The Pyrolytic Rearrangement of Two Cyclobutene Epoxides[1,2]

DAVID L. GARIN

Department of Chemistry, University of Missouri–St. Louis, St. Louis, Missouri 63121

The pyrolytic rearrangement of *exo*-bicyclo[3.2.0]hept-6-ene oxide (1) and *exo*-bicyclo[4.2.0]oct-7-ene oxide (6) have been investigated. At 420°, the former gives Δ^2-cyclopentenylacetaldehyde (2) in 50% yield. At 400°, the latter gives Δ^2-cyclohexenylacetaldehyde (7), 1-methylcyclohexene, and 3,4-tetramethylene-2,3-dihydrofuran (8). The corresponding cyclobutanones (10 and 11) were shown not to be intermediates. The structures of the products have been assigned on the basis of comparison with authentic samples and further chemical transformations.

There are many examples of the pyrolytic rearrangement of epoxides in the literature.[3,4] To our knowledge, there are but two reports on the pyrolysis of cyclobutene epoxides.[5] In the light of recent reports on the anomolous behavior of cyclobutene epoxides with regard to attack by various nucleophiles[6–9] and rearrangements caused by Lewis acids[9–11] the results of our work on the pyrolysis of *exo*-bicyclo[3.2.0]hept-6-ene oxide (1) and *exo*-bicyclo[4.2.0]oct-7-ene oxide (6) should be of some interest[12] (Scheme I).

Pyrolysis was affected by dropwise addition of the epoxide to a 12-in. vertical column of glass helices in a temperature-controlled oven under slow nitrogen flow. Optimum temperatures were considered to be those that gave complete conversion of the epoxide with the lowest number of products as determined by vapor phase chromatography.

Results

Pyrolysis of 1 at 420° gives a large number of high- and low-boiling products. A sample of the major constituent of the pyrolysate (50%) was isolated by preparative vpc. Analysis of its infrared and nmr spectra suggested Δ^2-cyclopentenylacetaldehyde (2) which was verified by comparison with an authentic sample and by reduction to the corresponding alcohol and comparison with 2-(Δ^2-cyclopentenyl)ethanol (4).

One of the minor products from the pyrolysate (5%) was isolated in impure form. The nmr spectrum showed a sharp aldehyde doublet at 9.2 ppm ($J = 5$ cps), no olefinic protons, and a methylene region that extended to 1.0 ppm. It seemed possible that the major substituent of this mixture was bicyclo[3.1.0]-hexane-6-carboxaldehyde (3), either *exo* or *endo* or a mixture of both. The mixture was reduced with

Scheme I
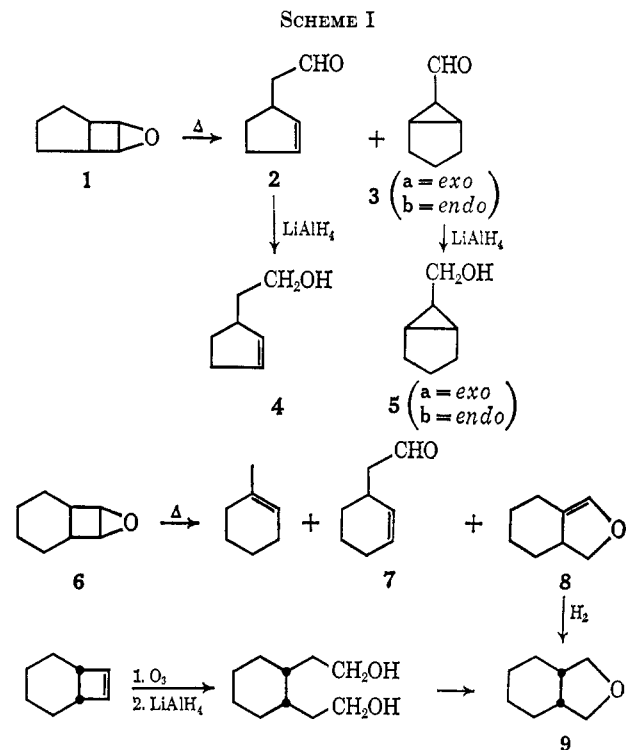
lithium aluminum hydride to the more stable alcohols. *exo*- and *endo*-bicyclo[3.1.0]hexane-6-methanols (5a, b) were synthesized for comparison.[13] The alcohols were analyzed by vpc on a THEED column at 125°.[14] Under these conditions, both *exo* and *endo* alcohols can be resolved. The major product from the reduction of the aldehyde (obtained from the pyrolysis of 1) was shown to be the *exo* isomer by comparison of retention times. The *endo* alcohol (5b) was not present. Samples of these alcohols were collected by preparative vpc. The infrared spectrum of the reduced aldehyde was superimposable with that of the authentic *exo* alcohol (5a) and differed from that of the *endo* alcohol (5b). Therefore, the aldehyde obtained from the pyrolysis of 1 is *exo*-bicyclo[3.1.0]hexane-6-carboxaldehyde (3a). The nmr spectrum of 5a shows a hydroxymethylene doublet at 3.3 ppm ($J = 7$ cps); that of 5b shows a hydroxymethylene doublet at 3.5 ppm ($J = 7$ cps).

Another minor product (2%), collected by preparative vpc, appeared to be an unsaturated ether (infrared spectrum: 3050, 1653, 1640, 1460, 1130, and 1028 cm^{-1}) but sufficient material could not be obtained to further characterize it.

(1) Presented in part at the Midwest Regional American Chemical Society Meeting, Columbia, Mo., Nov 1967.

(2) Portions of this manuscript were abstracted from the Ph.D. thesis of D. L. Garin, Iowa State University, 1964.

(3) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(4) An extensive review of epoxide chemistry can be found: A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1–523.

(5) G. Maier, *Chem. Ber.*, **96**, 2238 (1963); E. E. van Tamelen and D. Carty, *J. Amer. Chem. Soc.*, **89**, 3922 (1967).

(6) A. C. Cope and R. W. Gleason, *ibid.*, **84**, 1928 (1962).

(7) L. A. Paquette, A. A. Youssef, and M. L. Wise, *ibid.*, **89**, 5246 (1967).
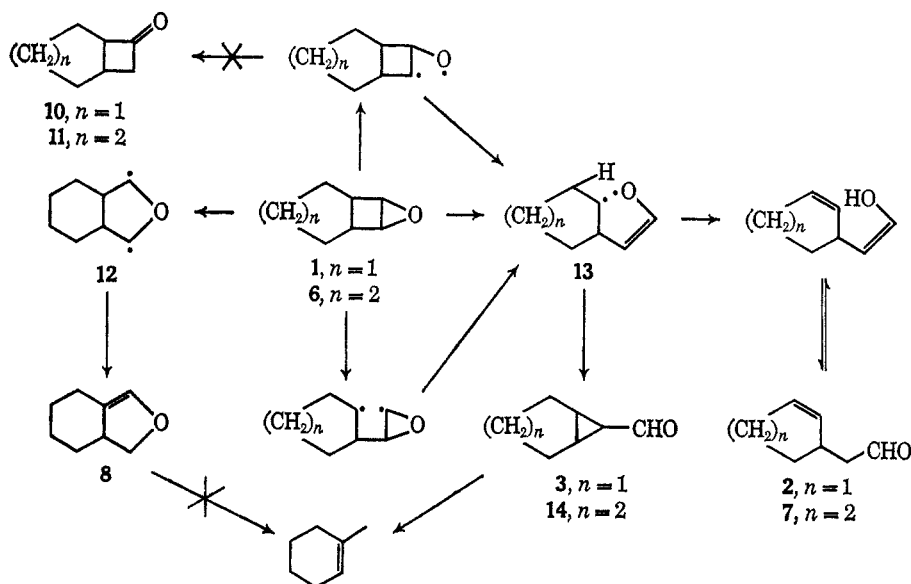
(8) A. Padwa, *ibid.*, **87**, 4205 (1965).

(9) W. R. Moore and C. H. Beede, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963, p 11M.

(10) J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1965).

(11) J. L. Ripoll and J. M. Conia, *Bull. Soc. Chim. Fr.*, 2755 (1965).

(12) Epoxides 1 and 6 were prepared by peracid oxidation of the corresponding olefins. Cope and Gleason[6] reported that the peracid oxidation of bicyclo[4.2.0]oct-7-ene gives both *exo* and *endo* epoxides with the *exo* isomer favored 87:13. The more rigid bicyclo[3.2.0]hept-6-ene would be expected to give an even greater predominance of the *exo* epoxide.

(13) K. B. Wiberg and A. J. Ashe, III, *J. Amer. Chem. Soc.*, **90**, 63 (1968).

(14) This is a 1-m, 0.25-in. diameter glass column utilizing tetrahydroxyethylenediamine (THEED) 1:3 on 60–80 firebrick. Retention times (min) at 125°: **5a**, 4.0; **5b**, 4.8.

SCHEME II

10, $n = 1$
11, $n = 2$

12

1, $n = 1$
6, $n = 2$

13

8

3, $n = 1$
14, $n = 2$

2, $n = 1$
7, $n = 2$

By comparison with 1, the pyrolysis of 6 at 400° was extremely clean giving three products which were separated and collected by preparative vpc. The low-boiling product (13%) was shown to be 1-methylcyclohexene by comparison with a prepared sample. The lesser of the two major products (31%) was identified as Δ^2-cyclohexenylacetaldehyde (7). The infrared and nmr spectra were consistent with this structure (aldehydic proton at 9.7 ppm, t, $J = 2$ cps; two olefinic protons at 5.5 ppm, multiplet). The 2,4-dinitrophenylhydrazone had mp 99.5–100° (lit.[15] mp 97°). Absorption of 1 mol of hydrogen gave cyclohexylacetaldehyde identified by its 2,4-dinitrophenylhydrazone derivative which had mp 123.5–125° (lit.[16] mp 124–125°). To distinguish between the Δ^2 and possible Δ^3 isomer, the aldehyde was reduced to the corresponding alcohol with lithium aluminum hydride and compared with authentic samples of 2-(Δ^3-cyclohexenyl)ethanol[17] and 2-(Δ^2-cyclohexenyl)ethanol.[18] Though similar, the infrared spectra of the two isomers differed in the fingerprint region. The infrared spectrum of the reduced aldehyde was identical with that of the Δ^2 isomer.

Unexpectedly, the major component of the pyrolysate (56%) appeared to be an enol ether. The infrared spectrum showed absorption at 1670, 1040, 920, and 835 cm^{-1}; the ultraviolet spectrum had λ_{max} 214 mμ (ϵ 6100) in 95% ethanol. Hydrogenation in ethyl acetate with 5% platinum oxide on carbon gave a single ether which was shown to be *cis*-hexahydrophthalan (9) by comparison with a sample synthesized from *cis*-bicyclo[4.2.0]oct-7-ene via ozonolysis,[19] reduction to *cis*-hexahydrophthalyl alcohol, and dehydration.[20,21] The infrared and nmr spectra of the dihydro

enol ether were superimposable with those of 9. Thus, the enol ether is 3,4-tetramethylene-2,3-dihydrofuran (8).

The pyrolysis of 6 at 400° (as well as 1 at 420°) repeatedly gave the same products in the same ratio. Pyrolysis on a column packed with glass wool (greater surface area) gave the same results as pyrolysis on glass helices. A similar lack of surface effects in epoxide pyrolyses has been reported.[22] Pyrolysis of 6 at lower temperature (350°) gives only 75% conversion of the epoxide with a smaller percentage of low-boiling product. Pyrolysis at higher temperature (450°) gives less of the two major products, several low-boiling products in higher yield, and other trace products. Pyrolysis at 500° gives much polymeric material.

Discussion

Schematically, it appears that the rearrangement to the aldehydes is occurring *via* initial breakage of either the C–O epoxide bond followed by breakage of the appropriate C–C bond of the cyclobutane ring, or *vice versa*. In Scheme II, homolytic bond cleavage is shown but the transformation could also be represented by heterolytic cleavage. The diradical intermediate 13 ($n = 1$) can account for the formation of 3, closing to the thermodynamically more stable *exo* isomer. The formation of the enol ether 8 is best represented by the cleavage of the C–C cyclobutanoxide bond to give the diradical intermediate 12 followed by two 1,2-hydrogen (or hydride) shifts or a 1,3-hydrogen shift. The apparent lability of this bond has been previously demonstrated.[6,7] The competitive nature of hydride shifts following the cleavage of a strained cyclobutane bond has been reported; e.g., the bromination of bicyclo[2.1.0]-pentane gives mainly *trans*-1,2-dibromocyclopentane.[23]

By analogy to other cycloalkene epoxides, the cyclobutene epoxides could rearrange to carbonyl compounds forming the corresponding cyclobutanone or a cyclopropanecarboxaldehyde (by ring contraction).[1,2] The possibility that the cyclobutanones were intermediates

(15) C. W. Whitehead, J. T. Traverso, H. R. Sullivan, and F. J. Marshall, *J. Org. Chem.*, **26**, 2814 (1961).

(16) J. Fried and R. C. Elderfield *ibid.*, **6**, 566 (1941).

(17) A sample was kindly supplied by the General Electric Research Laboratories, Schenectady, N. Y.

(18) This alcohol was obtained by reduction of the known Δ^2-cyclohexenylacetic acid: W von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

(19) J. L. Warnell and R. L. Shriner, *J. Amer. Chem. Soc.*, **79**, 3165 (1957).

(20) W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

(21) S. F. Birch, R. A. Dean, and E. V. Whitehead, *J. Org. Chem.*, **19**, 1449 (1954).

(22) C. K. Johnson, B. Dominy, and W. Reusch, *J. Amer. Chem. Soc.*, **85**, 3894 (1963).

(23) R. T. LaLonde, *ibid.*, **87**, 4217 (1965).

which further rearranged to products was eliminated by experiment. Bicyclo[4.2.0]octan-7-one (**11**) was prepared from bicyclo[4.2.0]oct-7-ene *via* the procedure of Brown and Garg.[24] Pyrolysis in the manner described for **6** gave a gas (assumed to be ketene) and cyclohexene as the only products. In a similar fashion, bicyclo[3.2.0]heptan-6-one (**10**) gave a gas and cyclopentene as the only products. This is analogous to the pyrolysis of cyclobutanone itself which is reported to give ketene and ethylene.[25]

The enol ether **8** was investigated as a possible source of 1-methylcyclohexene since dihydrofuran is reported to pyrolytically decompose to propene and carbon monoxide.[26] The pyrolysis of **8**, under reaction conditions similar to the pyrolysis of **6** but at slightly higher temperature (420°), gave a pyrolysate which was essentially unreacted enol ether. The unobserved cyclopropanecarboxaldehyde **14** may not be stable under reaction conditions and could be the source of the 1-methylcyclohexene. Cyclopropanecarboxaldehyde itself is known to rearrange pyrolytically to propene and carbon monoxide.[26] However, the injection of **14** (*exo* isomer)[27] into a gas chromatograph with the injection port heated to 475° produced no observable decomposition.

Both heat and Lewis acids can cause an epoxide to rearrange often giving identical products in different ratios.[1,2] It is interesting to note that the reaction of **6** with LiI gives **14** but no enol ether.[27,27a]

Experimental Section[28]

exo-Bicyclo[3.2.0]hept-6-ene Oxide (**1**).—The perbenzoic acid oxidation of bicyclo[3.2.0]hept-6-ene[29] (5.3 g, 0.056 mol) gave 4.0 g (65%) of colorless liquid, bp 61–62° (24 mm) [lit.[7] bp 84–85° (73 mm)]. Vpc analysis indicated the presence of only one component.

exo-Bicyclo[4.2.0]oct-7-ene Oxide (**6**).—Following the epoxidation procedure of Korach, Nielsen, and Rideout,[30] bicyclo[4.2.0]oct-7-ene[31] (8.3 g, 0.077 mol) was treated with 18 g of 40% peracetic acid solution[32] (0.095 mol) to give 4.1 g (43%) of colorless liquid: bp 71–73° (16 mm) [lit.[6] bp 82–84.5° (26 mm)]; infrared (neat), 3040, 942, 825, 809, and 760 cm⁻¹.

Pyrolysis of Liquid Epoxides and Ketones.—The liquid epoxide or ketone was drawn into a long-needle syringe. The needle was then inserted through a septum at the top of a vertical pyrolysis column. Twelve inches of the column were filled with ¹/₈-in. glass helices and encased in an oven maintained at 420° for **1** and **10** and 400° for **6** and **11**. The temperature was determined by attaching an iron–constantan thermocouple to the column and to a Rubicon potentiometer with reference temperature at 0°. The epoxide or ketone was allowed to drip onto the column at a

slow enough rate to prevent flooding (10–15 drops/min). The system was kept under a positive nitrogen pressure. The pyrolysate was trapped in a receiver kept at −70° (Dry Ice–acetone). Pyrolysate mixtures were separated and collected by vpc utilizing a Perkin-Elmer RX column at 75–150°.[28]

Δ²-Cyclopentenylacetaldehyde (**2**).—The major product from the pyrolysis of **1** displayed the following physical data: infrared (CCl₄), 3080, 2820, 2720, 1725, 1615, and 910 cm⁻¹; $\delta_{TMS}^{CCl_4}$ (in ppm) 9.7 (t, 1 H, *J* = 2 cps, CH₂CHO), 5.7 (multiplet, 2 H, =CH–), 3.05 (multiplet, 1 H, C=CCH<), integrates for ten total protons relative to two protons at 5.7 ppm. The infrared and nmr spectra were identical with that of an authentic sample obtained from the photolysis of norcamphor.[27,33] The 2,4-dinitrophenylhydrazone had mp 104–105° (lit.[34] mp 101–103°). A mixture melting point with the 2,4-dinitrophenylhydrazone of Δ²-cyclopentenylacetaldehyde had mp 103–105°.

2-(Δ²-Cyclopentenyl)ethanol (**4**) by the LiAlH₄ Reduction of **2**. —**2** (250 mg), obtained from the pyrolysis of **1**, was treated with lithium aluminum hydride in ether. Distillation, *in vacuo*, in a microdistillation apparatus gave 150 mg of a pure colorless liquid which displayed the following physical data: infrared (CCl₄), 3670, 3350, 3080, 1615, 1055, 970, and 910 cm⁻¹; $\delta_{TMS}^{CCl_4}$ (in ppm) 5.6 (multiplet, 2 H, =CH–), 3.6 (t, 2 H, *J* = 6.7 cps, CH₂-CH₂OH), integrates for twelve protons relative to two protons at 3.6 ppm. The infrared and nmr spectra were superimposable with those of known 2-(Δ²-cyclopentenyl)ethanol prepared by the lithium aluminum hydride reduction of Δ²-cyclopentenylacetic acid.[35] The α-naphthylurethan of the reduced aldehyde had mp 81–83° which showed no depression upon admixture with an authentic sample of the α-naphthylurethan of **4**.

2-(Δ²-Cyclopentenyl)ethanol (**4**) by the LiAlH₄ Reduction of Δ²-Cyclopentenylacetic Acid.—To a stirred slurry of 0.50 g of lithium aluminum hydride in 50 ml of ether was added 1.0 g of Δ²-cyclopentenylacetic acid.[35] After several hours, the excess hydride was quenched with a saturated aqueous solution of sodium sulfate. Hydrochloric acid (2 *N*) was added to hydrolyze the complex. The reaction mixture was filtered, and the ether layer was separated and dried (Na₂SO₄). Evaporation of the ether left 0.90 g of a viscous liquid. Analysis by vpc showed one product and some unreacted acid. A sample of the alcohol was collected from the gas chromatograph. Infrared and nmr spectra data are listed above.

Anal. Calcd for C₇H₁₂O: C, 74.95; H, 10.78. Found: C, 74.83; H, 11.09.

The α-naphthylurethan had mp 82–83°.

Anal. Calcd for C₁₈H₁₉O₂N: C, 76.84; H, 6.81; N, 4.98. Found: C, 77.00; H, 7.00; N, 5.25.

1-Methylcyclohexene.—The infrared spectrum of the olefin collected from the pyrolysis of **6** was found to be identical with that of authentic 1-methylcyclohexene, obtained by methyl Grignard addition to cyclohexanone and acid dehydration of the resulting alcohol.

Δ²-Cyclohexenylacetaldehyde (**7**).—The lesser of the two major products from the pyrolysis of **6** displayed the following physical data: infrared (CCl₄) 3030, 2860, 2710, 1725, 1685, 1650, 1435, and 835 cm⁻¹; $\delta_{TMS}^{CCl_4}$ (in ppm) 9.7 (t, 1 H, *J* = 2 cps, CH₂CHO), 5.5 (m, 2 H, =CH–). The 2,4-dinitrophenylhydrazone had mp 99.5–100.5° (lit.[15] mp 97°).

Anal. Calcd for C₁₄H₁₆O₄N₄: C, 55.25; H, 5.30. Found: C, 55.18; H, 5.06.

Hydrogenation of 50 mg of **7** with 5% palladium on charcoal gave a compound whose 2,4-dinitrophenylhydrazone had mp 123.5–125° (lit.[18] mp 124–125° for the 2,4-dinitrophenylhydrazone of cyclohexylacetaldehyde).

Reduction of **7**.—To a stirred slurry of 0.10 g of lithium aluminum hydride in 10 ml of ether was added a solution of 0.10 g of **7** in 5 ml of ether. A small amount of the resulting alcohol was collected from the gas chromatograph for spectral analysis. The infrared spectrum of this alcohol was compared with that of known 2-(Δ³-cyclohexenyl)ethanol[17] and 2-(Δ²-cyclohexenyl)ethanol and found to be identical with that of the latter.

2-(Δ²-Cyclohexenyl)ethanol.—Δ²-Cyclohexenylacetic acid[18] (3.0 g) was treated with 1.6 g of lithium aluminum hydride to give 2.45 g (91%) of a pure colorless liquid: bp 76–77° (2 mm) [lit.[36]

(24) H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2951 (1961).

(25) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *ibid.*, **76**, 6271 (1954).

(26) C. L. Wilson, *ibid.*, **69**, 3002 (1947).

(27) D. L. Garin, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1964.

(27a) NOTE ADDED IN PROOF.—The *endo* isomers of the bicyclic carboxaldehydes (**3** and **14**) rearrange to the respective unsaturated acetaldehydes (**2** and **7**) when injected into a gas chromatograph with the injection port heated to 230°.

(28) Melting points and boiling points are uncorrected. Nmr spectra were obtained on a Varian HR-60 spectrometer in CCl₄ with tetramethylsilane as internal standard. Except where otherwise noted, a Perkin-Elmer RX vpc column was used exclusively (a 2-m, 0.25-in. diameter column utilizing Ucon oil LB-550-X on diatomaceous earth). Percentage compositions refer to the relative areas observed for the different components.

(29) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

(30) K. M. Korach, R. D. Nielsen, and H. W. Rideout, *ibid.*, **82**, 4328 (1960).

(31) R. Srinivasan, *ibid.*, **84**, 4141 (1962); W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, **27**, 1910 (1962).

(32) FMC Corp., New York, N. Y.

(33) J. Meinwald and R. A. Chapman, *J. Amer. Chem. Soc.*, **90**, 3218 (1968).

(34) R. K. Hill and A. G. Edwards, *Tetrahedron Lett.*, 3239 (1964).

(35) C. R. Noller and R. Adams, *J. Amer. Chem. Soc.*, **48**, 2444 (1926).

(36) L. F. Fieser, M. T. Leffler, *et al.*, *ibid.*, **70**, 3195 (1948).

bp 74–75° (2 mm)]; infrared (CCl₄), 3300, 3030, 3010, 1645, 1448, 1432, 1138, 1067, 1049, 1010, 973, 888, 835, 720, 678, and 662 cm⁻¹.

3,4-Tetramethylene-2,3-dihydrofuran (8).—The major product (56%) from the pyrolysis of 6 displayed the following physical data: infrared (neat), 2910, 2850, 1670, 1470, 1445, 1100, 1085, 1060, 1040, 940, 920, 835, and 788 cm⁻¹; uv max (95% ethanol) 214 mμ (ε 6100).

The enol ether 8 (50 mg) was hydrogenated in ethyl acetate with 5% platinum oxide on charcoal to give essentially one compound as shown by vpc analysis. A sample of the saturated ether collected by preparative vpc showed the following physical data: infrared (CCl₄), 2930, 2860, 2670, 1590, 1480, 1450, 1135, 1082, 1060, 1030, 968, 926, and 892 cm⁻¹; δ$_{TMS}^{CCl_4}$ (in ppm) 3.6 (m, 4 H, CHO), 2.2 (broad, 2 H, >CH–), and 1.5 (broad single peak, 8 H, CH₂). Both infrared and nmr spectra were superimposable with those of cis-hexahydrophthalan (9).

cis-**Hexahydrophthalan (9).**—Following the procedure of Warnell and Shriner for the ozonolysis of an olefin,[19] bicyclo-[4.2.0]oct-7-ene[31] (0.50 g, 0.046 mol) in anhydrous ethanol (40 ml) was cooled in an ice bath and a stream of ozone in oxygen (2%) was passed through the solution for 0.5 hr. The ethanol solution was allowed to warm to room temperature and concentrated *in vacuo*. The crude liquid ozonide was dissolved in ether (5 ml) and added dropwise to a stirred suspension of lithium aluminum hydride (1.0 g) in ether (20 ml). The mixture was allowed to stir for 1 hr then refluxed for 0.5 hr. Excess hydride was quenched with water and 2 N hydrochloric acid (1 ml) was added. The solution was allowed to stir until hydrolysis was complete. The ether solution was filtered and dried (Na₂SO₄). Removal of the ether *in vacuo* gave 0.50 g of a colorless viscous liquid. A small amount of this liquid was dissolved in ether and induced to crystallize by keeping it in the freezer overnight. The white crystals had mp 40–42° (lit.[37] mp 42–43° for cis-hexahydrophthalyl alcohol).

Without further purification, the liquid diol was refluxed with 18% sulfuric acid (2 ml) for 20 min, in a manner similar to that reported[20,21] to give 0.40 g of a liquid with a terpenelike odor which was shown to be essentially one compound by vpc analysis. The infrared spectrum of 9 was identical with that published for *cis*-hexahydrophthalan.[38]

(37) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **28**, 1388 (1963).

Bicyclo[3.2.0]heptan-6-one (10).—Following the procedure of Brown and Zweifel for the hydroboration of a olefin,[39] bicyclo-[3.2.0]hept-6-ene[29] (18.2 g, 0.19 mol) yielded 17.0 g of a colorless liquid alcohol. Chromic acid oxidation[40] gave 13.0 g of crude product. Distillation afforded 5.0 g (24%) of colorless liquid: bp 65–70° (16 mm) [lit.[41] bp 162–166°]; infrared (CHCl₃), 1780 cm⁻¹. The semicarbazone derivative had mp 200–201.5° (lit.[41] mp 198.5–201°).

Bicyclo[4.2.0]octan-7-one (11).—Following the procedure of Brown and Garg for the conversion of olefins into ketones,[24] 3.0 g (0.028 mol) of bicyclo[4.2.0]oct-7-ene[31] gave 1.2 g (35%) of colorless liquid: bp 55–60° (4 mm) [lit.[6] bp 89–90.5° (25 mm)]; infrared (neat), 1780 cm⁻¹.

Pyrolysis of 10.—The pyrolysis of 0.40 g of 10 in the manner described above gave a gas and a low-boiling liquid. The liquid was analyzed by vpc on a Perkin-Elmer RX column[28] at 75°. The retention time of the liquid was identical with that of cyclopentene. A sample of the liquid was collected from the gas chromatograph. The infrared spectrum was superimposable with that of authentic cyclopentene.[42]

Pyrolysis of 11.—The pyrolysis of 0.25 g of 11 in the manner described above gave a gas and a low-boiling liquid. The liquid was analyzed by vpc on a Perkin-Elmer RX column[28] at 75°. The retention time of the liquid was identical with that of cyclohexene. A sample of the liquid, collected from the gas chromatograph, had an infrared spectrum which was superimposable with that of authentic cyclohexene.[42]

(38) J. Entel, C. H. Ruof, and H. C. Howard, *J. Amer. Chem. Soc.*, **74**, 441 (1952).
(39) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).
(40) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2952 (1961).
(41) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).
(42) Aldrich Chemical Co., Milwaukee, Wis.

Diels–Alder Adducts of 1,3-Dimethyl-1,3-cyclohexadiene

R. N. MIRRINGTON AND K. J. SCHMALZL

Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

The structures and stereochemistry of the major Diels–Alder adducts of 1,3-dimethyl-1,3-cyclohexadiene (2) with methyl vinyl ketone, methyl acrylate, and ethyl propiolate have been established as 4a, 4b, and 6d, respectively. Lactonization of acid 4c afforded either novel δ-lactone 7 or γ-lactone 8 as the major product depending on the conditions used. Lactone 7, the kinetically stable product, represents the first of such δ-lactones to be isolated in the bicyclo[2.2.2]octane series.

In connection with our work on the total synthesis of novel terpene skeletons, we required a supply of endo-1,5-dimethylbicyclo[2.2.2]oct-5-en-2-yl methyl ketone (4a). Although a Diels–Alder reaction between 1,3-dimethyl-1,3-cyclohexadiene (2) and methyl vinyl ketone would be expected[1] to yield 4a as the major product, we considered it necessary to make a detailed study of the nature of the adduct(s) from this reaction, particularly since no Diels–Alder adducts of 2 have been described previously, and because the stereochemical and structural integrity of 4a was vital for our future work.

Discussion

1,3-Dimethyl-1,3-cyclohexadiene.—The Grignard addition of methylmagnesium halide to 3-methyl-2-cyclohexen-1-one has been reported several times[2–6] and, except in two cases,[2,6] the product has been described as 1,3-dimethyl-1,3-cyclohexadiene (2). However, von Auwers[2] isolated carbinol 1, which could be dehydrated to a diene, considered by him to be 3. On the other hand, Thomas and Stoll[6] demonstrated by

(1) (a) H. L. Holmes, *Org. Reactions*, **4**, 60 (1948); (b) K. Alder, "Newer Methods of Preparative Organic Chemistry," Vol. 1, Interscience Publishers, New York, N. Y., 1948, p 381.

(2) K. von Auwers, *Ber.*, **46**, 2988 (1913).
(3) W. N. Haworth, *J. Chem. Soc.*, **103**, 1242 (1913).
(4) A. J. Birch, *ibid.*, 1642 (1947).
(5) (a) R. Y. Levina, N. P. Shusherina, K. D. Gir, and E. G. Treshchova, *Zh. Obshch. Khim.*, **24**, 1551 (1954); *Chem. Abstr.*, **49**, 11571 (1955). (b) R. Y. Levina, V. K. Daukshas, and T. P. Surikova, *Zh. Obshch. Khim.*, **30**, 2145 (1960); *Chem. Abstr.*, **55**, 8317 (1961).
(6) A. F. Thomas and M. Stoll, *Chem. Ind.* (London), 1491 (1963).