with chloroform) and a brown tar (eluted with 1:4-methanol-chloroform).

Anal. Calcd. for $C_{24}H_{28}O_4$(XIV) (380.46): C, 75.76; H, 7.42. Found: C, 76.04; H, 7.50.

Sodium Borohydride Treatment of the Enediol Sulfite (XIII).—To a colorless solution of 100 mg. of the enediol sulfite (XIII) in 7.5 ml. of 95% ethanol, was added 6 mg. of powdered sodium borohydride at room temperature. The solution turned yellow with evolution of hydrogen sulfide gas (detected with lead acetate paper). After complete solution of the borohydride, the solution was acidified with 1 *N* hydrochloric acid and extracted with ether. The ether layer was washed with water, 5% sodium bicarbonate solution, and again with water, then dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue (a yellow crystalline mass) was dissolved in petroleum ether (b.p. 30–60°) and chromatographed on 10 g. of silica gel. Elution with petroleum ether gave 80 mg. (93%) of mesitil and 5.4 mg. of crystalline sulfur. Mesitil resisted sodium borohydride reduction at room temperature, and gave hydromesitoin (XVI) smoothly only when boiled with sodium borohydride in 95% ethanol. Hydromesitoin (XVI), m.p. 205–206.5° (lit.,[21] 212–213°).

Anal. Calcd. for $C_{20}H_{26}O_2$ (298.41): C, 80.49; H 8.87. Found: C, 80.18; H, 8.55.

Bis(2,2′,4,4′,6,6′-hexamethyldesyl) Sulfite (X).—To a solution of 1.48 g. of mesitoin in 20 ml. of methylene chloride containing 0.8 ml. of pyridine, was added 0.35 ml. of thionyl chloride in 3 ml. of methylene chloride under agitation, at −20° in nitrogen. After being stirred for 2 hr., the reaction mixture was concentrated to dryness *in vacuo* at low temperature, and then extracted with dry benzene. The benzene solution was subjected to freeze-drying and gave a white powder, m.p. 200–202° (1.85 g.). Recrystallization of this powder from chloroform gave fluffy crystals, m.p. 202–204°, ν_{max} (cm.$^{-1}$): 1712 (C=O), 1205 (S=O).

Anal. Calcd. for $C_{40}H_{46}O_5S$ (638.83): C, 75.20; H, 7.26. Found: C, 77.96; H, 7.78.

On standing in the air for a long time, the color of this compound turned pale brown even in a refrigerator.

Reaction of Mesitoin with Sulfuryl Chloride.—To 400 mg. of mesitoin placed in a 50-ml. round-bottomed flask, cooled in an ice bath, was added 0.4 ml. of sulfuryl chloride, and the reaction mixture which was allowed to stand at 0° for 12 hr. solidified. After evacuation to remove the excess sulfuryl chloride, the mixture was dissolved in petroleum ether and chromatographed on 10 g. of silica gel. Elution with petroleum ether gave 11 mg. of colorless needles, m.p. 125°, and 20 mg. (5%) of mesitil, m.p. 118–119°. Elution with 1:9-benzene-petroleum ether gave 25 mg. of a colorless compound, m.p. 157–159°, ν_{max} (cm.$^{-1}$): 1704 (C=O), 1460, and 1168 (sulfate group ?).

Anal. Found: C, 65.0; H, 5.55.

Elution with 1:3 benzene-petroleum ether gave 186 mg. of a colorless compound, m.p. 159°, ν_{max} (cm.$^{-1}$): 3570 (OH), 1702 (C=O).

Anal. Found: C, 60.33; H, 5.48.

Crystalline products other than mesitil have not been identified yet, but the details of this reaction will be reported elsewhere.

Acknowledgment.—The author wishes to thank Professor Louis F. Fieser for the privilege and inspiration of working in his laboratory. This work was supported by grants from the National Cancer Institute of the National Institutes of Health (CY-1696) and the National Science Foundation.

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[21] R. C. Fuson, J. J. Denton, and C. E. Best, *J. Org. Chem.*, **8**, 64 (1943).

Equilibration of Bicyclic Alcohols

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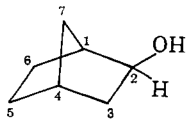
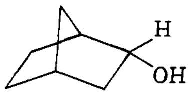
Equilibration under various conditions of *exo*- and *endo*-norborneol as well as isoborneol and borneol is reported. The equilibrium constants are linearly correlated with the relative rates of oxidation. A similar linear correlation is noted between the relative oxidation rates of epimeric cholestanols and their estimated relative stabilities.

In contrast to the extensive study of reactions of strained bicyclic systems there has been much less work on quantitative determination and analysis of this strain.[2] This paper is concerned with one aspect of the general problem, the measurement of the relative stability of *exo* and *endo* epimeric alcohols of [2.2.1]-bicycloheptane derivatives. These data are applied to the analysis of the rates of chromic acid oxidation of the bicyclic alcohols. As a result of this analysis and its extrapolation to the epimeric cholestanols an approximate but facile method for indirectly determining alcohol stability is developed.

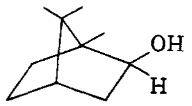
Results and Discussion



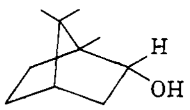
Ia



Ib



IIa



IIb

The relative stability of *exo*- and *endo*-hydroxyl group was determined at different temperatures for norborneol (Ia and Ib) and borneol (IIa and IIb) by equilibration of *exo–endo* mixtures with aluminum isopropoxide and analysis by gas–liquid chromatography.[3] In a series of control experiments it was determined that multiple ether extractions were required for representative sampling and it was shown that within our estimated error in composition (±1–3%) no molar response corrections were required for the chromatographic analyses. With borneol, which equilibrates more slowly than norborneol, the equilibrium composition was approached from both sides. The single

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[1] This paper is based in part on the dissertation of M. Sexton submitted in September, 1961, to the Graduate School of Cornell University in partial completion of the requirement for the M.S. degree.

[2] An unpublished calculation and correlation of the available data by H. Dauben assigns a strain energy of about 10 kcal./mole to bicycloheptane (H. Dauben, private communication).

[3] The experimental procedure was patterned after that of C. H. De Puy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960). These authors did not specify the amount of extraction employed. We found that multiple extraction was required.

TABLE I

PERCENTAGE *endo* ISOMER IN EQUILIBRATION OF BICYCLIC ALCOHOLS WITH ALUMINUM ISOPROPOXIDE[a]

Compound	Temp., °C.	% *endo*
Norborneol[b]	100	20[c]
	111	20
	116	22
	137	(23)[d]
Borneol	100	71
	137	69[c] (70)[d]
Dehydronorborneol[b]	100	*ca.* 45 ± 5 (53)[e]

[a] The reduction of bicyclic ketones has been reviewed by A. Rassat, *Tetrahedron Letters*, 21, 16 (1960). [b] De Puy and Story[3] obtained a 50:50 mixture for the norborneols and a 65:35 *endo exo* mixture for the dehydronorborneols. It is felt that the discrepancy may result from different extraction procedures. [c] Essentially identical results were obtained by equilibration with fluorenone and sodium; see text. [d] From reduction of norcamphor under special conditions; see text for details and implications. [e] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 77, 3034 (1955).

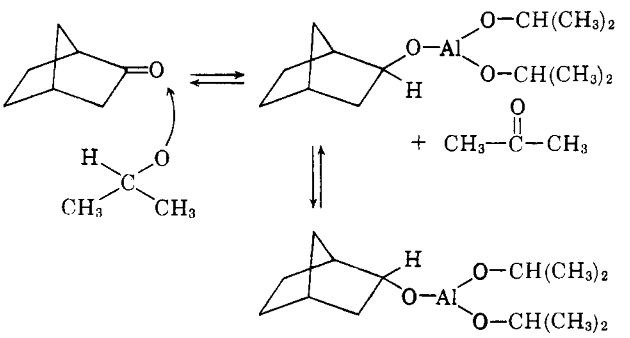
available norborneol mixture was equilibrated for periods at least 1.5 to 2 times longer than required for complete equilibration of the borneols. The results are summarized in Table I.

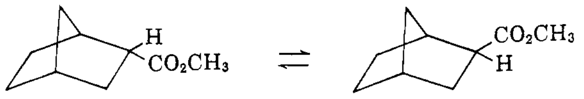
In a second series of runs borneol mixtures and norborneol mixtures were equilibrated using sodium and fluorinone in toluene. The resulting compositions were identical within experimental error to the corresponding aluminum isopropoxide equilibrations. Roberts, *et al.*,[4] report that a similar sodium–fluorinone equilibration at 111° of the norborneols gives 26% *endo*-norborneol. This is in reasonable agreement with our results (see Table I), particularly if allowance is made for their indirect analytical method.[5]

The identical results of the two equilibration procedures indicate that solvent has a negligible effect on the equilibrium compositions. Strong support for this conclusion is provided by the work of Takeshita and Kitajama[6] who found that (1) equilibration of the borneols at 190–200° in methanol, ethanol, isopropyl alcohol, or *t*-butyl alcohol gave 65% borneol and (2) reduction of camphor with aluminum isopropoxide in isopropyl alcohol at 88° gave 72% borneol at equilibrium. A plot of log K *vs.* $1/T$ of their data combined with ours gives a good linear correlation that is characterized by a ΔH of -1.00 kcal. and a ΔS of -0.88 e.u. with an average deviation of 0.004 in log K (about 0.2% in composition). Errors of ±1% in composition correspond to *ca.* ±0.3 kcal. in ΔH and ±0.5 e.u. in ΔS.

The data on the norborneols do not cover a sufficient temperature range to yield reliable ΔH and ΔS values but they do indicate a rough parallel to the borneol behavior with a similarly low dependence of log K temperature.

Camphor and norcamphor were reduced with aluminum isopropoxide in dry toluene without added acetone or alcohol in sealed tubes at 137°. The reaction mixture was cooled, hydrolyzed with cold dilute hydrochloric acid, and the alcohols analyzed as before. The camphor tubes required about eight days of heating at 137° to give a constant composition. These reductions and equilibrations (illustrated for norcamphor in equation 1) differ from the usual procedure by the absence of alcohol. If it is assumed that the generated acetone does not form significant amounts of enolate ester with the aluminum, then the actual materials equilibrated were the aluminate esters of the *endo* and *exo* alcohols. Since these equilibrium compositions were nearly identical with those obtained in the alcohol equilibrations, it seems necessary to conclude that an additional aluminum atom adds little to the steric requirements of the hydroxyl group.[7] It is interesting to note that equilibration[8] at 74–108° of *endo*- and *exo*-5-carbomethoxybicyclo[2.2.1]heptane (IIIa and IIIb) gave about the same ratio of epimers as the norborneols.





30% IIIa

70% IIIb

Cope[8] reported also that *endo*- and *exo*-5-carbomethoxybicyclo[2.2.1]heptene gave 52% of the *endo* isomer. An attempt was made to equilibrate dehydronorborneol with aluminum isopropoxide and with fluorenone–sodium. In both cases there was discoloration of the tubes in keeping with the known sensitivity of the intermediate ketone to basic reagents.[9] The approximate values of *ca.* 45 ± 5% obtained at 100° is in line with the ester equilibration. Roberts, *et al.*,[10] have reported 53% at 111°. These results also are in accord with the idea that atoms more than one atom removed from the ring have small steric requirements.

Application of Equilibrium Data to the Interpretation of Chromic Acid Oxidation Rates.—Kwart and Francis[11] have measured the rates of acid-catalyzed chromic acid oxidation of several alcohols in aqueous acetic acid; included were the borneols and 2-norborneols for which they obtained from the third-order kinetic term the ratios of 1.0:3.9:9.7:25:49 for cyclohexanol:*exo*-norborneol:*endo*-norborneol:borneol:isoborneol, re-

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[4] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.* **76**, 4501 (1954).

[5] A solution of the equilibrated alcohols was concentrated and then converted into a mixture of *endo*- and *exo*-*p*-bromobenzenesulfonates, which was analyzed kinetically.

[6] T. Takeshita and M. Kitajima, *Nippon Kagaku Zasshi*, **79**, 1472 (1958); *Chem. Abstr.*, **54**, 5729h (1960).

[7] This result is in marked contrast to the results of E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960), who found that the —OAlCl$_2$ had much larger steric requirements than an OH group. This difference could indicate either (a) that we had water present in spite of our precaution or (b) that, as Eliel and Rerick suggest, the —OAlCl$_2$ is swollen by solvent interaction. The smaller steric requirements of a —CO$_2$Et group compared to a —CO$_2$H is in keeping with suggestion b.

[8] A. C. Cope, E. Ciganek, and N. A. Le Bel, *ibid.*, **81**, 2799 (1959).

[9] S. J. Cristol and P. K. Freeman, *ibid.*, **83**, 4427 (1961).

[10] Table I, ref. *e*.

[11] H. Kwart and P. S. Francis, *ibid.*, **81**, 2116 (1959).

spectively.[12] In interpreting their data Kwart and Francis emphasized the relative instabilities of the intermediate chromate esters. Although this breakdown of chromic acid oxidation rates into an equilibrium term and a kinetic term is correct and revealing, it is possible to analyze the data in an alternative manner using another fundamental energetic relationship. For a two-step reaction involving a fast prior equilibrium followed by a slow decomposition of the intermediate, the rate of product formation is independent (subject to the conditions noted below)[13] of the relative stability of the intermediate. In qualitative terms this independence arises because a change in decomposition rate due to a change in stability of the intermediate is exactly compensated by a change in the concentration of the intermediate. Thus, the relative rates of oxidation of two alcohols under the same conditions are determined by the differences in relative stability of the alcohols and their transition states. As the transition states approach each other in energy, the ratio of oxidation rates approaches the equilibrium constant for the ground states. Conversely, a comparison of the equilibrium constant to the ratio of oxidation rates gives a measure of how nearly energetically equivalent are the two transition states.

Although the equilibrium and oxidation data are not at the same temperature, the low ΔH of the equilibration constants as well as the apparently low $\Delta\Delta H^*$ of the oxidation rates suggests that temperature differences may be ignored. Comparison of the relative rates of oxidation of an epimeric pair of alcohols with the corresponding equilibrium constant indicates that the transition states apparently have gone about two thirds of the way towards energetic equivalence. This does not mean that the oxygen atom has moved two thirds of the way towards its final position in the ketone product. Because of the high sensitivity of steric effects to the separation between interacting groups, small displacements greatly alter steric repulsions. Rough calculations of oxygen–hydrogen and oxygen–methyl interactions indicate that displacements of only *ca.* 0.3 Å. are required to reduce the steric repulsions to one third of their magnitude in the starting alcohol.[14] If 0.3 Å. is transformed into an angular displacement of the oxygen towards its final ketone position it corresponds to a rotation of about 12° (complete conversion to ketone requires a rotation of 109°/2 or 55°). It seems that in the transition state the hybridization of the remaining carbon–carbon bonds more nearly approximates the starting alcohol (*ca.* sp^3) than the final ketone (*ca.* sp^2).[15] It should be emphasized that the advantage of comparing epimeric alcohols is that rehybridization effects and electronic effects[16] tend to cancel.

As a further check on the validity of this approach,

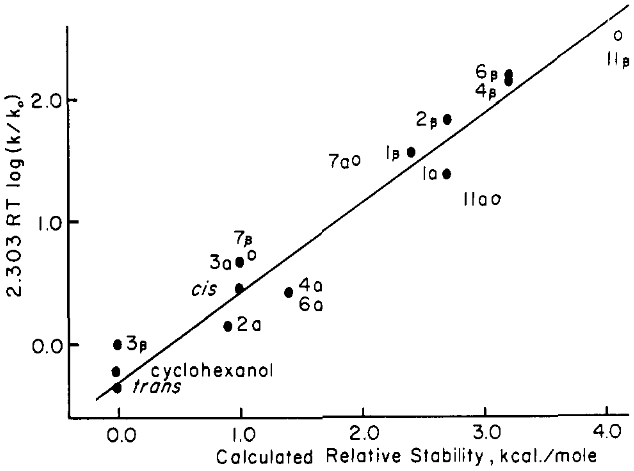

Fig. 1.—$\Delta\Delta F^*$ of alcohol oxidation *vs.* ΔF of alcohol stability.

the data of Schreiber and Eschenmoser[17] on rates of oxidation of six epimeric pairs of cholestanols have been examined in an approximate but analogous fashion. The relative stability of five of the pairs was estimated by applying conventional 1:3 diaxial repulsion contributions for the appropriate $H:CH_3$, $H:OH$, and $OH:CH_3$ interactions.[18] The reference state for each pair was the hypothetical structure in which the OH group and the H atom attached to the carbon bearing the OH group had been removed from the molecules.[22] For the 2-, 3-, 4-, and 6-epimeric alcohols. Comparison of the observed rate ratios with the estimated difference in stability indicates that the transition states have achieved roughly 90% energetic equivalence.[23] The treatment fails badly for the 1α, and 1β-cholestanols (a negative value is obtained). This, perhaps, is not surprising in view of the small difference in estimated stability (0.3 kcal./mole).

In the course of tabulating the rate–stability comparisons it was noted that in addition to the correlation between epimeric pairs of the alcohols there was a more striking correlation for the entire set of alcohols.[24] A plot of $\Delta\Delta F^*$ derived from the rate data *vs.* the calculated ΔF of alcohol stability is shown in Fig. 1. Also included are the points for cyclohexanol, *cis*- and *trans*-4-*t*-butylcyclohexanol,[25] and the previously unmanageable 1α- and 1β-cholestanols. The least squares slope is 0.74 (correlation coefficient, 0.95) with an average deviation of $\Delta\Delta F^*$ of 0.19 kcal./mole (*ca.* 35% in rate) or alternatively a deviation in the

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(12) Similar ratios may be derived from the data of Kwart and Francis[11] for the fourth-order terms.

(13) This holds only when the concentration of the intermediate is small compared to the concentration of the reactants. This condition should hold when the reaction follows good second-order kinetics.

(14) The calculation was made using rare gas repulsions as a measure of the interaction as discussed in Chap. 12 by F. H. Westheimer in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956. The geometry used was that of C. F. Wilcox, *J. Am. Chem. Soc.*, **82**, 416 (1960).

(15) This same point has been made in another way by Kwart.[16]

(16) H. Kwart, J. A. Ford, Jr., and G. C. Corey, *J. Am. Chem. Soc.*, **84**, 1252 (1962), and earlier work cited therein.

(17) J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **38**, 1529 (1955).

(18) The values used were 0.5 kcal./mole for $H:OH$,[19] 0.9 kcal./mole for $H:CH_3$,[20] and 2.2 kcal./mole for $OH:CH_3$.[19] The $H:OH$ value employed is at the upper limit of the observed range.[21]

(19) E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).

(20) D. S. Noyce and L. J. Dolby, *J. Org. Chem.*, **26**, 3619 (1961).

(21) E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960).

(22) The values calculated for 1α-, 1β-, 2α-, 2β-, 3α-, 3β-, 4α-, 4β-, 6α-, and 6β-cholestanol were 2.4, 2.7, 0.9, 2.7, 1.0, 0.0, 1.4, 3.2, 1.4 and 3.2 kcal./mole, respectively. Only the three interactions were considered and the cholestane nucleus was taken as composed of perfect chair cyclohexane units. Interactions like those occurring between the 1α-OH and the CH_2 at C-11 were treated as an $OH:CH_3$ interaction. The referee has kindly pointed out that the assumed perfection of the chairs is not only unreasonable for certain cases but unnecessarily restrictive; that it is necessary to assume only that the steroid conformation is the same as the appropriately substituted cyclohexane.

(23) The actual comparisons are contained graphically in Fig. 1.

(24) Such a correlation was proposed in semiquantitative form by Schreiber and Eschenmoser.[17]

(25) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

calculated ΔF of alcohol stability of 0.25 kcal./mole.[26] In view of the errors inherent in the estimations of ΔF and the neglect of any special factors like variable inductive effects, this is a surprisingly good fit and it supports the idea of relating alcohol stability to oxidation rate.

To the extent that relations like Fig. 1 are general for epimeric alcohols it is possible to estimate the composition of equilibrated epimeric alcohol mixtures from the oxidation rates of the pure alcohols.[27] Thus, if the oxidation rates of the four bicyclic alcohols are converted into alcohol stability ratios, it is calculated, using 0.74 as the factor for approach to energetic equivalence, that *at 30°* equilibrated norborneol mixtures would contain 22% *endo*-norborneol (20% observed at 100°) and equilibrated borneol mixtures would contain 71% borneol (71% observed at 100°).

Experimental

***d,l*-Borneol.**—*d,l*-Borneol (Aldrich) was crystallized twice from pentane [m.p. (sealed tube) 194–195.5°]. Gas chromatographic analyses indicated that it was a mixture of 79% borneol and 21% isoborneol.

***d,l*-Isoborneol.**—A solution of 25 g. (0.165 mole) of camphor in 85 ml. of anhydrous ether was added over a period of 1 hr. to a stirred, refluxing suspension of 7.5 g. (0.198 mole) of lithium aluminum hydride in 330 ml. of ether. The mixture was heated under reflux for 16 hr., then dilute hydrochloric acid was added until all of the solid dissolved. The ether layer was separated, dried over anhydrous magnesium sulfate, and evaporated. The resulting solid was crystallized twice from pentane to give 20 g. (80%) [m.p. (sealed tube) 192–194°] of a mixture of borneol and isoborneol. Gas chromatographic analysis indicated that the mixture was 11% borneol and 89% isoborneol.

***endo*-Norborneol.**—*endo*-Norborneol was prepared by lithium aluminum hydride reduction at −5 to 0° of norcamphor (Aldrich). The product was purified by sublimation and analysis by gas chromatography indicated that it contained 91% *endo*-norborneol and 9% *exo*-norborneol, m.p. (sealed capillary) 145–146°.

***exo*-Norborneol.**—The procedure of Schmerling[28] was followed to obtain *exo*-norborneol formate in 85% yield. To 30 g. (0.53 mole) of potassium hydroxide dissolved in 100 ml. of ethanol (95%) was added 38 g. (0.25 mole) of *exo*-norbornyl formate. The mixture was heated under reflux for 3 hr., cooled, and water added. The resulting oily layer was separated, diluted with ether and the ether solution concentrated until a solid separated. The solid was recrystallized at 0° from pentane and then sublimed to give 19 g. (67%) [m.p. (sealed capillary) 126–126.5°] of a solid that contained by gas chromatographic analysis 96% *exo*-norborneol and 4% *endo*-norborneol.

Gas Chromatographic Analysis.[3]—A 10-ft. column of 18% UCON H–B 2000 (a water-soluble monoalkyl ether of a mixed polyoxyethylene-oxy-propylene) on a support of Celite (30–60 mesh) was used to resolve the norborneols. Although this column did not give complete resolution, excellent agreement was obtained for a synthetic mixture of *exo*- and *endo*-norborneol. A mixture consisting of 0.0482 g. of 4% *endo*-norborneol and 96% *exo*-norborneol and 0.0458 g. of 91% *endo*-norborneol and 9% *exo*-norborneol analyzed for 54% *exo*-norborneol and 46% *endo*-norborneol, which is identical to the theoretical composition.

A 10-ft. commercial column of 20% LAC-446 (the adipate polyester of diethylene glycol partially cross-linked with pentaerythritol) on a support of Sil-o-cel C-22 diatomaceous earth firebrick (30–60 mesh) gave good resolution of the borneols.

Equilibration Experiments.[3]—Sealed test tubes were prepared that contained 0.3 g. (0.0015 mole) of aluminum isopropoxide, 0.005 ml. of acetone, 2 ml. of isopropyl alcohol, and 0.1 g. of the compound to be equilibrated. After the compound had been equilibrated for the indicated time the tube was chilled, and the contents dissolved in the minimum amount of cold 3 *M* hydrochloric acid. This solution was extracted three times with 5 ml. of ethyl ether. The ether layers were washed with a saturated sodium bicarbonate solution, water, and dried over anhydrous magnesium sulfate. The ether layer was condensed and used directly for the analysis. Control experiments on the known mixtures showed no change in composition after they were put through this treatment. The experiments did indicate the importance of using several extractions.

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[26] Also shown in Fig. 1 but not included in the calculation of the slope are the points for the 7α- and 7β-cholestanols and the 11α- and 11β-hydroxyallopregnanediones (3, 20).[17] The relative stabilities of the 7-epimers were estimated by taking the interactions with the C-17 CH_2 group to be one half of what they would have been if the D-ring had been six-membered. The 11-hydroxyallopreganediones were calculated as with the other epimers. The 11α-isomers deviate markedly (*ca.* 4 × the average deviation).

[27] One obvious restriction is that the epimers must react by the same mechanism. Most of the epimeric 1,2-diols discussed by Kwart[16] would fail.

[28] L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

Rearrangement Accompanying the Permanganate Oxidation of Ethyl *cis*-2,2,4,4-Tetracarbethoxycyclobutane-1,3-dimalonate[1,2]

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Potassium permanganate oxidation of the compound reported in the literature to be ethyl *cis*-2,2,4,4-tetracarbethoxycyclobutane-1,3-dimalonate (I) in acetic acid yields ethyl 1,5-hexadiene-1,1,3,3,4,4,6,6-octacarboxylate (II). A possible pathway for the transformation is suggested. Because of the different literature reports concerning the oxidation product its constitution was reinvestigated and established as correct.

During the course of an investigation aimed at the synthesis of cyclobutane-1,2,3,4-tetracarboxylic acid[5,6] the potassium permanganate oxidation of ethyl *cis*-2,2,4,4-tetracarbethoxycyclobutane-1,3-dimalonate (I) (*vide infra*) in acetic acid was undertaken as one step in a sequence. From the reaction, a compound, $C_{30}H_{42}O_{16}$, was obtained in a good yield. An attempt to distil this substance resulted in its conversion to ethyl 6-ethoxy-α-pyrone-3,5-dicarboxylate (IV). From the ozonolysis of $C_{30}H_{42}O_{16}$, ethyl ethane-1,1,2,2-tetracar-

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[1] Taken for the most part from the dissertation of G. C. Buzby, Jr. submitted in partial fulfillment of the requirements for the Ph.D. degree.

[2] Presented in part as Paper 125 before the Organic Division at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 14, 1960, Abstracts, p. 83-O.

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[4] To whom requests for reprints should be sent.

[5] R. Criegee and W. Funke, *Chem. Ber.*, **94**, 2358 (1961).

[6] G. W. Griffin, J. E. Basinski, and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 1012 (1962).