A correlation of molecular flexibility with ring size is also possible in both types of ethers III and IV. Compounds V, VI, and VII, which differ only in number of ring difluoromethylene groups (from four- to six-membered rings), vary in order of 0° F. viscosity in ring-size order of $6 \gg 4 > 5$. The same relationship in the Type IV ethers establishes the better fluid properties of perfluorinated cyclopentane and cyclobutane systems over cyclohexane systems.

The thermal stabilities of most of these ethers averaged about 500° F., although V and VII ethers had stabilities above 550° F., with the high fluorine content of both ether types resulting in good fire resistance properties. The perfluorocyclobutene trimer, XV, was an extremely mobile fluid with a viscosity of 117 cs. at −65° F., compared to the acyclic n-$C_{12}F_{26}$, which is a solid at 167° F. The thermal stability of XV was above 900° F., as measured by a pressure isoteniscope.

LITERATURE CITED

(1) Blake, E.S., Edwards, J.W., Hammann, W.C., Reichard, T.E., Ort, M.O., J. Chem. Eng. Data **6**, 87 (1961).
(2) Brice, T.J., Cohn, R.I., *J. Am. Chem. Soc.* **75**, 2921 (1953).
(3) Clayton, A.B., Roylance, J., Sayers, D.R., Stephens, R., Tatlow, J.C., *J. Chem. Soc.* **1965**, p. 7358.
(4) Faurote, P.D., Henderson, C.M., Murphy, C.M., O'Rear, J.G., Ravner, H., *Ind. Eng. Chem.* **48**, 445 (1956).
(5) Gash, V.W., Bauer, D.J., *J. Org. Chem.* **31**, 3602 (1966).
(6) Henne, A.L., Latif, K.A., *J. Ind. Chem. Soc.* **30**, 809 (1953).
(7) McKee, E.T., Crain, D.L., Crain, R.D., Betohlav, L.R., Braendlin, H.P., *J. Am. Chem. Soc.* **84**, 3557 (1962).
(8) Park, J.D., Dick, J.R., Lacher, J.R., *J. Org. Chem.* **28**, 1154 (1963).
(9) Park, J.D., Lacher, J.R., Dick, J.R., *Ibid.*, **31**, 1116 (1966).
(10) Park, J.D., Sharrah, M.L., Lacher, J.R., *J. Am. Chem. Soc.* **71**, 2337 (1949).
(11) Park, J.D., Snow, C.M., Lacher, J.R., *Ibid.*, **73**, 2342 (1951).
(12) Park, J.D., Wilson, L.H., Lacher, J.R., *J. Org. Chem.* **28**, 1008 (1963).
(13) Pruett, R.L., Bahner, C.T., Smith, H.A., *J. Am. Chem. Soc.* **74**, 1638 (1952).
(14) Rapp, K.E., Pruett, R.L., Barr, J.T., Bahner, C.T., Gibson, J.T., Lafferty, R.H., Jr., *Ibid.*, **72**, 3642, 3646, 4480 (1950).
(15) Shepard, R.A., Lessoff, H., Domijan, J.D., Hilton, D.B., Finnegan, T.F., *J. Org. Chem.* **23**, 2011 (1958).
(16) Stockel, R.F., Beachem, M.T., Megson, F.H., *Can. J. Chem.* **42**, 2880 (1964).
(17) West, R., Nin, H.Y., Ito, M., *J. Am. Chem. Soc.* **85**, 2584 (1963).

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Copper Chromite Reduction of Ethyl Pinonate

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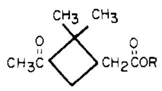
The effect of copper chromite catalyst on the hydrogenation of ethyl pinonate, ethyl 3-acetyl-2,2-dimethylcyclobutaneacetate was to reduce the carbonyl at 140° C., giving ethyl pinolate, some of which pyrolyzed and gave 3-vinyl- and 3-ethylidienecyclobutane derivatives before the carboxyl function was reduced to alcohol. The result was a mixture of 2,2-dimethyl-3-ethylcyclobutaneethanol and 2,2-dimethyl-3-(2-hydroxyethyl)-cyclobutaneethanol. Because the yield of mono alcohol was about 38% and of glycol only 34%, copper chromite reduction of ethyl pinonate is considered impractical.

A NUMBER of papers have emanated from this laboratory on the chemistry of *dl*-pinonic acid (I_A) and *dl*-pinolic acid (II_A). This report is closely related to some of the earlier work and was prompted by a request for a large sample of the glycol, 2,2-dimethyl-3-(2-hydroxyethyl)-cyclobutaneethanol (III) for evaluation as an intermediate for polyurethanes. Accordingly, a study of the copper chromite reduction of ethyl pinonate (I_B) was made as a preparative method for this glycol. When I_B was reduced, the reduction product was a mixture of III_A and 2,2-dimethyl-3-ethylcyclobutaneethanol (IV). The composition of each was obtained by comparing III_A and IV_A with materials made by alternate syntheses, III_B, III_C, and IV_B.

EXPERIMENTAL

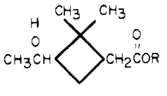
Boiling points, °C., are uncorrected. The carbon and hydrogen analyses were made by Galbraith Laboratories, Inc., Knoxville, Tenn. The GLPC data were obtained from (A) a column ⅛ inch by 15 feet, packed with 30% Carbowax 20M on Chromosorb W, or (B) a column 3/16 inch by 12 feet, packed with 20% Carbowax 20M on Gas Chrom Q.

2,2-Dimethyl-3-(2-hydroxyethyl)cyclobutaneethanol (III). A. Ethyl pinonate, I_B, 360 grams (1.65 mole) n_D^{20} 1.4526 [lit. 1.4526 (*4*)], prepared by the esterification of *cis-dl*-pinonic acid with ethanol in toluene using *p*-toluenesulfonic acid as a catalyst, was reduced with lithium aluminum hydride



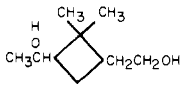
I_A R=H

I_B R=C$_2$H$_5$



II_A R=H

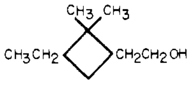
II_B R=C$_2$H$_5$



III_A FROM COPPER CHROMITE REDUCTION OF I_B

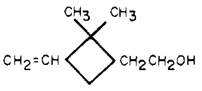
III_B FROM THE LAH REDUCTION OF I_B

III_C FROM THE LAH REDUCTION OF II_A

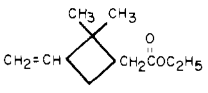


IV_A COPPER CHROMITE REDUCTION OF I_B

IV_B HYDROGENATION OF V



V



VI

(LAH) in accordance with Park *et al.* (*2*), except that decomposition of the LAH complex was accomplished by dropwise addition of water so that the solids agglomerated and settled quickly when stirring was interrupted. Treatment with mineral acid was unnecessary. The product was isolated by filtering to remove the sludge, washing the sludge with ether, evaporating ether, and distilling, 210 grams of I_B, 73.9%. n_D^{20} 1.4754. Anal. Calcd., $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.93, H, 11.90.

The chromatogram from the GLPC analyses, column A or B, had four peaks with relative peak areas of 34.4, 7.6, 2.5 and 1.0. The GLPC chromatogram of I_B, column A, had two peaks with relative areas of 4 to 1.

B. Solid pinolic acid (II_A), m.p. 104° C. from water, 2.0 grams (0.011 mole) was reduced similarly with LAH and gave 1.65 gram of product, 100%. The GLPC chromatogram, column A, had two peaks with relative areas of 6.8 to 1. These had the same retention times as peaks 1 and 2 above.

C. Copper Chromite Reduction of II. Ethyl pinonate, I_B, 586 grams (2.8 moles), was reduced neat in a rocking-type pressure reactor at 140° C. with 4 to 5000 p.s.i. of hydrogen and 58 grams of barium promoted copper chromite powdered catalyst (Girdler G-22). A sample was taken, dissolved in benzene, and filtered to remove the catalyst. After removal of solvent, analyses of the residue by GLPC and by infrared spectroscopy indicated the presence of a substantial amount of II_B. The entire batch was worked up like the sample and recharged in the pressure reactor with 50 grams of fresh catalyst, hydrogen added at 3,000 p.s.i., and heated to 275° C. After about five hours, the reactor was allowed to cool and the product dissolved in benzene, filtered, and distilled. Two batches were combined, giving 372 grams of slightly impure IV_A, 38.2%, b.p. 92–96° C., 3.0 mm., n_D^{20} 1.4497, and 331 grams of III_A, 34.4%, b.p. 136–138° C., 2.0 mm. Hydroxyl equivalent calcd. for $C_{10}H_{20}O_2$: 86.13. Found: 88.1, n_D^{20} 1.4699. The composition of the lower-boiling fraction was confirmed by comparing the GLPC chromatogram, column B, and infrared spectrum with that of IV_A obtained from hydrogenation of the vinyl derivative, V (below).

The GLPC chromatogram, column A or B, for the higher-boiling fraction had the same four peaks as the glycol obtained by the LAH reduction of ethyl pinonate above. Since the relative peak areas (1.67, 1, 8, and 1.67) were different, it is assumed the same four isomers are present, but in different amounts. The glycols III_A, III_B, and III_C had identical infrared spectra.

2,2-Dimethyl-3-vinylcyclobutaneethanol (V). Ethyl 2,2-dimethyl-3-vinylcyclobutaneacetate (VI)[4], 19.4 grams (0.1 mole), was reduced with 6 grams LAH, as above. A colorless slightly viscous liquid was obtained, 14 grams, 91%, b.p. 78–79° C. at 2 mm., n_D^{20} 1.4646. There were strong vinyl bands in the infrared at 908, 1649, and 3010 cm.$^{-1}$. Anal. Calcd. for $C_{10}H_{18}O$: C, 77.68; H, 11.77. Found: C, 78.01; H, 11.47.

2,2-Dimethyl-3-ethylcyclobutaneethanol (IV_B). The vinyl compound V, 2.0 grams, in ethanol was reduced with hydrogen, 30 p.s.i., using platinum oxide catalyst. Isolating the product gave 1.93 grams, n_D^{20} 1.4491.

DISCUSSION

Ethyl *dl*-pinonate made by direct esterification of *cis* I_A is a mixture of cis and trans isomers in a ratio of 4 to 1. Similarly, *dl*-pinolic acid used in this work was a mixture of cis and trans isomers. Thoi (*5*), Trave (*6*), and other workers have assigned the name of *cis-dl*-pinonic and *cis-dl*-pinolic acids to the high-melting isomers (105° C. for both pure acids). The lower-melting or liquid materials were assigned to the trans configuration. The relative amounts of the isomers of esters of either of the acids used in this work were readily discernible by GLPC. Nomenclature of these authors is used in this report.

Both I_B and II_A were reduced with LAH to obtain III_B and III_C for comparison with III_A. The product III_C had two peaks in its GLPC chromatogram, and must have been a mixture of cis and trans isomers. The chromatogram from III_B had four peaks, two of which had the same retention times as the isomers of III_C. Accordingly, the glycol III_B must have contained the cis and trans isomers of III_C, and it is reasonable to expect the presence of two diastereomers isomeric with the above cis and trans isomers. No subsequent work, however, has been done to establish this. The chromatogram of III_A had four peaks with retention times identical to those of III_B, but the relative composition as represented by the peak areas of the chromatogram was somewhat different. The elemental analyses, hydroxyl equivalent, and infrared spectral analyses are in support of the structure III_A as assigned.

Park *et al.* (*2*) used LAH reduction of a number of similar materials giving a number of hydroxyalkyl and olefinic substituted gem-dimethylcyclobutanes without complications from isomerization or rearrangement. Park and coworkers also studied the pyrolysis and rearrangement of II_A (*3*). Data in this report and accumulated data in this laboratory show that products of rearrangement would be discernible by GLPC. From the evidence presented, there seems to be little doubt that III_A and III_B are mixtures of glycols as described.

The mono-alcohol IV_B was prepared by hydrogenation of the vinylcyclobutane derivative, V, which in turn was obtained from LAH reduction of VI prepared and described by Lewis and his collaborators (*1*). Since the ester, VI, was a cis-trans mixture, IV_B and V were also mixtures. Comparison of IV_A from the copper-chromite reduction with IV_B by GLPC and infrared spectroscopy leaves little doubt that IV_A is a cis-trans mixture like IV_B.

The formation of IV_A is believed to be simple and direct. During copper-chromite reduction of I_B, adsorption of hydrogen was quite rapid at 140° C. Letting the reaction cool to stop the reaction and examining a sample by GLPC and infrared spectroscopy showed the presence of an appreciable amount of II_B. Hydrogenation was continued. No appreciable amount of hydrogen up-take was observed until the temperature reached 250° C. The ketone was reduced at about 140° C., giving ethyl pinolate, some of which pyrolyzed at the higher reaction temperature. Hydrogenolysis rather than pyrolysis is not precluded; however, the conditions were practically the same as those described by Park *et al.* for the pyrolysis of pinolic acid (*3*). If pyrolysis occurred, the resulting 3-vinyl- and 3-ethylidenecyclobutane derivatives would hydrogenate, resulting in IV_A.

In view of the results obtained, use of a copper-chromite reduction for the preparation of III_A on a large scale seems impractical because of the susceptibility of pinolic acid to pyrolysis.

LITERATURE CITED

(1) Lewis, J.B., Settine, R.L., Mayne, R.Y., Hedrick, G.W., *J. Med. Chem.* **11**, 955–7 (1968).
(2) Park, J.D., Allphin, N.L., Jr., Choi, S., Settine, R.L., Hedrick, G.W., *Ind. Eng. Chem. Prod. Res. Develop.* **4**, 149 (1965).
(3) Park, J.D., Settine, R.L., Hedrick, G.W., *J. Org. Chem.* **27**, 902 (1962).
(4) Parkin, B.A., Jr., Hedrick, G.W., *J. Org. Chem.* **25**, 1417 (1960).
(5) Thoi, Le-Van, *Ann. Chim. (Rome)* **10**, 35 (1931).
(6) Trave, R., *Chim. Ital.* **85**, 908 (1958).

RECEIVED for review September 9, 1968. Accepted March 21, 1969. Mention of commercial products is for identification only and does not constitute endorsement by the U. S. Department of Agriculture over those of other manufacturers.