The Oxidation of Maleopimaric Acid with Alkaline Permanganate[1,2]

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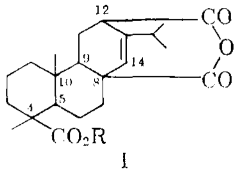
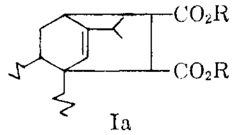
Chemical and nuclear magnetic resonance studies were used to show that the major product, A ($C_{24}H_{32}O_6$) obtained in the alkaline permanganate oxidation of maleopimaric acid has the structure V and not the structures previously suggested. A second product isolated in this oxidation has been shown to have structure IX. Further oxidation of A gave a dihydroxylactone diacid for which the revised structure VIII is proposed. Maleopimaric acid gave a crystalline bromolactone, XI. The absolute configuration of V is given.

The oxidation of maleopimaric acid, I (R = H),[4] by alkaline permanganate was first reported by Arbusov[5] and later by Ruzicka and Lalande.[6] The latter workers were unable to confirm the earlier work and isolated as the main oxidation product a substance A, $C_{24}H_{32}O_6$ (m.p. 211–212°). Titration showed A to contain two free carboxyl groups which readily formed the dimethyl ester. An unreactive double bond was indicated by the tetranitromethane test. The two remaining oxygen atoms were assumed to belong to an unreactive lactone group, largely by analogy with related ozonolysis studies.

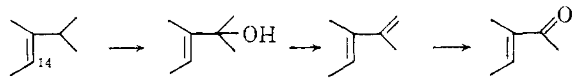


I

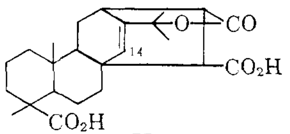


Ia

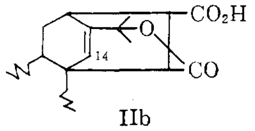
Ruzicka and Kaufmann[7] convincingly showed that ozonolysis of the trimethyl ester of the acid corresponding to maleopimaric acid (Ia, R = CH_3) led to degradation of the isopropyl side chain to give a diene and an α,β-unsaturated ketone. This was believed to occur *via* the intermediate alcohol as follows



When methyl maleopimarate, (I, R = CH_3) was treated with ozone, three products were isolated; the dimethyl ester of one of these products was reported to be identical with the dimethyl ester of A.[6] On the basis of this evidence structure IIa or IIb was suggested for A.[6] During the course of another investigation we had occasion to repeat the permanganate oxidation of maleopimaric acid and found that neither of these proposed structures was consistent with our results.



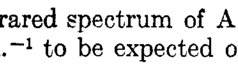
IIa



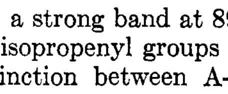
IIb

Following the earlier procedure[6] we isolated A of identical properties to those previously described. The infrared absorption spectra of A and its dimethyl ester showed strong bands at 1780 cm.$^{-1}$ indicating the presence of γ-lactones. Since both of Ruzicka's structures contain δ-lactones they cannot be correct.

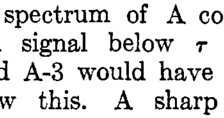
There are three possible structures containing a γ-lactone and one double bond, A-1, A-2, and A-3. Structures A-2 and A-3 are inconsistent with the hindered nature of the double bond and the infrared spectrum of A lacks a strong band at 890 cm.$^{-1}$ to be expected of the isopropenyl groups in A-2 and A-3. A clear distinction between A-1, A-2, and A-3 was possible using n.m.r. spectroscopy. The spectrum of A contained only a single hydrogen signal below τ 6.0 (Table I) whereas A-2 and A-3 would have two hydrogens resonating below this. A sharp six hydrogen signal at τ 8.22 in addition to those for the methyl



A-1



A-2



A-3

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[1] This investigation was supported by Grant NSF-G14512 from the National Science Foundation (L.H.Z.) and by the National Research Council of Canada (J.P.K.).

[2] Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, September 3–8, 1961.

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[4] Maleopimaric acid is the Diels–Alder adduct arising from the resin acids and the dienophile maleic anhydride.

[5] The earlier work is reviewed in Sir John Simonsen's, "The Terpenes," Vol. 3, Cambridge University Press, Cambridge, 1952, p. 439.

[6] L. Ruzicka and W. A. Lalande, Jr., *Helv. Chim. Acta*, **23**, 1357 (1940).

[7] L. Ruzicka and St. Kaufmann, *ibid.*, **23**, 1346 (1940).

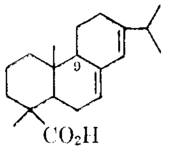
hydrogens on ring A again was incompatible with structures A-2 and A-3.

The data in Table I indicate a small upfield shift for the C-14 protons in A and its dimethyl ester as compared to the model compounds 1 and 2, whereas the protons of the isopropyl methyl groups of A and its dimethyl ester appear about 0.8 p.p.m. downfield from those of the model compounds 1, 2, and 3. The signals for the C-14 protons in structures IIa and IIb would be expected to appear at about the same field as in the model compounds 1 and 2, whereas the signals for the isopropyl methyl protons in IIa and IIb should occur at lower field as compared to the model compounds since the lactone group will exert some influence. However, this deshielding would be expected to be about 0.4 p.p.m. rather than the observed 0.8 p.p.m.[8] On the other hand, it has been observed that the peaks for the isopropyl methyl protons in neoabietic acid, IV, fall about 0.7 p.p.m. downfield from those of the isopropyl methyl protons of abietic acid, III,[9] a situation clearly consistent with ours. On the basis of the infrared and n.m.r. observations we propose structure V (R = H) for A. In V the C-14 proton is not vinylic but is deshielded by an acyloxy group. Such protons have been observed to appear in the n.m.r. in the region observed.[8] Further chemical work lends support to structure V.

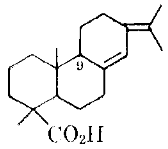
TABLE I
SELECTED N.M.R. PEAKS IN τ UNITS[a]

		Proton assignments	
	Compound	C-14[b]	Isopropyl methyls
1.	I (R = CH_3)	4.55	Doublet centered at 9.07
2.	I-a (R = CH_3)	4.68	Doublet centered at 8.94
3.	Abietic acid, III	...	Doublet centered at 9.04
4.	A (V, R = H)	4.92	8.24
5.	A dimethyl ester (V, R = CH_3)	5.00	8.22
6.	B (VI)	5.68	Doublet centered at 8.35
7.	XI	5.40	...

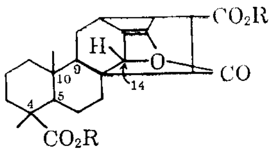
[a] See Experimental for details. [b] These peaks appear at the lowest field in each of the spectra and are therefore assigned to the C-14 protons.



III



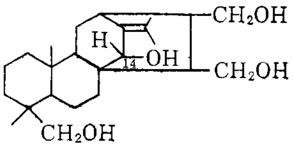
IV



V

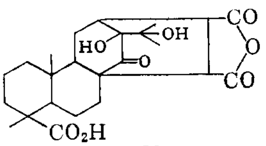
When A was reduced with lithium aluminum hydride a white crystalline compound, B (m.p. 252–253°), was obtained which showed strong absorption in the infrared at 3425 cm.$^{-1}$ (O—H) but no absorption in the 1800–1675-cm.$^{-1}$ region (C=O).

The peak at lowest field in the n.m.r. spectrum of B appeared at τ 5.68 (Table I). If Ruzicka's structures IIa or IIb correctly represented A then the reduction product of A should show a vinylic proton as the peak at lowest field in its n.m.r. spectrum. In the absence of other unsaturation, the observed signal at τ 5.68 is not likely due to a vinyl proton. If structure V were correct for A, then the structure B would be VI and the n.m.r. would be expected to show a peak at low field due to the proton at C-14. The change in chemical shift from τ 5.0 to τ 5.68 on reduction is consistent with the origin of this signal in the hydrogen on secondary carbon carrying an ester and alcohol function, respectively. The elemental analysis and active hydrogen and molecular weight determinations for B were in satisfactory agreement with structure VI ($C_{24}H_{40}O_4$). We were unsuccessful in attempts to oxidize B to an α,β-unsaturated ketone. This observation is not surprising in view of the hindered nature of the C-14 position.

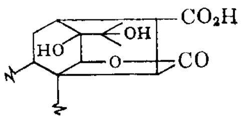


VI

The earlier workers[6] found that further oxidation of A with three equivalents of alkaline permanganate gave a product $C_{24}H_{32}O_8$ (m.p. 307–308°) in poor yield, for which structure VII was postulated. The evidence in support of VII was very meager, consisting in essence in the formation of a diacetate and in its consumption of *approximately* one molar equivalent of standard base under mild conditions and three molar equivalents under more drastic conditions. No derivatives of the C-14 carbonyl group were obtained.



VII



VIII

In our hands this substance was found to titrate as a dibasic acid under even the mildest conditions. In addition, the characteristic anhydride doublet in the infrared spectrum which was to be expected if VII was correct, was absent and instead a strong singlet at 1776 cm.$^{-1}$ was present. In view of these observations structure VIII is suggested for

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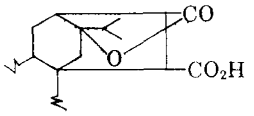
[8] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959.

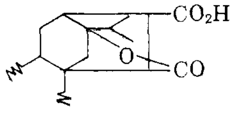
[9] J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4762 (1960).

this product of further oxidation. This structure could arise from V by simple hydroxylation of the double bond. Since VIII was obtained in such low yield it has not been possible to investigate it further. Attempted ozonolysis of V gave only recovered starting material. These observations indicate the hindered nature of the double bond in V.

In addition to A, Ruzicka and Lalande[6] isolated, in low yield, a second lactone ($C_{24}H_{34}O_6$, m.p. 252–253°) in the oxidation of maleopimaric acid with less than two equivalents of permanganate. Structures IX and X were suggested for this lactone. We have found that the infrared spectra of this lactone and its dimethyl ester

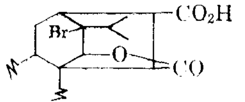


IX

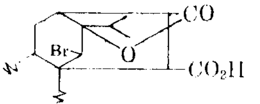


X

show strong bands at about 1779 cm.$^{-1}$ and the n.m.r. spectrum of the dimethyl ester showed no peaks below τ 6.3. These data indicate the presence of a γ-lactone and the tertiary nature of the noncarboxyl lactone oxygen atom. Structure IX can therefore be assigned to the lactone. Structure X has been suggested for a lactone (m.p. 317°) obtained by acidification of the disodium salt (pH 6.2) of maleopimaric acid.[10] The lactones IX and X are not oxidation products of I but arise simply by addition of one or the other of the carboxyl groups of Ia (R = H) to the double bond presumably during the work-up in acidic media. A similar reaction occurs when I is treated with bromine in an alkaline medium (pH 9). In this latter case there is immediately formed a bromolactone for which two plausible structures XIa and XIb can be offered. The infrared spectrum of the dimethyl ester of the bromolactone showed a



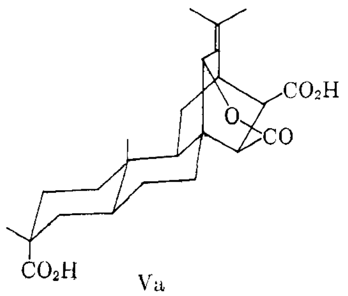
XIa



XIb

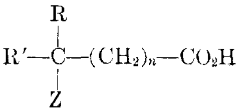
strong band at 1783 cm.$^{-1}$ (γ-lactone) and the lowest peak in its n.m.r. spectrum appeared at τ 5.40 (Table I). The spectral data do not allow a clear distinction to be made between XIa and XIb.

It is now possible to define completely the absolute configuration of the compounds discussed in this paper by the use of recent reports from other laboratories. The stereochemistry at C-4, C-5, and C-10 must be the same as in the resin acids. There has been some confusion as to the stereochemistry at C-9 in these adducts since malepimaric[5] acid has been reported to arise from levopimaric acid and from abietic acid which were reported to differ in stereochemistry at C-9.[11] However, recent work has shown that these two resin acids both have an α-hydrogen at C-9.[12, 13] The formation of the various lactones mentioned above shows that the anhydride moiety of I is *cis* to the double bond as would have been predicted on the basis of the known stereochemical selectivity of the Diels–Alder reaction.[14] The remaining ambiguity, the stereochemistry at C-8 and C-12, is determined by the approach of the dienophile in the Diels–Alder reaction. Evidence to support the back-side approach of the dienophile is now available from several sources. Burgstahler and co-workers[13] have shown that the C ring in levopimaric acid is skewed in such a manner that the β face is shielded by the angular methyl group at C-10, while the α face is free for attack by the dienophile. Ayer and Stothers[15] have made a careful study of the position at which the C-10 methyl protons in compounds such as I, V, and IX resonate in the n.m.r. as compared to the C-4 methyl protons and have concluded that the double bond in I and V shield the C-10 methyl protons, with the shielding being less in V than in I. This observation again requires that the dienophile enter from the α (rear) side and V therefore should be pictured sterically as shown below.



Va

The mechanism of the formation of V is interesting. Kenyon and Symons[16] studied the oxidation of carboxylic acids containing a tertiary carbon atom, XII (Z = H; n = 0,2), and observed that hydroxy carboxylic acids, XII (Z = OH), were obtained in good yields only in concentrated alkaline



$$R'-\overset{R}{\underset{Z}{C}}-(CH_2)_n-CO_2H$$

XII

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(10) G. Brus, Le-van-Thoi, H. Francois, and C. Fines, *Peintures' Pigments, Vernis*, **29**, 36 (1953).

(11) W. Klyne, *J. Chem. Soc.*, 3072 (1953).

(12) W. H. Schuller and R. V. Lawrence, *J. Am. Chem. Soc.*, **83**, 2563 (1961).

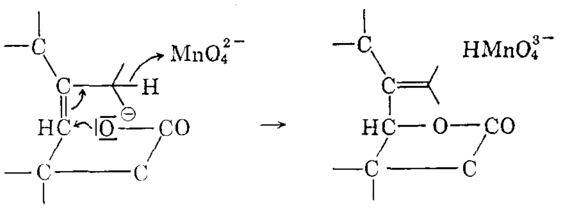
(13) A. W. Burgstahler, H. Ziffer, and U. Weiss, *ibid.*, **83**, 4660 (1961).

(14) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(15) Private communication from Professor W. A. Ayer of the University of Alberta.

(16) J. Kenyon and M. C. R. Symons, *J. Chem. Soc.*, 2129, 3580 (1953).

permanganate and in very poor yields in dilute alkaline media. If optically active acids were used only inactive hydroxy acids were obtained from the concentrated alkaline permanganate solutions. In contrast, manganate in dilute alkaline solution gave good yields of the hydroxy acid and also retention of optical activity. The concentrated alkaline permanganate oxidation of either *exo*- or *endo*-norbornane-2-carboxylic acid has been recently shown to give only norbornane-2-*exo*-hydroxy-2-*endo*-carboxylic acid.[17] The oxidation of I to give V is conducted with dilute alkaline permanganate and the product is isolated in excellent yield (~90%). This fact and the observed stereospecificity of the reaction suggest that the oxidizing agent may be manganate ion formed by the action of hydroxide ion on permanganate ion (probably formed only very slowly under these conditions). Thus a mechanism similar to that suggested by Kenyon and Symons[16] may apply here with an allylic rearrangement occurring in this case.



$$HMnO_4^{3-} + H_2O \longrightarrow MnO_2 + 3OH^-$$

Experimental

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Analyses were performed by Dr. A. Bernhardt (Mülheim, Germany). Infrared spectra were run on a Beckman IR-5 spectrophotometer. All gas chromatographs were run at 280° using a column 1/8 in. × 5 ft. of 5% SE-30 on acid-washed Chromosorb W with a hydrogen flame detector and a hydrogen flow rate of 26 ml./min. and a nitrogen flow rate of 28 ml./min. The wood rosin was kindly supplied by Dr. G. I. Keim of Hercules Powder Co.

Nuclear Magnetic Resonance Measurements.—The n.m.r. spectra of compounds 1–5 (Table I) were run on a Varian 40-Mc. high resolution spectrometer and those of 6 and 7 were run on a Varian A60. Tetramethylsilane was used as an internal standard with its peak taken as 10.0 units on the Tiers τ scale. All samples were run in deuterochloroform except for 6 which was insoluble in this solvent and was therefore run in dimethyl sulfoxide. In order to determine whether this latter solvent had any significant effect on the chemical shifts, compound 5 (Table I) was run in both solvents. The difference in the positions of the peaks was small.

Maleopimaric Acid, I (R = H).—Maleopimaric acid is now commercially available from Distillation Products Industries, Eastman Kodak Co., but most of the material used in this work was prepared directly from wood rosin by known procedures.[5] The maleopimaric acid was crystallized several times from acetic acid and dried at 100–130° and 1 mm. (in order to remove solvent of crystallization) and had the following properties: m.p. 229–230°; $[\alpha]^{25}\text{D}$ −28.1° (*c*, 3.41 in $CHCl_3$); $\nu_{\text{max}}^{\text{KBr}}$ 1845, 1779, 1710 cm.$^{-1}$, reported[5]: m.p. 226–227°; $[\alpha]\text{D}$ −29.6° ($CHCl_3$). Methyl ester, I (R = CH_3), found: m.p. 214–215°; $[\alpha]^{25}\text{D}$ −28.7 (*c*, 3.71 in $CHCl_3$), $\nu_{\text{max}}^{\text{mull}}$ 1840, 1770, 1730 cm.$^{-1}$. reported[5]: m.p. 216–217°; $[\alpha]\text{D}$ −28.9 ($CHCl_3$); single peak in gas chromatography with retention time of 13 min.

Refluxing I (R = CH_3) in methanol gave the half acid ester, m.p. 154–155°, $\nu_{\text{max}}^{\text{KBr}}$ 1734, 1712 cm.$^{-1}$ which on heating at its melting point was reconverted to I (R = CH_3) of identical physical properties to those mentioned above.

Anal. Calcd. for $C_{25}H_{34}O_5$: C, 72.43; H, 8.27. Found: C, 72.31; H, 8.19.

An ethereal solution of diazomethane converted the half-acid ester into the known trimethyl ester of I; the latter was also prepared directly from I. A solution of I in excess phosphorus trichloride was allowed to stand at room temperature for 4 hr., after which the solution was taken to dryness, methanol added to the residue, and the solution refluxed for 2 hr. Concentration and addition of water gave crystalline trimethyl ester (compound 2 of Table I) which after recrystallization had m.p. 103–104° (reported 103°),[5] yield, 65%; single peak in gas chromatography with retention time of 11.5 min.

Oxidation of Maleopimaric Acid, I, with Alkaline Permanganate. Lactone V.—Maleopimaric acid (20 g.) was added to a solution prepared by dissolving 6 g. of sodium hydroxide in 100 cc. of water. This solution was cooled to 10° and to it was added a cold solution prepared by dissolving 11.2 g. of potassium permanganate (2.1 equivalents of oxidizing agent) in 300 cc. of water. The reactants were allowed to stand at 10° overnight, after which the precipitated manganese dioxide (6.2 g.) was removed by filtration and the filtrate neutralized (pH 6.8) with carbon dioxide. Concentration of the filtrate to 250 cc. and acidification (pH 1) with dilute hydrochloric acid gave the crude lactone V (R = H) as a white precipitate. It was later found to be more convenient to remove the precipitated manganese dioxide by passing gaseous sulfur dioxide through the solution until all of the manganese dioxide had dissolved, and then to acidify with hydrochloric acid and proceed as described above. Drying at room temperature and 1 mm. gave 19 g. of V (R = H), m.p. 190–195°, which after two recrystallizations gave the analytical sample, m.p. 211–212° (reported[6]: 211–212°), $[\alpha]\text{D}$ −37.3° (*c*, 3.25 in methanol), yellow color with tetranitromethane, no decolorization of bromine in carbon tetrachloride solution, $\nu_{\text{max}}^{\text{KBr}}$ 1780, 1750, 1710, 1675 (weak) cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{32}O_6 \cdot 1/4H_2O$: C, 68.46; H, 7.78. Found: C, 68.39; H, 7.83.

A sample of V (R = H) which had been dried at 100° and 1 mm. to remove the water of solvation gave the following neutralization equivalents: Calcd. for dibasic $C_{24}H_{32}O_6$: 208. Found: 201, 202, 200.

Treatment of V (R = H) with ethereal diazomethane gave the dimethyl ester, V (R = CH_3), which after two recrystallizations from methanol–water and extensive drying gave m.p. 185° (reported[6]: m.p. 182–184°), $\nu_{\text{max}}^{\text{KBr}}$ 1770, 1740, 1710, 1675 (weak) cm.$^{-1}$, single peak in gas chromatography with retention time of 14.6 min.

Anal. Calcd. for $C_{26}H_{36}O_6$: C, 70.24; H, 8.16; O, 21.60. Found: C, 70.31; 70.35; H, 8.18, 8.23; O, 21.63, 21.80.

Attempts to hydrogenate V (R = H) at atmospheric pressure using palladium-on-charcoal or platinum-on-charcoal catalysts met with no success. Under the same conditions maleopimaric acid also could not be hydrogenated. An attempt to isolate acetone by the ozonolysis of V (R = H) was also unsuccessful.

Isolation of IX in Oxidation of Maleopimaric Acid.—When the oxidation of maleopimaric acid was run using less than two equivalents of permanganate, small amounts of lactone IX were isolated. In a typical run using one equivalent of permanganate, the crude oxidation product gave 10% of IX, m.p. 252–254° (reported[6]: m.p. 250–252°), $\nu_{\text{max}}^{\text{KBr}}$

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[17] H. Kwart and G. D. Null, *J. Am. Chem. Soc.*, **82**, 2348 (1960).

1770, 1739, 1709 cm.$^{-1}$, no color with tetranitromethane. Treatment of an ether solution of IX with an ethereal diazomethane solution gave the dimethyl ester, m.p. 218–219° (reported[6]: m.p. 218–220°), ν_{max}^{KBr} 1779, 1739, 1709 cm.$^{-1}$.

Oxidation of Lactone V with Alkaline Permanganate. Preparation of VIII. Procedure A.—The conditions used by Ruzicka and Lalande[5] were followed exactly in this procedure and VIII was isolated as previously reported in very low yield. The product VIII, m.p. 310° (reported[5]: 307–308°) was found to have ν_{max}^{KBr} 3450, 1775, 1720, 1150 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{34}O_8$: C, 63.98; H, 7.61. Found: C, 64.29; H, 7.24.

Procedure B.—In this procedure maleopimaric acid was oxidized directly with five equivalents of permanganate under the conditions described for the preparation of V. The product isolated was identical in infrared and melting point with that isolated by procedure A and was obtained again in very low yield.

Equivalent weight calcd: monobasic, 450; dibasic, 225; tribasic, 149. Found on titration in the cold: 237, 241. Found at room temperature: 178, 173. Titrations were run with 0.0982 *N* and 0.0098 *N* sodium hydroxide, respectively.

Reduction of V with Lithium Aluminum Hydride. Preparation of VI.—Three grams of dry lactone V in ether was added slowly to an ether solution containing 6 g. of lithium aluminum hydride. After refluxing overnight, ethyl acetate was added to destroy the excess lithium aluminum hydride and the solution was acidified with dilute sulfuric acid. The ether layer was separated, dried over sodium sulfate, and concentrated to a small volume, which on cooling gave 0.66 g. of white needles, m.p. 200–205°. Recrystallization from methanol–water gave the analytical sample of B, m.p. 207–209°, positive tetranitromethane test, negative test with bromine in carbon tetrachloride, ν_{max}^{KBr} 3425 (O—H), 1665 (C=C) cm.$^{-1}$; $[\alpha]_D$ −57.2° (*c*, 3.00 in methanol), single peak in gas chromatography with retention time of 12.5 min.

Anal. Calcd. for $C_{24}H_{40}O_4$: C, 73.43; H, 10.27; O, 16.30; active hydrogen (4), 1.02; mol. wt. 393. Found: C, 73.78; H, 10.16; active hydrogen, 0.90; mol. wt. (Rast), 371.

B did not give a 2,4-dinitrophenylhydrazone with a methanolic–hydrogen chloride solution of the test reagent and aqueous hydrochloric acid and *p*-toluenesulfonic acid in benzene gave only negligible amounts of carbonyl-containing products.

Attempts to show that B was an allylic alcohol by oxidation to an *α,β*-unsaturated ketone with manganese dioxide and chromic anhydride failed to give any products that showed absorption in the ultraviolet region.

Reaction of I with Bromine in Alkaline Solution. Preparation of XI.—This bromolactone was prepared by a procedure recently reported by Grovenstein,[18] *et al.* The bromolactone (m.p. 225–228°) was found to decompose readily.

Anal. Calcd. for $C_{24}H_{33}O_6Br$: C, 57.95; H, 6.69. Found: C, 57.54; H, 6.70.

It was found more convenient to convert the crude bromolactone directly to its dimethyl ester with diazomethane. In a typical run 2 g. of I gave 1.5 g. of the dimethyl ester, m.p. 233–236°, ν_{max}^{KBr} 1783, 1736, 1727 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{37}O_6Br$: C, 59.42; H, 7.09; Br, 15.20. Found: C, 59.03; H, 6.93; Br, 15.24.

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Oxidation of Monomeric and Polymeric Sulfhydryl Compounds[1]

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Using a spectrophotometric procedure, the relative rates of oxidation of a series of thiols were determined based on the observed rate of reduction of a dye, sodium 2,6-dichlorobenzeneoneindophenol. In aqueous pH 10 buffered solution, 2,2-dimethyl-4-(*p*-mercaptophenyl)valeric acid and a saponified copolymer of vinyl thiolacetate and methyl methacrylate were oxidized at approximately the same rate while 2,2-dimethyl-4-mercaptovaleric acid was oxidized about two times as fast. In dimethylformamide solution, 2,3-butanedithiol was oxidized approximately 61 times as fast as 2,6-heptanedithiol. These results have been compared to previous work reported and are discussed in terms of the ease of sulfur participation and disulfide formation.

From our previous work and that of Barron,[4] it is clear that a neighboring mercaptan group will influence the rate of oxidation of a polymercaptan in a very specific way. Thus, it was found that 2,4-di(*p*-mercaptophenyl)pentane was oxidized more than six times as fast as *p*-thiocresol.[5] It was suggested that two thiol groups existing as parts of the same molecule in juxtaposition may give rise to some type of participation. Likewise a polymer of *p*-mercaptostyrene gave an increased oxidation rate slightly higher than the model dimercapto system, 2,4-di(*p*-mercaptophenyl)pentane.

In confirmation of Barron's[4] earlier findings, it was found that 2,4-pentanedithiol was oxidized faster than 2,5-hexanedithiol, both of which were oxidized faster than the monothiol 2-mercaptoethanol.[1] It was suggested that facile ring forma-

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[1] This is the 23rd in a series of papers on new monomers and polymers. For the previous paper in this series, see C. G. Overberger, J. J. Ferraro, and F. W. Orttung, *J. Org. Chem.*, **26**, 3458 (1961).

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