eluting first with 30–60° petroleum ether, then petroleum ether progressively richer in diethyl ether (up to 60:40). Using this technique, *cis*-2-phenylcyclopentanol (VI) was first eluted and subsequently further purified by distillation, bp 113–115° (2 mm).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.42; H, 8.71. Found: C, 81.45; H, 8.42.

trans-2-Phenylcyclopentanol[7] was also purified and both alcohols assayed for deuterium (when AlD_3 was used) by nmr spectroscopy[5] (see discussion).

B. Inverse Addition of Ethereal Alane[8] to 1-Phenylcyclopentene Oxide (V).—To a solution of 0.212 g (1.59 mmoles) of aluminum chloride in 50 ml of anhydrous ether at 0° was added 0.2 g (4.76 mmoles) of $LiAlD_4$. This solution was stirred at room temperature for 0.5 hr, whereupon it was added dropwise to a solution of 3.06 g (19.1 mmoles) of 1-phenylcyclopentene oxide (V) in 50 ml of anhydrous ether. The reaction mixture was brought to reflux for 1 hr followed by hydrolysis with 5% aqueous hydrochloric acid solution. The ether layer was separated and washed with a saturated solution of aqueous bicarbonate, then water, followed by drying over magnesium sulfate.

The ether was distilled and the residue was subjected to alumina chromatography and vpc analysis as above.

C. Reaction of 1-Phenylcyclopentene Oxide (V) with AlH_3/THF Reagent.[6]—To 50 ml of anhydrous THF was added 1.14 g (30 mmoles) of $LiAlH_4$ at 0°. To this solution was added 1.47 g (0.80 cc) of 100% H_2SO_4 slowly *via* a syringe, while the solution was stirred vigorously. Hydrogen evolution was indicated by means of a gas bubbler. The solution was stirred at room temperature for 1 hr, followed by standing overnight in an atmosphere of nitrogen to permit the lithium sulfate precipitate to settle.

The THF solution was removed carefully (cloudy, owing to some Li_2SO_4 that had not settled) by a syringe and injected into a dry, three-neck, 200-ml, round-bottom flask fitted with a syringe cap, reflux condenser to which a gas bubbler was connected, and an inlet tube. To the AlH_3/THF solution was added 0.5 g (3 mmoles) of 1-phenylcyclopentene oxide (V) in 10 ml of THF in *ca.* 10 sec. This reaction mixture was stirred under a nitrogen atmosphere for 1 hr at room temperature whereupon it was hydrolyzed with methanol followed by work-up with Rochelle's salt (sodium potassium tartrate) solution to break up the trimethoxyaluminum complex. The THF solution was then separated and dried over magnesium sulfate. Solvent evaporation afforded 0.4 g of crude product; alumina chromatography and vpc analyses were then carried out as above.

It should be noted that this method of preparing alane in THF gave results with styrene oxide identical with those obtained by Brown and Yoon:[8] 74% α-phenylethanol and 26% β-phenylethanol.

Registry No.—Alane, 7784-21-6; V, 10294-00-5; VI, 2362-73-4; IX, 1198-34-1; AlD_3, 10294-03-8.

The Generation of Angular Methyl Groups in Fused-Ring Systems[1]

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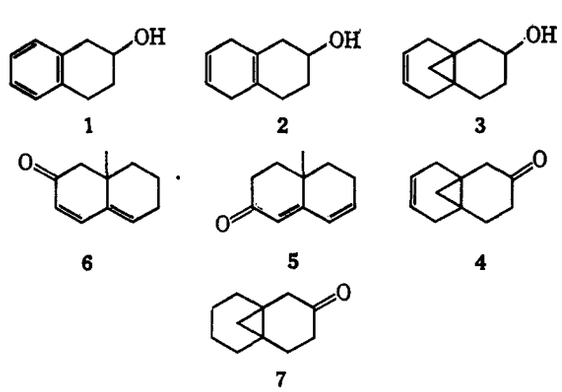
Received December 1, 1966

A stereospecific method for introducing an angular methyl group, which uses the known stereospecificity of the Simmons–Smith cyclopropanation with subsequent opening of the cyclopropane to form a methyl group is discussed. Base-catalyzed ring opening of tricyclo[4.4.1.$0^{1,6}$]undec-8-en-3-one (4) leads to self-condensation. Acid-catalyzed ring opening of ketone 4 gives both possible ring-opened ketones in a ratio depending upon the acid used.

One of the major problems that one faces in the total synthesis of the terpenes and steroids is the stereospecific introduction of angular methyl groups. The key to success in most work to date is the elaboration of a methylcyclohexanone *via* the Robinson annelation[2] or various modifications[3] of the basic theme. Although this general approach has enjoyed success as a route to fused cyclic systems possessing an angular methyl group, as pointed out by Marshall and Fanta, it is also often plagued by low yields and impure products.[4] Some versatility is also lost in that one must always engage in annelating a new ring, rather than being able to introduce a methyl group to a suitably fused, preformed array.

It has been previously observed that cyclopropane rings could be opened smoothly to give angular methyl groups.[5] These observations plus the recently accumulated knowledge that in the Simmons–Smith reaction[6] certain polar groups may direct formation of the cyclopropyl ring *cis* to themselves[7] suggests that a synthetic sequence could be designed involving a stereospecifically formed cyclopropane ring and its subsequent selective opening to produce an angular methyl group. We chose to investigate, as a model, the conversion of 1 to 5. While this investigation was in progress, a similar scheme was shown to be of value in the conversion of estradiol to 10α-testosterone.[8]



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Results and Discussion

The Birch reduction of 1,2,3,4-tetrahydro-2-naphthol (**1**) gave as expected in high yield 1,2,3,4,5,8-hexahydro-2-naphthol (**2**). At this stage there was some concern about the Simmons–Smith reaction on **2**, since the reagent could react *a priori* with either of the two double bonds. It was anticipated though on the basis of the reported increase in rate of reaction of homoallylic alcohols[7a] that the major proportion of the methylene transfer reagent would be directed to the central double bond of **2**. After some preliminary experimentation, it was found that treatment of **2** with a 2 *M* ratio of the reagent accomplished almost exclusive addition to the central double bond giving a nearly quantitative yield of monoadduct, which was >95% pure by vapor phase chromatography (vpc) analysis. Structure **3**, *cis*-tricyclo[4.4.1.0^{1,6}]undec-8-en-3-ol, was assigned to the product on the basis of spectral properties. Its nuclear magnetic resonance (nmr) spectrum contained an AB quartet (τ_A 9.68, τ_B 9.31, J = 4.5 cps) for the cyclopropyl hydrogens and a multiplet of equal intensity for the olefinic hydrogens at τ 4.52. We assign the *cis* configuration of the alcohol and cyclopropane ring by analogy with previous work,[7a,b] which has shown the directing power of the OH group. The compound was homogeneous to vpc and thin layer chromatography under all conditions tried.[9]

Conversion of **3** to the desired tricyclo[4.4.1.0^{1,6}]-undec-8-en-3-one (**4**) was accomplished smoothly in 89–91% yield by the Jones reagent.[11] Ketone **4** formed a yellow 2,4-dinitrophenylhydrazone. Its spectral properties were consistent with the structure proposed. In the nmr there still appeared an AB quartet for the cyclopropane hydrogens, shifted slightly from that found for **3**, centered at τ 9.48 (J = 5 cps) and a multiplet of equal area at τ 4.60 could be assigned to the olefinic hydrogens. A new singlet appeared at τ 7.62 and could be assigned to the two hydrogens of the isolated methylene next to the carbonyl group. Confirmation of the structure of **4** came from saturation of the isolated double bond using prereduced platinum oxide in ether and stopping the hydrogenation after the uptake of 1 mole of hydrogen/mole of compound. Other solvents (ethanol and ethyl acetate) and/or other catalysts gave mixtures of ring-opened products as evidenced by the loss of the characteristic AB pattern in the nmr spectrum. The saturated ketone **7** formed a 2,4-dinitrophenylhydrazone with the same melting point as that reported[5b] and gave an nmr spectrum identical with that found by Starr and Eastman.[12]

Both acid- and base-catalyzed ring opening of cyclopropanes had been reported.[5,7] Treatment of **4** with various bases gave disappointing results. When the conditions were strong enough to yield other than starting material, only dark, polymeric materials were obtained. These gave indication on the basis of their infrared spectra of having undergone not only ring opening but also self-condensation reactions. This type of opening was not pursued any further.

On the other hand, acid-catalyzed opening of the cyclopropane ring in **4** led to more encouraging and interesting results. Treatment of **4** with hydrochloric acid in acetic acid yielded two isomeric ketones. They were separated by preparative vpc and assigned structures **5** and **6** on the basis of the following evidence.

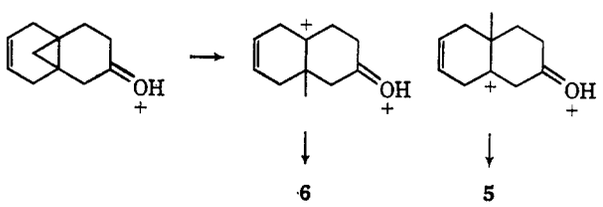
The expected product of the ring opening (**5**) was a known compound with a reported maximum in the ultraviolet of 281 mμ.[13] Our ketone had a maximum at 283 mμ and in addition formed a brick red 2,4-dinitrophenylhydrazone with the same melting point as that reported.[13]

The second ketone (**6**) also had infrared absorption characteristic of an unsaturated ketone. However, it gave an ultraviolet absorption maximum at 290 mμ which agrees exactly with that reported for the chromophore found in $\Delta^{3,5}$-cholestadien-2-one.[14] The nmr spectrum provided confirmation of structure **6**, 6,-7,8,6a-tetrahydro-8a-methyl-2(1H)-naphthalenone. It included a three hydrogen singlet (τ 8.89) for the angular methyl, a two hydrogen singlet (τ 7.79) assigned to the isolated methylene at C-1, a one hydrogen triplet for the olefinic hydrogen at C-5 (τ 4.05, J = 4 cps) and two one hydrogen doublets of an AB pattern (τ 4.30 and 3.20, J = 10 cps); the higher field resonance was assigned to the proton at C-3 and the lower to the hydrogen at C-4.[15]

The two ketones accounted for at least 98% of the monomeric products formed by the acid-catalyzed isomerization. The ratio of **5**:**6** was interestingly dependent upon the acid used in the reaction. Hydrochloric acid–acetic acid gave 3.4:1 ratio of **6**:**5**, perchloric acid–acetic acid gave 1.3:1 ratio and boron trifluoride etherate–acetic acid gave a 1:1 ratio. It may be possible to find conditions which will produce a predominance of either **5** or **6** at will.

It was of interest that two isomerized ketones were obtained in unequal proportions. An explanation for this observation may lie in the fact that **4** probably is to a large extent protonated on oxygen in the acid solution. If this is the species that undergoes ring opening, then the more stable of the two positive intermediates leading to **5** and **6** should be the one which gives **6**. It has the greater separation of formal charges.

The difference in the ratio of **5**:**6** obtained with different acids may reflect the degree to which the ketone **4** is protonated in each case.



(9) It is of interest to interject a comment here about the preparation of the Zn–Cu couple used to carry out the cyclopropanation. We have found the most reproducible, highly active couple is prepared by the method of LeGoff, using the 30 mesh zinc.[10] This paper seems to have been overlooked by recent workers.

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A second cyclopropyl ketone, tricyclo[4.3.1.0^{1,6}]-dec-3-en-8-one (**9**), was donated to us for this study

9 **10**

by Dr. Phillip Radlick.[16] Similar acid treatment of **9** gave, because of its symmetry, one product in 81% yield, **10**, 4,5-dihydro-3a-methylinden-2(3H)-one. Infrared absorption was consistent with it being a conjugated, five-ring ketone. A maximum at 272 mμ was in agreement with that calculated for the chromophore present in **10**.[17] The nmr spectrum of **10** showed a three hydrogen singlet at τ 8.82 for the quaternary methyl group, a two hydrogen singlet at τ 7.84 for the isolated methylene, and a one hydrogen singlet at τ 4.32 for the olefinic C-3 hydrogen; the remaining olefinic hydrogens at C-4 and C-5 appeared as an AB pattern, which was further split by the methylene at C-6, giving rise to two pairs of triplets centered at τ 3.72 (C-5) and 3.40 (C-4), J_{AB} = 10 cps, $J_{vicinal}$ = 4 cps, and $J_{allylic}$ = 2 cps.

Experimental Section[18]

1,2,3,4-Tetrahydro-2-naphthol (1).—The procedure of Dominguez for the reduction of β-naphthol to 5,6,7,8-tetrahydro-2-naphthol gave in our hands mainly **1**.[19] Omitting the addition of base to the reduction mixture gave 5,6,7,8-tetrahydro-2-naphthol.

1,2,3,4,5,8-Hexahydro-2-naphthol (2).—Ammonia (1 l.) was condensed in a flask fitted with a Dry Ice condenser and containing 34.46 g (0.233 mole) of **1** dissolved in a mixture of 125 ml of ethanol and 100 ml of diethyl ether. Sodium (21.4 g, 0.845 g-atom) was added in small pieces over about 45 min. At the end of the addition, the blue color of dissolved sodium persisted for 15 min. After the blue color disappeared the Dry Ice condenser was removed, allowing the ammonia to evaporate slowly at room temperature. To the residue was added 1.5 l. of water and the mixture was extracted several times with fresh portions of methylene chloride. The organic layers were combined, dried over magnesium sulfate, and evaporated on a rotary evaporator to yield 32.6 g of a light yellow oil, whose nmr showed no aromatic hydrogens. Distillation under nitrogen at 0.1 mm gave a small forerun, 83–85° (1.2 g), and a main fraction, 85–87° (31.2 g), which crystallized on standing in the refrigerator, mp 45–47°.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.88; H, 9.32.

p-Nitrobenzoate had mp (from ethanol) 107–109°.

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.72; N, 4.67. Found: C, 68.08; H, 5.58; N, 4.81.

***cis*-Tricyclo[4.4.1.0^{1,6}]undec-8-en-3-ol (3).**—The Simmons–Smith reaction was carried out by the method of LeGoff.[10] To a stirred suspension of Zn–Cu couple (39 g, 0.60 g-atom) in 100 ml of *dry* ether was added approximately 6 ml of methylene iodide. The mixture was intermittently heated with an infrared lamp until initiation of a reaction was evidenced by continued reflux of the ether after withdrawal of the heat. A mixture of **2** (41.0 g, 0.272 mole) and the remainder of 142.2 g (0.53 mole) of methylene iodide was dropped into the reaction at a rate which maintained a gentle reflux. The reaction was refluxed an additional 4 hr and allowed to cool to room temperature. To the gray mixture was added *cautiously* with stirring a saturated solution of ammonium chloride. (If this addition is carried out carefully, a granular precipitate forms from which the ether solution containing the product can be decanted. The amount of ammonium chloride which needs to be added varies from reaction to reaction.) The ether solution was decanted and the precipitate was washed several times with fresh ether. The combined ether extracts were washed twice with saturated ammonium chloride, twice with saturated sodium bicarbonate, dried over magnesium sulfate, and evaporated on a rotary evaporator to give 44.8 g of a spicy smelling syrup which was >95% pure monoadduct by vpc analysis.

Tricyclo[4.4.1.0^{1,6}]undec-8-en-3-one (4).—The crude product from the cyclopropanation was oxidized directly without further purification by the Jones reagent.[11] Compound **3** (44.8 g in 400 ml of acetone) was cooled to 0° with an ice bath. Jones reagent was added slowly from a buret while the mixture was stirred magnetically. The addition was discontinued when the color of the solution turned from green to orange; 75 ml of the reagent was required. The acetone was decanted from a green precipitate and removed on a rotary evaporator at room temperature. The residue from the evaporation was partitioned between water and ether and the water was extracted with several portions of fresh ether. The combined ether extracts were washed with saturated sodium bicarbonate, dried over magnesium sulfate, and evaporated under vacuum. Distillation of the product at 0.5 mm gave, after a small forerun, 25.9 g of **4** bp 71–74°. This reaction was carried out several times on a 10-mmole scale with yields of 89–91%. Compound **4** showed infrared absorption at 5.84 and 6.05 μ and formed a yellow 2,4-dinitrophenylhydrazone, mp 154–156°.

Hydrogenation of 4. Compound 7.—Platinum oxide (13 mg) was prereduced in 10 ml of ether. To the suspension was added 164 mg of **4**. Slightly more than the theoretical amount of hydrogen was taken up in 40 min when the uptake had ceased. The catalyst was filtered and the ether was evaporated to give a quantative yield of **7**. Its nmr spectrum was identical with that of an authentic sample.[12] The product formed a yellow 2,4-dinitrophenylhydrazone, mp 154–155° (lit.[5b] 154–155°), confirming the structure of **4**.

Attempted Base-Catalyzed Ring Opening of 4.—Heating **4** with potassium *t*-butoxide in dimethyl sulfoxide under a variety of conditions gave only starting material or dark polymeric material. Apparently self-condensation of the ketone takes place.

Only starting material was recovered from treatment of **4** with an excess of dimsyl sodium in dimethyl sulfoxide. The ketone was also stable to neutral, activity I alumina, being chromatographed unchanged.

Acid-Catalyzed Ring Opening of 4. Compounds 5 and 6.—To 25 ml of a 1:3 mixture of concentrated HCl–acetic acid was added 1.62 g of **4**. The solution was refluxed *under nitrogen* for 3 hr, cooled to room temperature, and poured into 150 ml of water. The water was extracted with three portions of ether. The combined ether extracts were washed with saturated sodium bicarbonate, dried over magnesium sulfate, and evaporated under vacuum to give 1.67 g of a dark yellow oil. Kugelrohr distillation [bp 80° (0.1 mm)] gave 686 mg of a clear, mobile liquid which consisted of a small amount (<5% relative to other components) of **4** and two new ketones, **5** (23%) and **6** (77%), as shown by vpc. Both showed infrared absorption characteristic of doubly unsaturated ketones: **5**, λ_{max}^{film} 6.0, 6.18, 6.30 μ; **6**, λ_{max}^{film} 5.98, 6.12, 6.32 μ. Their ultraviolet spectra were significantly different: **5**, λ_{max}^{MeOH} 283 mμ (ε 21,000); **6**, λ_{max}^{MeOH} 290 mμ (ε 16,200). Each formed a 2,4-dinitrophenylhydrazone: **5**, mp 188–190° (lit.[13] mp 187–190°); **6**, mp 125–127°.

Anal. Calcd for $C_{17}H_{18}H_4O_4$: C, 59.64; H, 5.30. Found: C, 59.57; H, 5.40.

Essentially the same conditions were used for the ring opening using other acids, *i.e.*, equivalent acid concentrations.

Acid-Catalyzed Ring Opening of 9. Compound 10.—Using the same conditions as above, 150 mg of **9** was subjected to acid-catalyzed ring opening. Work-up and Kugelrohr distillation [bp 85° (0.1 mm)] gave 116 mg (78%) of a slightly yellow oil, which showed only one peak on the vpc; infrared absorption λ_{max}^{film} 5.90, 6.15, 6.32 μ; ultraviolet absorption λ_{max}^{MeOH} 272 mμ

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(17) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press Ltd., London, 1964, pp 60–66.

(18) Analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. Vpc was carried out using 20% XE-60 (60–80 Chromosorb W) columns and a Wilkens A90P instrument. Infrared spectra were determined on a Perkin-Elmer Model 137 Infracord. Ultraviolet spectra were determined on a Cary Model 14. Nmr spectra were recorded on a Varian A-60, with tetramethylsilane as an internal standard.

(19) X. A. Dominguez, I. C. Lopez, and R. Franco, *J. Org. Chem.*, **26**, 1625 (1960). This paper describes the preparation of an extremely active Raney nickel catalyst with allows the above hydrogenation to be carried out in a low-pressure Parr shaker; *cf.* G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947).

(ε 20,300). It formed a maroon 2,4-dinitrophenylhydrazone, mp 162–163°.

Anal. Calcd for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.79; H, 4.91; N, 16.80.

A second experiment using boron trifluoride etherate as the acid catalyst gave the same product in 81% isolated yield.

Registry No.—2, 10271-04-2; 3, 10294-80-1; 4, 10271-05-3; 2,4-dinitrophenylhydrazone of 4, 10271-06-4; 5, 10271-07-5; 6, 10271-08-6; 2,4-dinitrophenylhydrazone of 6, 10271-09-7; 10, 10271-10-0; 2,4-dinitrophenylhydrazone of 10, 10271-11-7.

Rearrangement of α-Bromocamphoric Anhydride[1a-c]

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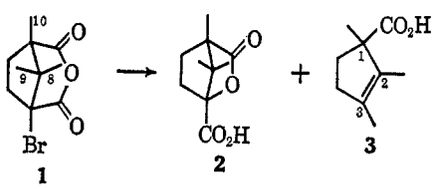
Received September 29, 1966

α-Bromocamphoric anhydride (1) is converted by aqueous sodium carbonate into camphanic acid (2) and the rearranged product laurolenic acid (3). Camphanic acid is not converted to laurolenic acid under the same conditions, and thus is not an intermediate in the rearrangement. D-(−)-α-Bromocamphoric anhydride-9,9,9-d_3 was prepared from D-(+)-isoketopinic acid (14) by lithium aluminum deuteride reduction of the corresponding methyl ester to 9-hydroxyisoborneol-2,9,9-d_3, selective preparation of the 9-*p*-toluenesulfonate, lithium aluminum deuteride reduction to D-(−)-isoborneol-2,9,9,9-d_4, Sarett oxidation to D-(+)-camphor-9,9,9-d_3 (shown to be optically pure), oxidation with selenium dioxide and then alkaline hydrogen peroxide to D-(+)-camphoric acid-9,9,9-d_3, and bromination. Rearrangement of this labeled bromo anhydride produced D-(+)-laurolenic acid in which the deuteriomethyl group is located exclusively at the 2 position. Consequently the rearrangement involves stereospecific migration of the methyl which is *cis* to the carboxyls of α-bromocamphoric acid. These results indicate that methyl migration is concerted with bromide loss, and that neither α-carboxylate participation in bromide loss (through an α-lactone or its mechanistic equivalent) or carbene formation is involved.

In 1885 Fittig and Woringer reported that α-bromocamphoric anhydride (1) was converted by boiling water into a mixture of an unsaturated acid, laurolenic acid (called lauronolic acid in the older literature), and the lactonic acid, camphanic acid (2).[2] Aschan[3] found that the yield of laurolenic acid was improved somewhat at higher pH, and that the α-chloro anhydride gave similar results. The correct structure for laurolenic acid (3) was first suggested by Lapworth,[4] and this assignment has been confirmed by subsequent physical and degradative evidence[5-9] and our recent synthesis.[10]



Although laurolenic acid is the minor product of the bromo anhydride hydrolysis (15% yield), it is in many respects the more interesting owing to the unusual combination of structural changes which accompany its formation. The rearrangement of bromonorcedrenedicarboxylic acid[11,12] is the only other known reaction in which a 1,2-methyl migration accompanies loss of bromide and carbon dioxide from an α-bromo acid. In order to allow a mechanistic interpretation of this unusual rearrangement we wished to learn (a) whether there is any stereospecificity of methyl migration, and if so which methyl migrates, and (b) which of the two carboxyl groups is lost, since the symmetry of this system (unlike that of the cedrene derivative) does not allow an unequivocal *a priori* assignment. We have attempted to answer these questions by studying the rearrangement of suitably labeled α-bromocamphoric anhydride. At this time we are able to report that the methyl migration is completely stereospecific, involving only the methyl which is *cis* to the two carboxyl groups; work is in progress which will ascertain whether carboxyl loss is equally specific.

One of the initial points to be established about the bromo anhydride rearrangement was that camphanic acid (2) is not an intermediate in the formation of laurolenic acid (3). It is known, for example, that laurolenic acid is produced upon pyrolysis of the lactonic acid.[2,3,9,13,14] However, the conditions which convert the bromo anhydride reproducibly to 14–16% laurolenic acid and 55–65% camphanic acid leave camphanic acid unchanged. Thus its intermediacy in the bromo anhydride rearrangement is excluded, and the two products are formed by competitive reaction pathways.

(1) (a) Abstracted in part from the Ph.D. dissertation of A. P. L., Indiana University, 1966; (b) supported in part by National Science Foundation Research Grant GB-1606; (c) presented in part at the 2nd Midwest Regional Meeting of the A. C. S., Lawrence, Kan., Oct 27–28, 1966; (d) U. S. Government Grantee, 1960–1962, administered by the Institute of International Education; Coulter Jones Scholar, University of Arkansas, 1965–1966; (e) correspondence regarding this work should be directed to W. L. M. at this address.

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