.[7] In most instances hydride attack takes place principally at the carbonyl group adjacent to the more highly substituted carbon atom. Thus, the reduction of *cis*-1-methylcyclohexane-1,2-dicarboxylic acid anhydride (I) to

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