

From the reaction of piperonal, chloroform and sodium methoxide in excess methanol at temperatures below 30°, a small amount (4 g. from 37 g. of piperonal) of 3,4,3',4'-di-(methylenedioxy)-deoxybenzoin, m.p. 114° after recrystallization from ethanol was obtained. The literature melting point is 114.5°.<sup>12</sup>

$\alpha$ -Methoxy-*m*-nitrophenylacetic acid was obtained first as the crude acid, and this was distilled at 163–166° at 1.5 mm. Recrystallization of the distillate from benzene gave yellow crystals, m.p. 109–110°. From 10 g. of *m*-nitrobenzaldehyde, 0.6 g. (4% of theor.) was obtained.

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>O<sub>3</sub>N: C, 51.19; H, 4.29; -OCH<sub>3</sub>, 14.69; neut. equiv., 211. Found: C, 51.35; H, 4.07; -OCH<sub>3</sub>, 14.62; neut. equiv., 210.

$\alpha,\beta$ -Di-(*p*-nitrophenyl)-glycidic acid was obtained as the sodium salt by treating *p*-nitrobenzaldehyde in the usual way and attempting to precipitate the sodium acid salt. From 19 g. of *p*-nitrobenzaldehyde, 4 g. was obtained. Acidification yielded the free acid, m.p. 188–190° after recrystallization from 50% aqueous ethanol.

*Anal.* Calcd. for C<sub>15</sub>H<sub>10</sub>O<sub>7</sub>N<sub>2</sub>: C, 54.55; H, 3.05; neut. equiv., 330. Found: C, 54.66; H, 3.16; neut. equiv., 328.

*p*-Cyano- $\alpha$ -methoxyphenylacetic acid was isolated as the ammonium salt by treating the crude acid (6 g. from 10 g. of *p*-cyanobenzaldehyde, 48% of theor.) with ammonium hydroxide. The ammonium salt was recrystallized from a 95:5 ethyl acetate-ethanol mixture. It melted at 154–155°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>N<sub>2</sub>: C, 57.68; H, 5.81; N, 13.4; -OCH<sub>3</sub>, 14.91. Found: C, 57.47; H, 5.91; N, 13.2; -OCH<sub>3</sub>, 15.06.

$\alpha$ -Methoxy-(1-naphthalene)-acetic acid was isolated as a mixture of the normal sodium salt and the free acid by following the general procedure for precipitating sodium acid salts, but omitting the acetone and water washes. Acidification of an alkaline solution of the mixture yielded the free acid, m.p. 149–150° after recrystallization from 50% aqueous ethanol. From 40 g. of 1-naphthylaldehyde, 31 g. (49% of theor.) was obtained.

*Anal.* Calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>: C, 72.21; H, 5.60; -OCH<sub>3</sub>, 14.33; neut. equiv., 216. Found: C, 72.37; H, 5.51; -OCH<sub>3</sub>, 14.01; neut. equiv., 216.

$\alpha$ -Methoxy-(2-naphthalene)-acetic acid was isolated as the sodium acid salt, m.p. 243–244°, neutral equivalent 457 compared with the theoretical value of 454, after recrystallization from 50% aqueous ethanol. From 5 g. of the 2-naphthylaldehyde, 2 g. (24% of theor.) was obtained. The free acid was obtained by dissolving the sodium acid salt in dilute sodium hydroxide solution and acidifying with an excess of 2 *N* hydrochloric acid. The acid melted at 98.5–99.5° after recrystallization first from hot water and then from ligroin (b.p. 60–80°).

(12) I. Allen and J. S. Buck, *J. Am. Chem. Soc.*, **52**, 310 (1930).

*Anal.* Calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>: C, 72.21; H, 5.60; -OCH<sub>3</sub>, 14.33; neut. equiv., 216. Found: C, 72.18; H, 5.56; -OCH<sub>3</sub>, 14.43; neut. equiv., 219.

The 2-naphthaldehyde was prepared by a Sommelet reaction on 2-(bromomethyl)-naphthalene. It was purified by means of its sodium bisulfite addition product.

$\alpha$ -Methoxy-(2-thiophene)-acetic acid was obtained first as the crude acid (11 g. from 10 g. of thiophene-2-carboxyaldehyde). This was converted to the sodium acid salt by treatment with the theoretical amount of 20% sodium hydroxide solution, and the sodium acid salt was recrystallized from absolute ethanol. The sodium hydrogen di-( $\alpha$ -methoxy-2-thiopheneacetate) melted at 207–210° dec., and had a neutralization equivalent of 364 compared with a theoretical value of 366. Three grams of the acid salt, washed with acetone but not recrystallized, was obtained (20% of theor.). The ammonium salt was made from the free acid obtained by acidifying the sodium acid salt. The ammonium salt melted at 145–146° dec. after recrystallization from acetone. This melting point value was obtained by placing the capillary in melting point bath at 140° with the temperature rising 2° per min.

*Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>SN: C, 44.43; H, 5.86; N, 7.51; -OCH<sub>3</sub>, 16.40. Found: C, 44.73; H, 6.04; N, 7.60; -OCH<sub>3</sub>, 16.13.

$\alpha$ -Methoxy- $\alpha$ -phenylpropionic acid was isolated as a mixture of the normal sodium salt and the free acid. There was obtained 8.2 g. (16% of theor.) from 30 g. of acetophenone. The free acid was an oil. The ammonium salt melted at 175–176° after recrystallization from a 3:1 ethyl acetate-ethanol solution containing ammonia.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>N: C, 60.89; H, 7.67; N, 7.10; -OCH<sub>3</sub>, 15.74. Found: C, 61.09; H, 7.46; N, 6.98; -OCH<sub>3</sub>, 15.42.

**Preparation of Salts.**—Using 50% aqueous methanol as the solvent, one molar solutions were made up using the acids prepared or their ammonium salts, with the exception of 2,6-dichloro- $\alpha$ -methoxyphenylacetic acid which was obtained in insufficient amounts. The acid solutions were half neutralized with ammonium hydroxide. To four drops of each solution was added an equivalent amount of a one molar solution in 50% aqueous methanol of one of the chlorides of magnesium, lithium, potassium, rubidium or cesium. The two precipitates observed were voluminous and formed within 30 min.

The solubility data were determined by evaporating known values of saturated solutions to dryness or, in the case of the acid salts, by titrating a sample of the saturated solution.

**Acknowledgment.**—It is a pleasure to acknowledge the financial aid received from the Union Carbide Company.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

## The Importance of Steric Effects in the Baeyer-Villiger Oxidation

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From a study of the peroxidation of 1-methylnorcamphor, leucouche, camphor and epicamphor, it has been possible to demonstrate the importance of two types of steric effects on the course of the Baeyer-Villiger reaction.

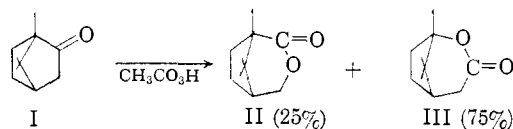
The mechanism of the Baeyer-Villiger reaction has been a subject of considerable current interest.<sup>1–5</sup> From the established migrational apti-

- (1) A. Rassat and G. Ourisson, *Bull. soc. chim. France*, 1133 (1959).
- (2) J. Meinwald, M. C. Seidel and B. C. Cadoff, *J. Am. Chem. Soc.*, **80**, 6303 (1958).
- (3) J. Meinwald and E. Frauenglass, *ibid.*, **82**, 5235 (1960).
- (4) R. R. Sauer, *ibid.*, **81**, 925 (1959).
- (5) M. F. Hawthorne, W. D. Emmons and K. S. McCallum, *ibid.*, **80**, 6393 (1958); and M. F. Hawthorne and W. D. Emmons, *ibid.*, **80**, 6398 (1958).

tude sequence for alkyl groups, 3° > 2° > 1°, it appears that electronic effects are the dominant factors in controlling the course of the reaction. Although several authors<sup>3,6–8</sup> have discussed the importance of steric effects, there are no examples

- (6) J. T. Edward and P. F. Morand, *Can. J. Chem.*, **38**, 1325 (1960).
- (7) M. F. Murray, B. A. Johnson, R. R. Pederson and A. C. Ott, *J. Am. Chem. Soc.*, **78**, 981 (1956).
- (8) J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

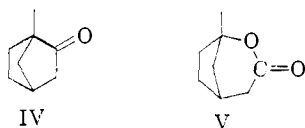
of systems whose oxidation can be said to be sterically controlled. The possibility that steric effects might be enhanced in bicyclic ketones is evident from the results with camphor (I). An abnormally large amount of the "wrong" lactone (II) is formed when one considers the relative migratory aptitudes for ethyl *vs.* *t*-butyl (1/560).<sup>5</sup>



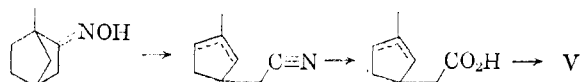
In order to evaluate more systematically this possibility several model ketones were oxidized with buffered peracetic acid; namely, 1-methylnorcamphor, fenchone and epicamphor.

### Results

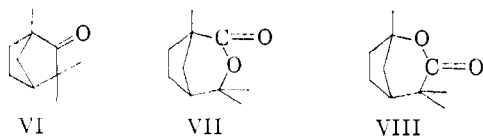
**1-Methylnorcamphor.**—Reaction of 1-methylnorcamphor (IV)<sup>9</sup> with peracetic acid gave lactone V exclusively as far as could be determined by gas chromatography and infrared spectroscopy.



For comparison, an authentic sample of lactone V was prepared from the oxime of 1-methylnorcamphor. The two samples had identical infrared spectra and retention volumes and showed no melting point depression on admixture.



**Fenchone.**—A mixture of *ca.* 60% VII and 40% VIII was obtained on oxidation of fenchone (VI). The product mixture could not be separated by crystallization or chromatography, but analysis



could be made by gas chromatography. The reference samples were prepared according to directions given by Semmler from  $\beta$ - and  $\alpha$ -fencholenic acids (IX and X).<sup>10</sup> The lactones produced in this manner contained impurities, but the major products corresponded to the lactones from fenchone.

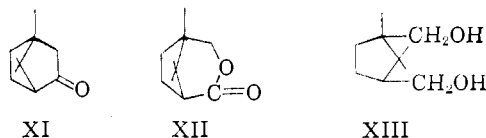


**Epicamphor.** *d,l*-Epicamphor (XI) was prepared from bornyl chloride according to Bredt and Pinten.<sup>11</sup> The peroxidation product was obtained

(9) S. Beckmann, R. Schaber and R. Bamberger, *Ber.*, **87**, 997 (1954).

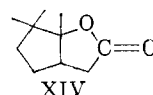
(10) F. W. Semmler, *ibid.*, **39**, 2851 (1906); see also D. S. Tarbell and F. C. Loveless, *J. Am. Chem. Soc.*, **80**, 1963 (1958).

(11) J. Bredt and P. Pinten, *J. prakt. Chem.*, **115**, 45 (1927).



as a crystalline solid in 94% yield. The material was homogeneous on three different gas chromatography columns and had a retention volume and infrared spectrum identical with that of an authentic sample of *d*- $\beta$ -campholide (XII).<sup>12</sup> Further confirmation of the assigned structure was obtained by comparison of the glycol XIII prepared by reduction with lithium aluminum hydride with that of an authentic sample prepared from camphoric anhydride.

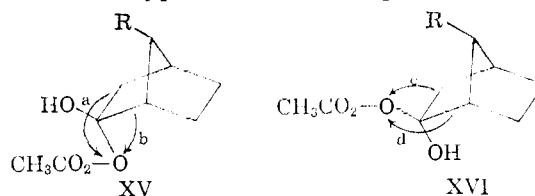
At this point it was imperative that a quantitative analysis of the lactone products from camphor be undertaken. Since it was not possible to resolve II and III by gas chromatography, the crude mixture was subjected to isomerization with dilute sulfuric acid.<sup>4,13</sup> The resulting mixture contained  $\alpha$ -campholide and dihydro- $\beta$ -campholenolactone (XIV) in a ratio of 1 to 3,<sup>14</sup> and was not affected by further treatment with acid. The original oxidation mixture must therefore have contained 75% III and 25% II.



### Discussion

Two interesting conclusions can be drawn from this study: (1) steric effects can compete successfully with electronic effects in controlling the outcome of the Baeyer-Villiger reaction, and (2) an  $\alpha$ -methyl group on a bridgehead appears to have an unusually large rate-retarding effect.

The steric arguments have been discussed in detail by Meinwald and Frauenglass.<sup>3</sup> Thus, camphor and epicamphor would be expected to form adducts of type XV and fenchone and 1-methylnorcamphor would be expected to form adducts of type XVI. Decomposition of the



adducts by paths b and c can be shown to lead to lactones *via* transition states which resemble boat forms and decomposition *via* paths a and d leads to lactones *via* transition states resembling chain forms. The nature of the group R should have a profound effect on the relative amounts of the two types of decompositions.

(12) We are deeply indebted to Prof. J. Vène, University of Rennes, for a gift of this material.

(13) M. Harispe and D. Mea, *Bull. soc. chim. France*, 1562 (1960), recently reported that  $\alpha$ -campholenic acid gives III on lactonization. There can be little doubt that the product is actually XIV since we showed earlier<sup>4</sup> that III is not stable in dilute acid.

(14) While this result affects the magnitude of the effect of acid on the migratory ratios it does not affect the over-all conclusions reached earlier.<sup>4</sup> See also ref. 5.

Application of these steric arguments leads to a consistent picture if one considers the results from the standpoint of a competition between steric and electronic effects. This is clearly illustrated by a comparison of the results obtained from camphor oxidation with those from oxidation of 1-methylnorcamphor and epicamphor. Steric and electronic factors both favor the same lactone (V) with 1-methylnorcamphor. The shift in product composition toward the electronically unfavored lactone in camphor oxidation suggests steric intervention since the electronic environments of the two ketones are essentially identical. Diminution of the electronic competition from 3° vs. 1° in camphor to 2° vs. 1° in epicamphor results in almost complete formation of the electronically unfavored lactone.

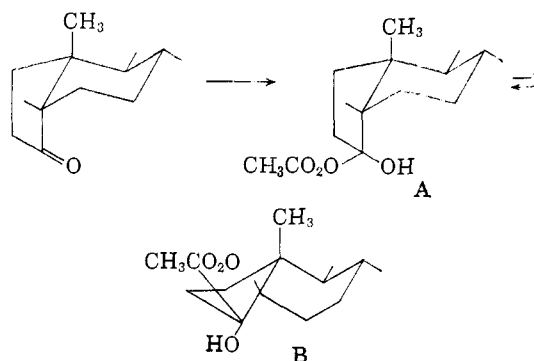
Even more striking is the comparison between norcamphor and epicamphor both of which have essentially the same electronic environment about the carbonyl group. The product from the former is virtually exclusively the electronically favored lactone,<sup>3</sup> while the latter ketone leads almost exclusively to the sterically favored product.

No large steric forces of the types described above can be operative during the oxidation of fenchone since they would be expected to favor formation of lactone VIII which is actually formed to the extent of only 40%. It appears that hydrogen on carbon 7 has little effect on the collapse of the intermediate of type XVI.

In addition to the steric effects described above, a more subtle steric effect is operating through  $\alpha$ -methyl groups on the adjacent bridgehead. This effect is manifested by changes in the over-all rate of oxidation. Examination of the experimental data reveals that those ketones which do not possess  $\alpha$ -methyl groups on the bridgehead (norcamphor, epicamphor) oxidize considerably faster than those which do (camphor, fenchone and 1-methylnorcamphor). Although this fact in itself is not particularly surprising, it is rather interesting that the effect is strong enough to overcome the expected rate-retarding effect of the *gem*-dimethyl group. More data are needed before the magnitude of this effect can be quantitatively estimated, but these results strongly suggest that a substantial amount of the steric hindrance about the carbonyl group of bicyclic ketones such as camphor is due the bridgehead methyl group. Very possibly the decreases in rate are caused by a decreased concentration of the adducts due to eclipsing of the addend with the methyl group.<sup>16</sup>

The steric argument has been criticized recently on the basis of some results taken from the oxidation of an A-norsteroidal ketone.<sup>3</sup> It was found that the electronically favored lactone was formed *via* what appears to be the sterically unfavorable transition state. Extension of these steric arguments to non-rigid systems is not yet warranted. The case at hand, for example, can be rationalized by assuming ring inversion from A to B which would lead to the observed products.

(15) O. H. Wheeler, R. Cetina and J. Z. Zabicky, *J. Org. Chem.*, **22**, 1153 (1957), have discussed similar effects in connection with equilibrium studies of cyanohydrin formation.



**Acknowledgment.**—We wish to thank the Research Corp., New York, for generous financial support.

### Experimental<sup>16</sup>

**1-Methylnorcamphor** was prepared by oxidation of 1-methylnorborneol<sup>9</sup> with chromium trioxide<sup>17</sup> and had b.p. 54–55° (9 mm.) (lit.<sup>18</sup> b.p. 60–62° (15 mm.)).

The oxime had m.p. 84–85° after crystallization from ethanol–water and sublimation.

*Anal.* Calcd. for C<sub>8</sub>H<sub>13</sub>NO: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.77; H, 9.34; N, 9.77.

**Oxidation of IV with Peracetic Acid.**—To a solution of 8.1 g. (0.065 mole) of 1-methylnorcamphor in 50 ml. of glacial acetic acid containing 3 g. of anhydrous sodium acetate was added 20 ml. (*ca.* 0.12 mole) of 40% peracetic acid.<sup>19</sup> The slurry was stirred vigorously and kept in the dark for 30 days at room temperature. Dilution with water was followed by ether extraction. The combined extracts were washed with sodium bicarbonate solution and water. After removal of the ether there was obtained 3.94 g. of crude lactone V. Gas chromatography (190°, silicone and carbowax) did not reveal more than one lactone. Chromatography on alumina followed by crystallization from low-boiling petroleum ether at –70° gave 3.8 g. (42%) of colorless needles, m.p. 35–36°, which showed a carbonyl maximum (Nujol) at 5.7  $\mu$ .

*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 68.54; H, 8.63. Found: C, 68.30; H, 8.69.

The same product could be prepared in about the same yield by running the reaction in the presence of sulfuric acid<sup>4</sup> rather than buffered solution for 2 hr. at 0°.

**Synthesis of Lactone V.**—A mixture of 6.0 g. of 1-methylnorcamphor oxime and a solution of 1 ml. of sulfuric acid in 40 ml. of water was heated at reflux for 3 hr. The layers were separated and the aqueous phase extracted with ether to give 5 g. of a mixture which contained nitrile (4.4  $\mu$ ) and 1-methylnorcamphor. The structure of the nitrile was assigned on the basis of analogy with the same cleavage on camphor oxime and the absence of infrared absorption characteristic of exocyclic methylene groups at *ca.* 11  $\mu$ . An attempt to remove the carbonyl impurity with Girard T reagent was not completely successful since the C, H analysis of the product b.p. 62–64° (19 mm.) was about 1% low in carbon.

The nitrile (1.2 g.) was hydrolyzed in refluxing methanol containing 5.0 g. of potassium hydroxide and 3 ml. of water. There was obtained 1.4 g. of crude acid which was purified by molecular distillation. Cyclization was effected at 27° in 30 ml. of glacial acetic acid containing 1 ml. of concentrated sulfuric acid for 4 days. Dilution with water followed by ether extraction and bicarbonate wash gave 0.65 g. of lactone from 1.0 g. of acid. The infrared spectrum and vapor chromatogram were identical with the lac-

(16) All gas chromatographic analyses were determined on the Aerograph, Wilkins Instrument Co., at a flow rate of 60 ml. of helium per minute. Infrared data are taken from an Infracord, Perkin-Elmer Corp., model 137. Elemental analyses are by G. Robertson, Florham Park, N. J.

(17) W. A. Mosher and E. O. Langerak, *J. Am. Chem. Soc.*, **73**, 1302 (1951).

(18) L. Ruzicka, *Ber.*, **50**, 1362 (1917).

(19) Obtained from the Becco Chemical Division, Buffalo, N. Y.

tone from peroxidation. Crystallization from petroleum ether gave a solid, m.p. 33–34° undepressed on admixture with V.

**Oxidation of Fenchone with Peracetic Acid.**—Fenchone (60 g., 0.40 mole) in glacial acetic acid (300 ml.) containing 10 g. of anhydrous sodium acetate was treated with 80 ml. (ca. 0.48 mole) of 40% peracetic acid and the resulting mixture was kept in the dark for 14 days. Dilution with water was followed by ether extraction. The extracts were washed with sodium bicarbonate solution, washed with water and dried over sodium sulfate. Evaporation of the ether gave an oil which was distilled to give 12 g. of fenchone and 17.5 g. (35%) of lactones. The gas chromatogram of the crude lactone mixture (150°, Craig butanediol-succinate) showed two poorly resolved peaks in the approximate ratio of 60:40. The larger area corresponded to lactone VII and the smaller to lactone VIII (see below). The mixture was purified by crystallization at –78° from low-boiling petroleum ether followed by sublimation and had m.p. 61–63°. Semmler<sup>20</sup> reports m.p. 68–69° and 77–78° for VII and VIII, resp.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C, 71.39; H, 9.59. Found: C, 71.02; H, 9.67.

Methanolysis of 5 g. of the lactone mixture with 50 ml. of absolute methanol containing a drop of fuming sulfuric acid gave a mixture of methyl esters which on saponification gave an acid whose infrared spectrum was very similar to that of  $\beta$ -fencholenic acid. The S-benzylthiouronium salt had m.p. 134–135° but may not be homogeneous.

*Anal.* Calcd. for C<sub>18</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S: C, 64.69; H, 7.80; N, 8.37. Found: C, 64.49; H, 7.99; N, 8.16.

**Rearrangement of Fenchone Oxime.**—Fenchone oxime was prepared essentially by the method of Wallach.<sup>20</sup> The crude oxime (90 g.) was added to a solution of 18 ml. of concentrated sulfuric acid in 450 ml. of water and heated at reflux for 1.5 hr. The layers were separated and the aqueous phase was extracted with pentane. The combined organic product showed three main peaks in addition to fenchone on gas chromatographic analysis (180°, carbowax).<sup>21</sup> The nitriles could not be completely separated by fractional distillation through a column of glass helices (460 × 10 mm.). Two main fractions were collected in addition to fenchone: 14 g., b.p. 103–112° (22 mm.), and 15 g., b.p. 112–114° (22 mm.) (lit.<sup>21</sup> for  $\alpha$ -fencholenitrile, b.p. 100–102° (19.5 mm.)).

The two fractions were hydrolyzed separately by the procedure which was reported by Cockburn to effect separation of  $\alpha$ - and  $\beta$ -fencholenitrile.<sup>22</sup> Each fraction was heated for 2 days with 60 g. of potassium hydroxide in 250 ml. of ethanol. Evaporation of the ethanol followed by addition of water and ether extraction gave mixtures of acidic and neutral products. From the low-boiling fraction there was obtained 8.5 g. of acidic material (presumably  $\beta$ -fencholenic acid) and 4.5 g. of neutral material (presumably  $\alpha$ -fencholenamide). The high-boiling fraction gave essentially no neutral material and 15 g. of acidic product, presumably  $\beta$ -fencholenic acid. The S-benzylthiouronium salt had m.p. 135–136° and did not depress the melting point

of the salt prepared from the lactones. Hydrolysis of the crude  $\alpha$ -fencholenamide was effected by heating at reflux for 4 hr. in 50 ml. of diethylene glycol containing 5 g. of potassium hydroxide. Dilution with water followed by ether extraction gave 4 g. of crude  $\alpha$ -fencholenic acid.

The two acids were lactonized by swirling 1-g. samples in 10 ml. of concentrated sulfuric acid for 2 minutes. Dilution with water was followed by ether extraction. The ether extracts were washed with sodium carbonate solution, water and then evaporated to give 0.75 g. of crude lactone VII from IX and 0.6 g. of crude lactone VIII from X. The major peaks of the gas chromatograms of these products (150°, Craig) corresponded to the peaks of the two lactones from the peracid oxidation of fenchone. A considerable amount of another product appeared in the gas chromatogram of the lactone VII which appears to be a five-membered lactone (carbonyl max. at 5.6  $\mu$ ). The mixture of lactones had the correct analysis for a lactone after chromatography and molecular distillation.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.68.

*d,l*-Epicamphor was prepared according to reference 11. The gas chromatogram (150°, silicone) exhibited one peak and the infrared spectrum showed carbonyl absorption (Nujol) at 5.7  $\mu$ ; m.p. oxime 100–101° (lit.<sup>23</sup> m.p. 98–100°).

**Oxidation of *d,l*-Epicamphor with Peracetic Acid.**—A solution of 30 ml. of glacial acetic acid, 2 g. of anhydrous sodium acetate and 6 g. (0.04 mole) of epicamphor was treated with 13 ml. (ca. 0.078 mole) of 40% peracetic acid and allowed to stand for 5 days at room temperature. Dilution with water was followed by extraction with ether to give 6.3 g. (94%) of *d,l*- $\beta$ -campholide, m.p. 213–216° (lit.<sup>24</sup> m.p. 218–220°, 216–217° and 218°). Gas chromatography on the three columns at 220° showed only one peak. The same peak appeared on the chromatogram (Carbowax) of the sample of *d*- $\beta$ -campholide supplied by Prof. Vène.<sup>12</sup> The infrared spectra of the two in chloroform were virtually identical; carbonyl maximum 5.8  $\mu$ . Recrystallization from petroleum ether raised the melting point to 216–218°, mixture melting point with Vène's sample, 219–221°.

The crude lactone was reduced with lithium aluminum hydride in ether to give the diol XIII in quantitative yield, m.p. 133–134° after recrystallization from methylene chloride-ether. The infrared spectrum was identical with that of an authentic sample (m.p. 135.5–137.5°) prepared from camphoric anhydride,<sup>4</sup> and no depression of melting point was observed on admixture of the two samples. The two samples had the same retention times on the silicone and carbowax columns at 220°.

**Oxidation of Camphor.**—Camphor was oxidized according to the usual procedure.<sup>4</sup> The crude product (2.76 g.) was isomerized by treating with 60 ml. of glacial acetic acid containing 4 ml. of concentrated sulfuric acid. After 20 hr. at 25° half of the solution was processed<sup>4</sup> to give 1.25 g. of a 3:1 mixture of XVI and II (and camphor) (208°, silicone). The second half of the isomerization solution was heated for 1.5 hr. on the steam-bath and quenched to give 1.15 g. of a mixture which had the same analysis as the first half.

(20) O. Wallach, *Ann.*, **263**, 129 (1891).

(21) R. W. Cottingham, *J. Org. Chem.*, **25**, 1473 (1960), has shown that the pure  $\alpha$ -oxime leads only to  $\alpha$ -fencholenitrile. The oxime used here undoubtedly contains both forms of the oxime. The third nitrile formed is probably a double bond isomer.

(22) G. B. Cockburn, *J. Chem. Soc.*, **75**, 501 (1899)

(23) R. Furness and W. H. Perkin, *J. Chem. Soc.*, **105**, 2024 (1914).

(24) A. Haller and H. Blanc, *Compt. rend.*, **141**, 697 (1905); J. Brecht, *J. prakt. Chem.*, **95**, 63 (1917); and F. Salman-Legagneur and J. Vène, *Bull. soc. chim. France*, **4**, 448 (1937).