

Neighboring-Group Participation in Pyrolytic *trans* Eliminations

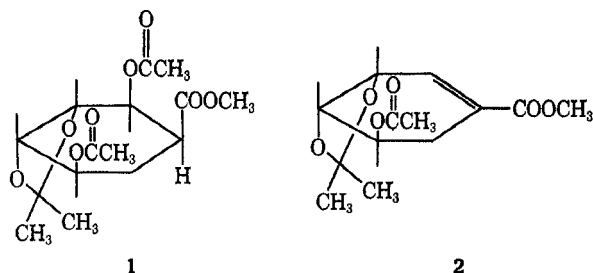
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Pyrolytic elimination of acetic acid from a series of methyl 2-acetoxy-*trans*-decalin-3-carboxylates (3-6) demonstrated that *trans* elimination occurs to give  $\alpha,\beta$ -unsaturated esters when the acetoxy and carbomethoxy groups are *cis*. The facility with which methyl 1 $\epsilon$ -methyl-2 $\alpha$ -acetoxy-*trans*-decalin-3 $\epsilon$ -carboxylate (6) produced methyl 1-methyl-*trans*- $\Delta^2$ -octalin-3-carboxylate (10) in quantitative yield leads to the postulation of neighboring-group participation in this elimination. A plausible mechanism for this assist is given.

In a previously reported stereospecific synthesis of D-(–)-shikimic acid<sup>1,2</sup> we based the stereochemistry

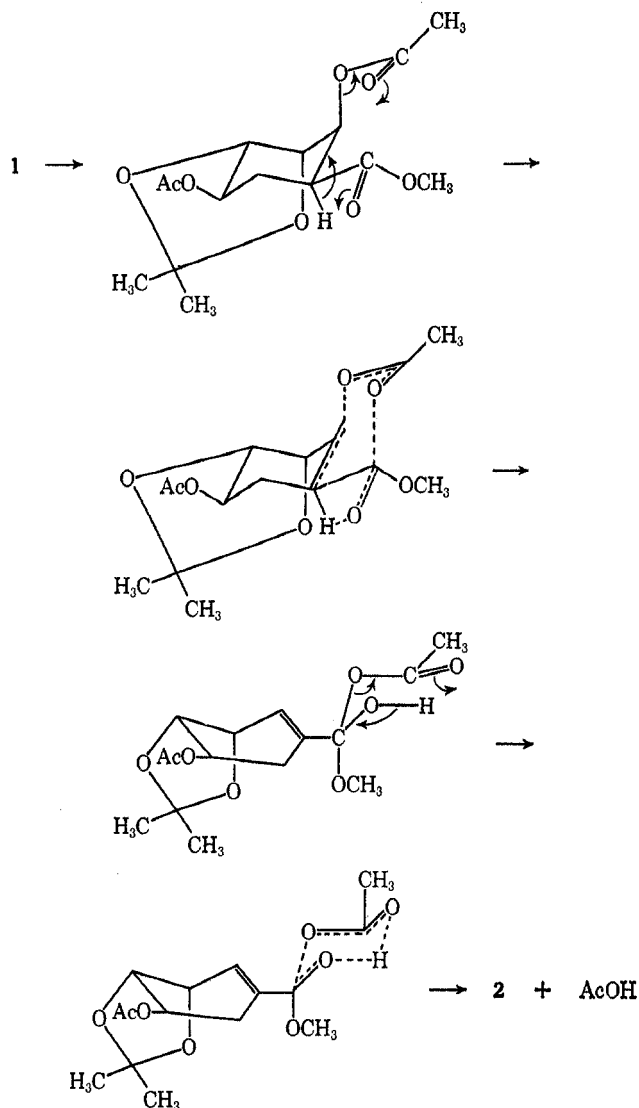


of the C-1 hydrogen atom (C-1 carboxy group) in the intermediate 1 on the fact that the latter, when heated to 285° in a sealed Pyrex tube, underwent pyrolytic elimination of acetic acid to give DL-methyl-3-O-acetylshikimate acetonide (2) in 95% yield. In an essentially identical synthetic sequence reported by Raphael and coworkers,<sup>3</sup> this acetonide was depicted as 1 with the C-1 carboxy group *cis* to the adjacent C-2 acetyl group. These authors also reported that although acetic acid elimination could be effected partially by conventional base catalysis, it occurred in 80% yield when the acetate 1 was pyrolyzed in the presence of magnesium oxide at 290°.

Subsequent nmr investigations<sup>4-6</sup> indicated that structure 1 is correct; in benzene solution the 100-MHz spectrum gives an eight-lined pattern at  $\delta$  2.83-3.20 with coupling constants of 11.5, 4.0, and 3.0 cps for the C-1 proton.

It thus appeared that the reported pyrolytic elimination of acetic acid<sup>2,3</sup> was a *trans* diaxial elimination in contrast to the more usual *cis* ester pyrolyses.<sup>7,8</sup> A possible mechanism is the concerted cyclic rearrangement depicted in col 2.

Although *trans* pyrolytic eliminations have been reported,<sup>9-12</sup> this unique neighboring-group participa-



tion required further investigation using model compounds.

The *trans*-decalin system, considered to be rigid, was selected and the four acetoxy decalincarboxylates 3-6 were prepared and pyrolyzed under conditions similar to those used with the shikimate acetonide precursor, 1. The stereochemistry of the decalins was established by nmr analysis.

Compounds 3-5 were prepared from the common precursor, *trans*-2-decalone-3-carboxylic acid (12), which was obtained by carboxylation of *trans*-2-decalone via the potassium triphenylmethide reagent, followed by condensation with carbon dioxide.<sup>13</sup>

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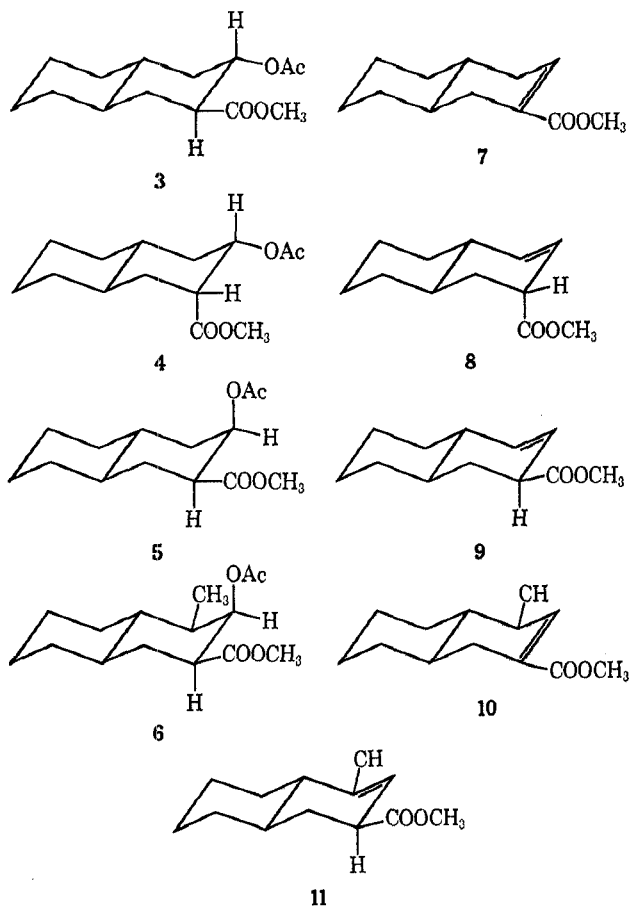
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Reduction of **12** with sodium amalgam<sup>14,15</sup> gave the *trans*-hydroxy acid **13** in 25% yield, along with a small amount of the *cis* acid **18** (R = H). Esterification of

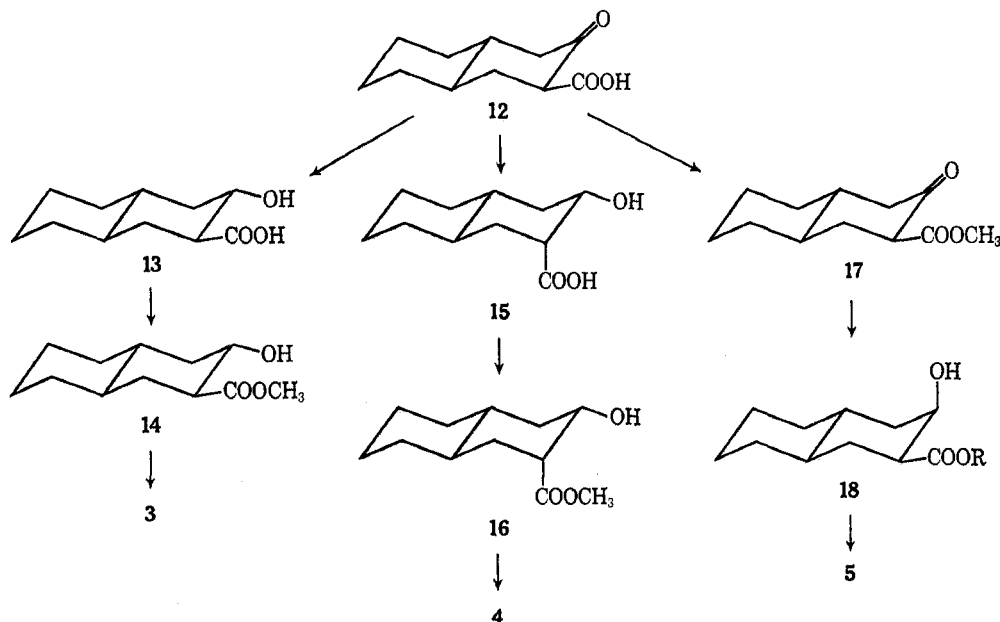
nals appear at  $\delta$  4.30 and 2.70.<sup>15,16</sup> Earlier reports of the course of the sodium amalgam reduction of **12** are somewhat conflicting: Sicher and coworkers<sup>14</sup> suggested that the *cis*- $\beta$ -hydroxy acid **18** (R = H) was the product obtained, while Pavia and coworkers<sup>15</sup> reported a mixture of hydroxy acids, **13** and **15**, from the same reaction. The mixture was converted into **13** by epimerization of the methyl esters with sodium methoxide followed by saponification.

Hydrogenation of **12** under basic conditions, using a ruthenium catalyst, gave the hydroxy acid **15**. This was then methylated and acetylated to give **4**. In the nmr spectrum of **4** there appeared a pair of overlapping triplets at  $\delta$  4.87 and 4.69 ( $J = 10.5$  and  $6.0$  cps, respectively) and a broad symmetrical signal at  $\delta$  3.05 ( $W_{1/2} = 11$  cps). Such a pattern would be expected from an axial H-2 and an equatorial H-3.<sup>17</sup>

It is noteworthy that while the nmr spectra of **3** and **4** are very similar in the H-2 region ( $\delta$  4.80–4.90), each exhibiting a broad signal of base of *ca.* 25 cps for this region, they differ markedly in the H-3 region. The observed chemical-shift difference of 0.65 ppm corresponds to the expected chemical-shift difference between an axial and an equatorial proton, the equatorial proton absorbing at the lower  $\delta$  value.<sup>17</sup>

Conversion of **12** into the methyl ester **17**, followed by hydrogenation under neutral conditions, gave the *cis*-hydroxy ester **18** (R = CH<sub>3</sub>), which was acetylated to yield **5**. The nmr spectrum of **5** exhibited an absorption at  $\delta$  5.35 ( $W_{1/2} = 7$  cps) and another broad multiplet at  $\delta$  2.45, both being in agreement with the structure indicated.

The preparative route to the acetoxy ester **6** involved the intermediate *anti-trans*-1-methyl-2-decalone ob-



**13** with diazomethane, followed by acetylation with acetic anhydride and pyridine, gave **3** in good yield. The nmr spectrum of **3** exhibited two broad bands centered at  $\delta$  4.92 and 2.40 corresponding to H-2 and H-3, respectively. In the free hydroxy acid **13**, these sig-

nals are obtained by the stereospecific synthesis recently described by Turner and coworkers.<sup>18</sup> They established that the equatorial position is the thermodynamically preferred

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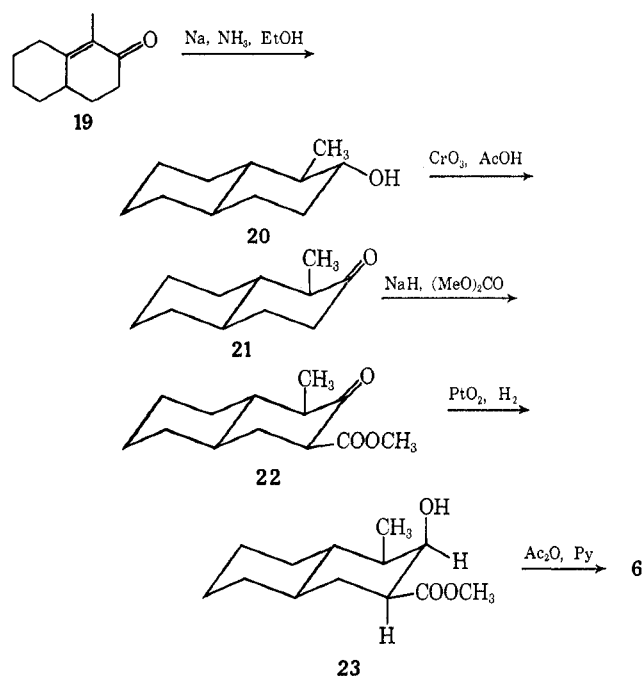
(18) R. B. Turner, R. B. Miller, and J. L. Lin, *J. Amer. Chem. Soc.*, **90**, 6124 (1968).

TABLE I

	Acetate				
	1 <sup>a</sup>	3	4	5	6
Tube length, cm	...	35	35	34	27
Pressure, mm	...	$2 \times 10^{-4}$	$3 \times 10^{-4}$	$2.5 \times 10^{-4}$	$5 \times 10^{-4}$
Pyrolysis temp, °C	290	310-315	310-315	340-345	350-355
Pyrolysis period, min	...	200	300	240	240
Sample size, mg	...	380	263	106	192
Materials obtained from pyrolysate, mg	...	212	230	98	175
Yield of olefin, %	80	25	25	20	90

<sup>a</sup> The data for 1 are repeated<sup>2</sup> here for the purpose of comparison.

orientation for the methyl group. This observation holds for the corresponding alcohol as well as for the ketone. The reaction of *anti-trans*-1-methyl-2-decalone with sodium hydride and dimethyl carbonate<sup>19</sup> gave



the keto ester 22, which underwent hydrogenation in the presence of platinum dioxide followed by acetylation to give the acetoxy ester 6. The nmr spectrum of 6 showed an absorption at  $\delta$  5.45 ( $W_{1/2} = 7$  cps) and a broad multiplet centered at  $\delta$  2.75 (assigned to H-2 and H-3, respectively), which were similar to those exhibited by 5 and consistent with the proposed structure.

Of the possible olefinic pyrolysis products 7-11, only the  $\alpha,\beta$ -unsaturated ester 7 is reported in the literature.<sup>20</sup> It was prepared from the corresponding acid and used as a reference in the vapor phase chromatographic analysis of the pyrolysis products.

### Results and Discussion

The pyrolyses were run in Pyrex tubes ( $0.8 \times 35.0$  cm) evacuated to *ca.*  $10^{-4}$  mm before sealing; temperatures were 310-350°; reaction times varied from 1 to 5 hr (see Table I). The pyrolysis product mixtures were analyzed by gas-liquid partition chromatography (glpc) and by infrared, nmr, and mass spectral determinations.

(19) E. J. Corey, R. B. Mitra, and H. Uda, *J. Amer. Chem. Soc.*, **86**, 485 (1964).

(20) W. R. Vaughan and R. Caple, *ibid.*, **86**, 4928 (1964).

When pyrolyzed for 1 hr, the *cis* acetate 3 gave small amounts of the  $\alpha,\beta$ -unsaturated olefin 7, as indicated by glpc, but the bulk of the starting material was recovered unchanged. A 3-hr pyrolysis period at 310-315° produced *ca.* 25% elimination to give again mainly 7, but significant charring also occurred. Prolonged pyrolysis did not push the elimination to completion. Glpc analysis of the product mixture indicated the presence of two other products in minor amounts. A sharp  $6.05\text{-}\mu$  C=C absorption was present in the infrared spectrum of the pyrolysate.

A 1-hr pyrolysis period left 4 essentially unaffected, though trace amounts of 7 and one other product was detectable by glpc. Pyrolysis for 4 hr at 310-315° caused *ca.* 25% elimination without appreciable charring. The major product was again 7, though three other minor constituents were present in the product mixture.

When pyrolyzed for 1 hr at 310°, 5 gave three products in small yield. Of these, one was 7 and another had a retention time equal to that of one of the minor products in the pyrolysis of 3. The relative abundance of the latter to 7 was 1.4:1.0. A 4-hr pyrolysis period at 340-345° changed this ratio to 0.8:1.0 (*i.e.*, the relative proportion of the more thermodynamically stable 7 increased at higher temperatures and longer reaction time). Charring was slight. The overall yield of olefinic materials from the 4-hr pyrolysis was *ca.* 20%.

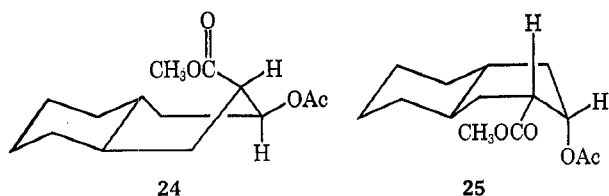
When subjected to a 4-hr pyrolysis at 350°, 6 underwent almost complete elimination to the  $\alpha,\beta$ -unsaturated ester 10, with negligible charring. One other minor product was present in the pyrolysate. The structure of the major product 10 was proven by infrared and nmr spectral analysis and by the mass spectrum of the product mixture. The infrared spectrum exhibited absorptions at 5.82 and 6.06  $\mu$ ; the relative area of the olefinic hydrogen peak at  $\delta$  6.80 in the nmr spectrum was 0.9; the mass spectrum of the product mixture showed a parent peak at  $m/e$  208. Glpc analysis, on both LAC 446 and DEGS columns, indicated a minimum purity of 95%.

The starting acetate was either recovered or its presence was established by glpc in all runs. No evidence (glpc or spectral) for epimeric forms could be obtained.

Of the possible olefinic products 7-11, 7 and 10 are the most thermodynamically stable. In addition, assuming the possibility of *trans* elimination, the acidity of H-3 suggests that 7 is the major product from 3-5. With 6, where the only elimination pathways available are *trans*, the predominant product would be expected to be 10. The results indeed suggest that the overriding factors governing the direction of elimination in these systems are the thermodynamic stability of the

olefinic product and the acidity of the leaving proton.<sup>7,21</sup> Here the two factors reinforce each other. However, the striking features in this series of reactions are (A) the similarity of the products (*ca.* 25% yield of mixtures of olefins from the pyrolysis of **3-5**); (B) the contrast between the latter and the near quantitative yields of pure products from the pyrolysis of **1** and **6**.

The above observations suggest that, while the conformations of **1** and **6** are fixed, by the five-membered ring and the methyl group, respectively, **3-5** may be present as a mixture of boat-chair conformers at the elevated temperatures utilized for pyrolysis. Under the conditions of the reaction, competing elimination mechanisms may be operative. Thus **5**, in which the carboxy-assisted *trans*- $\beta$  elimination can occur, could be in equilibrium with the conformer **24** in which the *trans*-*e,e* elimination mechanism can operate. Similarly, **4**, in which *trans*-*e,e* elimination occurs, would be in equilibrium with the conformer **25**. The latter can now undergo carboxy assisted *trans*- $\beta$  elimination. In **3**, where the acidic  $\beta$  proton is *cis* to the leaving group, other conformers are less likely to be important in the elimination reaction.



As noted above, one of the minor products from the pyrolysis of **3** also appeared in the pyrolysate of **5**, and in relatively higher proportion. Furthermore, in the latter pyrolysis, higher temperature and longer reaction time increased the proportion of **7** at the expense of this material. We surmise that this product is the  $\beta,\gamma$ -unsaturated ester **9**. Thus there would appear to be two types of elimination occurring in **5**. At 310° normal *cis* elimination toward C-1 predominates, producing 60% **9** in the olefinic product mixture. At 340° *trans* elimination accounts for 55% of the olefinic product mixture.

Initial formation of **9** by normal *cis* elimination followed by rearrangement to the more stable **7** seems unlikely; it has been demonstrated that such isomerization does not occur in the cyclohexane system,<sup>11,22</sup> and presumably this observation holds true for the decalin system. In **6**, where the conformation is fixed and in which *cis* elimination is blocked, the almost exclusive formation of **10** offers a further example of the assisted *trans*- $\beta$ -elimination mechanism.

### Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. Refractive indexes were measured on a Carl Zeiss refractometer. Infrared spectra were recorded on a Beckman IR-8 infrared spectrophotometer. Nmr spectra were measured on a Varian A-60 spectrometer, using tetramethylsilane (TMS) as internal standard. Chemical shifts were expressed in terms of  $\delta$  in parts per million. Gas-liquid partition chromatography (glpc) was conducted on an

F & M Model 810-19 analytical gas chromatograph, using a flame detector and 0.125 in.  $\times$  4 ft columns, packed with 5% w/w diethylene glycol adipate (LAC-446, F & M) on Gas-Chrom P (70-80 mesh, Applied Science Laboratories, Inc.) normally at 170°. Helium carrier gas flow was *ca.* 75 ml/min at 40 psi. Microanalyses were performed on an F & M Carbon Hydrogen Nitrogen Analyzer Model 185 in this department and by the Huffman Laboratories, Inc., Wheatridge, Colo. Mass spectral determinations were done on an Finnegan 1050 spectrometer.

*trans*-2-Decalone-3-carboxylic Acid (**12**).—A suspension of potassium triphenylmethide reagent in ether was prepared by the method of Hauser and coworkers.<sup>13</sup> To this reagent, cooled in an ice bath, was rapidly added a solution of *trans*-2-decalone, bp 75-77° (0.03-0.04 mm),  $n_D^{20}$  1.4829, yield 16.9 g (0.11 mol), in 35 ml of diethyl ether. The mixture was stirred for 15 min and the resulting white suspension was poured onto crushed Dry Ice (300 g). The mixture was stirred occasionally until the Dry Ice had completely evaporated. More diethyl ether was added to make a thin paste. It was extracted with cold 10% aqueous sodium hydroxide (three 100-ml portions). The alkaline aqueous extracts were washed with diethyl ether, cooled in an ice bath, acidified with concentrated hydrochloric acid, and extracted with diethyl ether (three 100-ml portions). The ethereal extracts were washed with water, filtered through anhydrous magnesium sulfate, and evaporated to dryness *in vacuo*. The product was obtained, mp 100-106° (lit. mp 108-111°, 100-105°,<sup>16</sup> 90° dec<sup>16</sup>), yield 24 g. The infrared spectrum was similar to those previously reported.<sup>15</sup> The crude material was used in subsequent reactions without further purification.

*trans*-2e-Decalol-3e-carboxylic Acid (**13**).<sup>14,15</sup>—The keto acid **12** (8.7 g, 44.33 mmol) was dissolved in aqueous sodium carbonate (20 g in 150 ml of water) and the resulting solution was diluted to a volume of 700 ml. Sodium amalgam (3.5%, 600 g) was added and the mixture was allowed to stand at 25° with occasional shaking for 4.5 days. The aqueous phase was decanted and filtered. The mercury and excess amalgam were washed with water. The filtrate and washings were combined, washed with dichloromethane (two 100-ml portions), cooled in ice, acidified with concentrated hydrochloric acid at 5-6°, saturated with sodium chloride, and extracted with diethyl ether (four 100-ml portions). The ethereal solution was filtered through anhydrous magnesium sulfate and evaporated to dryness *in vacuo*; 8.2 g of crystalline material was obtained. Recrystallization from acetone gave the *trans*-hydroxy acid, mp 173-174.5° (lit. mp 175-176°,<sup>15</sup> 177.5-179°<sup>14</sup>), yield 1.9 g. Concentration of the mother liquid gave a second crop of 0.2 g; the total yield was 2.1 g (23.8%).

Methyl *trans*-2e-Decalol-3e-carboxylate (**14**).—A solution of diazomethane in diethyl ether (25 ml) generated from N-methyl-N'-nitro-N-nitrosoguanidine (Aldrich, 1.5 g, 10.2 mmol) and 2 N potassium hydroxide solution (25 ml) was mixed with absolute ethanol (15 ml) and added to a solution of the hydroxy acid **13** (0.878 g, 4.43 mmol) in diethyl ether and absolute ethanol (15 ml each). The mixture was stirred at room temperature for 2 hr. A few drops of concentrated hydrochloric acid were added to destroy the excess diazomethane. The reaction mixture was evaporated to dryness *in vacuo*. The residue was taken up in diethyl ether (30 ml), washed with 10% aqueous sodium carbonate solution (10 ml) and water (two 10-ml portions), filtered through anhydrous magnesium sulfate, and evaporated to dryness. Upon drying over phosphorus pentoxide *in vacuo*, the oily residue solidified in featherlike needles, yield 0.9 g (4.24 mmol, 95.7%).

Methyl 2e-Acetoxy-*trans*-decalin-3e-carboxylate (**3**).—The hydroxy ester **14** (1.4 g, 6.59 mmol) was dissolved in dry pyridine (8 ml). The solution was mixed with acetic anhydride (7.0 g, 68.56 mmol) and refluxed under anhydrous conditions for 1 hr. The reaction mixture was evaporated *in vacuo* at 60°. The oily residue thus obtained was stirred with water (10 ml) at room temperature for 1.5 hr and extracted with ethyl acetate (four 10-ml portions). The extracts were washed with water (two 5-ml portions) and filtered through anhydrous magnesium sulfate, and the solvent was removed. The oily residue was dried over phosphorus pentoxide *in vacuo*, yield 1.65 g (6.49 mmol, 98%). Vacuum distillation afforded the pure acetate: bp 82-84° (0.04-0.05 mm);  $n_D^{20}$  1.4742; nmr  $\delta$  4.92 ( $W_{1/2}$  = 23 cps) and 2.40.

Anal. Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>: C, 66.12; H, 8.72. Found: C, 66.20; H, 8.98.

*trans*-2e-Decalol-3a-carboxylic Acid (**15**).<sup>18</sup>—The keto acid **12** (2.8 g) was dissolved in 5% sodium carbonate solution (120

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(22) W. J. Bailey and R. A. Baylouny, *ibid.*, **81**, 2126 (1959).

ml) and ruthenium dioxide (500 mg, 54%) was added. This was hydrogenated in a Parr shaker for 3 days. The catalyst was then removed and the solution was washed with ethyl acetate. The aqueous solution was neutralized with hydrochloric acid and extracted with ethyl acetate. The solution was dried over magnesium sulfate and the solvent was removed, leaving a yellow oil. Crystals, mp 128–131°, were obtained from benzene.

**Methyl 2e-Acetoxy-trans-decalin-3a-carboxylate (4).**—The acetate 4 was prepared from the corresponding hydroxy acid 15 (0.68 g, 3.46 mmol) by esterification with diazomethane followed by refluxing the ester with acetic anhydride and pyridine, as described above. The product was a light yellow, oily liquid, (0.63 g after drying over phosphorus pentoxide and sodium hydroxide pellets at 0.15 mm, 2.46 mmol, 71% overall yield):  $n_D^{20}$  1.4751; nmr  $\delta$  4.78 (a pair of overlapping triplets in a five-lined pattern,  $J = 10.5$  and 6 cps) and 3.05 (symmetrical and broad,  $W_{1/2} = 11$  cps). Thin layer chromatography on silica gel showed a single spot when developed by two solvent mixtures: chloroform-ethyl acetate (3:2) and chloroform-acetone (9:1). Glpc indicated at least 95% purity.

**Methyl trans-2-Decalone-3-carboxylate (17).**—An ethereal solution of diazomethane, prepared as before from N-methyl-N'-nitro-N-nitrosoguanidine (13.5 g, 91.8 mmol), was added to a solution of the crude keto acid 12 (13.6 g, 69.3 mmol) in diethyl ether (100 ml). The reaction mixture was stirred in an ice bath for 1 hr. The ethereal solution was then washed with water and saturated aqueous sodium chloride and filtered through anhydrous magnesium sulfate; the solvent was removed. The crude product was a yellow liquid,  $n_D^{20}$  1.4999, yield 12.45 g (59.2 mmol, 85.4%). Distillation gave a colorless liquid: bp 96–97° (0.5 mm) [lit.<sup>23</sup> bp 126–129° (3 mm)];  $n_D^{20}$  1.5006; ir (CCl<sub>4</sub>) 5.7, 5.82, 6.02, and 6.19  $\mu$  [lit.<sup>15</sup> ir (CHCl<sub>3</sub>) 5.75, 5.85, 6.04, and 6.21  $\mu$ ]; nmr 715 cps (enolic proton) (lit.<sup>15</sup> 724 cps in CDCl<sub>3</sub>). The product solidified in white needles upon storage at 3°.

**Methyl trans-2a-Decalol-3e-carboxylate (18).**—The keto ester 17 (3.1 g, 14.8 mmol) was dissolved in absolute ethanol (40 ml) and mixed with platinum oxide catalyst (Engelhard Industries, Newark, N. J., 0.5 g, 85.48%). The mixture was hydrogenated in a Parr shaker at 25°. The calculated amount of hydrogen was absorbed in 30 min. Removal of the catalyst by filtration through Celite followed by evaporation of the solvent *in vacuo* afforded the hydroxy ester 18 as a white, crystalline solid in a quantitative yield of 3.3 g, mp 91–93° from carbon tetrachloride (lit.<sup>14</sup> mp 95–96° from acetone).

**Methyl 2a-Acetoxy-trans-decalin-3e-carboxylate (5).**—The crude hydroxy ester 18 (3.3 g, 14.8 mmol) was acetylated with acetic anhydride in dry pyridine as described above. Purification of the product obtained as an oil, by vacuum distillation and by chromatography (both column and gas phase), was unsuccessful. However, 5 separated as crystals upon prolonged standing. It was recrystallized from petroleum ether (bp 30–60°), giving white prisms: mp 62.5–63.5°; nmr  $\delta$  5.35 (pyramid,  $W_{1/2} = 7$  cps) and 2.45 (multiplet).

*Anal.* Calcd for C<sub>14</sub>H<sub>22</sub>O<sub>4</sub>: C, 66.12; H, 8.72. Found: C, 66.40; H, 8.62.

**Methyl trans- $\Delta^2$ -Octalin-3-carboxylate (7).**—The free acid<sup>20</sup> (64 mg, 0.355 mmol) was esterified with diazomethane generated from N-methyl-N'-nitro-N-nitrosoguanidine (76 mg, 0.517 mmol) by the usual procedure. The crude product was a colorless liquid: yield 41.2 mg (0.212 mmol, 60%);  $n_D^{25}$  1.4953 (lit.<sup>20</sup>  $n_D^{25}$  1.4963); ir (CHCl<sub>3</sub>) 5.86 and 6.06  $\mu$ . Glpc showed that the crude product was slightly contaminated by one substance, probably the free acid.

**1-Methyl- $\Delta^{1,9}$ -octal-2-one<sup>24</sup> (19).**—1-(2-Oxocyclohexyl)pentan-3-one<sup>25</sup> (5 g, 23 mmol) was cyclized in hydrochloric acid by the method of Shunk and Wilds.<sup>24</sup> The product was obtained as an

oil and was distilled *in vacuo*, bp 80–82° (ca 0.1 mm) [lit.<sup>26</sup> bp 150–155° (18 mm)], yield 3.5 g (78%).

**trans-anti-trans-2-Hydroxy-1-methyldecalin (20).**<sup>18</sup>—The ketone 19 (5.9 g, 36 mmol) was reduced with sodium in liquid ammonia by the method of Turner, *et al.*<sup>18</sup> The crude product was distilled *in vacuo*, bp 80–85° (1.5–2 mm). The material condensed as a white, crystalline solid in the receiver, mp 52–55° (lit.<sup>18</sup> mp 55–57°), yield 3.7 g (67%).

**anti-trans-1-Methyl-2-decalone (21).**<sup>18</sup>—The alcohol 20 was oxidized with chromium trioxide in dilute acetic acid by the method of Turner.<sup>18</sup> The product (2.8 g, 80%) was a clear liquid whose infrared and nmr spectra were consistent with 1-methyl-2-decalone.

**Methyl anti-trans-1-Methyl-2-decalone-3-carboxylate (22).**<sup>19</sup>—To sodium hydride (8.0 g, 0.18 mol, 54% in mineral oil dispersion) in dry dioxane (100 ml) was added dimethylcarbonate (23.4 g, 0.23 mol) in dry dioxane (60 ml). The mixture was stirred and heated to 80–85°, and to it was added 1-methyl-2-decalone (21, 8.3 g, 0.05 mol) in dioxane (75 ml) over a 1-hr period. The heating and stirring was continued overnight, and the mixture was then cooled in ice and dissolved in aqueous acetic acid. The solution was concentrated on a rotary evaporator and the residue was dissolved in 20 ml of water. The resulting mixture was extracted with ether and the ether extracts were washed with aqueous sodium bicarbonate and aqueous sodium chloride. Drying (MgSO<sub>4</sub>) followed by removal of the ether left a yellow oil, bp 90–96° (60% yield), whose infrared spectrum was consistent with that expected for the keto ester.

**Methyl 1e-Methyl-trans-2a-Decalol-3e-carboxylate (23).**—To the keto ester 22 (2 g, 8.9 mmol) in redistilled ethanol (30 ml) was added platinum dioxide (0.63 g). The material was hydrogenated in a Parr shaker for 5.5 hr. The product was distilled, bp 134–135.8° (3 mm). The distillate crystallized on standing, mp 78–79° (30% yield of crystalline product). The infrared and nmr spectra were consistent for the hydroxy ester.

**Methyl 1e-Methyl-2a-acetoxy-trans-decalin-3e-carboxylate (6).**—To the hydroxy ester 23 (2 g, 8.9 mmol) in dry pyridine (7 ml) was added acetic anhydride (10 ml). The mixture was heated at 155–160° for 45 min. The acetate was isolated as described above. Vacuum distillation gave a clear oil, bp 140° (3.2 mm), which crystallized on standing in the cold: mp 47–48°; yield 25%; nmr  $\delta$  5.48 (pyramid,  $W_{1/2} = 7$  cps) and 2.82 (multiplet).  
*Anal.* Calcd for 6: C, 67.25; H, 8.96. Found: C, 67.48; H, 8.90.

**Pyrolysis of the Acetates.**—The conditions used in the pyrolysis of the acetonide in the shikimic acid synthesis (1) were employed. The acetates were placed separately in Pyrex tubes of 8-mm i.d., evacuated to pressures of ca.  $3 \times 10^{-4}$  mm, and sealed. The tubes were heated in an electric furnace at temperatures indicated in Table I, p 1354. The oily products were dissolved in reagent grade ethyl acetate, treated with anhydrous sodium carbonate powder, and filtered. The filtrates were analyzed by glpc. The presence of olefinic substances in the pyrolysates was confirmed by the sharp ir band near 6.05  $\mu$ , which was absent in the infrared spectra of the starting acetates.

**Registry No.**—3, 23757-87-1; 4, 23757-89-3; 5, 23757-88-2; 6, 23757-90-6; 7, 1204-87-1; 15, 23757-92-8; 17, 23757-93-9; 22, 23757-94-0; 23, 23757-95-1.

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