$[\alpha]D$ −129°; uv, λ_{max} (ϵ), 247 (11,800), 255 (13,100), 264 (8,800, sh) nm; nmr δ 5.59 (1H, m), 5.80 (1 H, m) ppm.

Anal. Calcd for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.40; H, 12.10.

When this compound was chromatographed over SiO_2–$AgNO_3$, it was transformed into **4** and **16**.

Maleic Anhydride Adduct from 15.—The diene (50 mg) and maleic anhydride (50 mg) were dissolved in xylene (0.5 ml) and the mixture was heated for 8 hr at 135° in a sealed tube. The solvent was then evaporated under reduced pressure and the residue refluxed for 2 hr with 1.5 *M* methanolic potassium hydroxide (6 ml). After cooling the undissolved material (10 mg, diene **4**) was filtered off and the filtrate, diluted with water and acidified with 2 *N* hydrochloric acid, was extracted with ether. Evaporation of the dried ($MgSO_4$) extract afforded 38 mg of residue, which was dissolved in ether and precipitated with methanol to obtain an amorphous powder, mp 150–155°, $[\alpha]D$ +43°.

Anal. Calcd for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99. Found: C, 78.55; H, 9.78.

Isomerization of Dienes with Hydrochloric Acid in Ethanol.—Each diene (50 mg) was dissolved in ethanol (50 ml) containing 36% hydrochloric acid (5 ml). The solution was refluxed for 1.5 hr and the reaction product was isolated in the usual way. Yields were almost quantitative. Dienes **12**, **13**, and **14** afforded **3**; dienes **15** and **16** afforded **4**.

Catalytic Hydrogenations.—Each diene (50 mg) was dissolved in a mixture of cyclohexane (30 ml) and acetic acid (10 ml) and the solution was stirred under hydrogen in the presence of 5% Pt–C catalyst (0.15 g), for the given time. The catalyst was then filtered off, the filtrate was diluted with water, and the product was isolated in the usual way. Diene **3** (stirring time 0.5 hr) afforded **9** and A′-neogammacer-16-ene.[2] Diene **3** (stirring time 7 hr) and diene **14** (stirring time 3 hr) afforded **9**. Diene **13** (stirring time 7 hr) afforded a mixture containing (glpc) 20% **9**, 50% 21αH-A′-neogammacerane (moretane), 16% 21βH-A′-neogammacerane (hopane), and 14% unidentified product. Dienes **4**, **15**, and **16** (stirring time 5 hr) afforded **17**.

Registry No.—**4**, 3608-05-7; **5**, 1615-92-5; **6a**, 22847-67-2; **6b**, 22847-68-3; **7**, 22922-40-3; **12**, 22847-69-4; **13**, 22847-70-7; **14**, 22847-71-8; **15**, 22847-72-9; **16**, 22847-73-0; maleic anhydride adduct of **15**, 22847-74-1.

Acknowledgments.—We wish to thank Professor G. Berti for his continued interest in this work, Dr. P. L. Barili for the glpc analyses, Dr. V. Nuti for the elemental analyses, and Dr. G. Ceccarelli (Istituto di Chimica Fisica) for the nmr spectra. This work was supported by a grant from the Consiglio Nazionale delle Ricerche.

Experiments Directed toward the Total Synthesis of Terpenes. XIV. An Interpretation of the Transmogrification of 4β,7aα-Dimethyl-1α-hydroxy-4α-phenyl-4,5,6,7-tetrahydro-2-indanone by Base[1]

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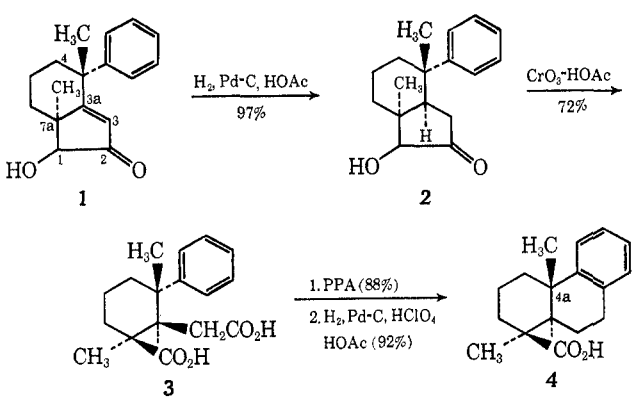
Received August 4, 1969

The base-catalyzed rearrangement of the unsaturated hydroxy ketone **1** has been shown to generate the diosphenol **31** in virtually quantitative yield. The process involves epimerization of the tetrasubstituted C-7a carbon of the tetrahydro-2-indanone ring system and probably entails initial reverse aldolization and subsequent recombination to the epimeric unsaturated hydroxy ketone **30** prior to diosphenol formation. The structure of the diosphenol **31** was determined by degradation to the hexahydro-2-indanone **22**, which was, in turn, synthesized independently. Oxidation of the diosphenol **31** and then polyphosphoric acid catalyzed cyclization of the resulting anhydride **35** produced the benzobicyclo[3.3.1]nonane skeleton **36**. Evidence in favor of this structure was obtained by degradation of the acid **36** to the hydrocarbon **38**. Single-crystal X-ray structural analyses of the *p*-bromobenzoates of the unsaturated hydroxy ketones **1** and **30** and the diosphenol **31** are reported, and the driving force of the rearrangement reaction is discussed in terms of the steric crowding in the hydroxy ketone **1**.

In the recently described stereoselective synthesis of deoxypodocarpic acid (**4**)[3] from these laboratories,[4] the unsaturated hydroxy ketone **1** was a key intermediate. Catalytic hydrogenation of the conjugated double bond served to introduce the last required center of asymmetry at C-3a and generate the saturated hydroxy ketone **2** in good yield. The further transformation of this saturated ketone **2** to the desired deoxypodocarpic acid (**4**) and its derivatives was then unexceptional and the sequence that was developed provides an excellent route for the synthesis of these tricyclic acids. During the course of this investigation and before the catalytic hydrogenation of the unsaturated ketone **1** had been



(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, Grant PRF 2481C; and also to U. S. Public Health Service, Grant GM 12121, and to National Science Foundation, Grant GB 6617X, for support of the X-ray crystallography work.

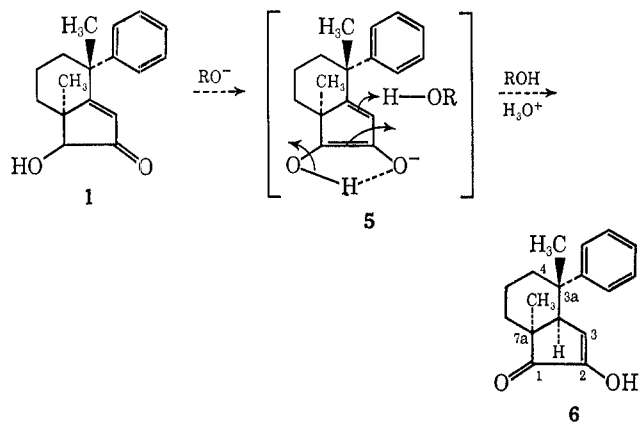
(2) (a) National Science Foundation Teaching Assistant Summer Fellow, 1966; National Institutes of Health Trainee, 1966; Research Fellow of the Institute of General Medical Sciences, National Institutes of Health, U. S. Public Health Services, 1966–1968. (b) National Defense Education Acts Predoctoral Fellow, Department of Biology.

(3) The structural formulas containing one or more asymmetric carbon atoms depict one diastereoisomer, but refer to racemic compounds throughout. Each racemate is arbitrarily represented by the diastereoisomer that has the C-4 (hydroindan series) or C-4a (phenanthrene series) methyl group in the β configuration. In the text the (±) prefix will be omitted and intermediates are to be assumed to be racemic.

(4) F. Giarrusso and R. E. Ireland, *J. Org. Chem.*, **33**, 3560 (1968).

fully developed, the authors attempted[5] an alternate scheme for the conversion of this ketone **1** into the diacid **3**. While the result of this attempt did not lead to a useful alternative to the hydrogenation step, the outcome was unexpected and occasioned the further investigation reported here.

Consideration of the functional array present in the unsaturated hydroxy ketone **1** suggests the formal possibility that an α diketone (diosphenol **6**) might result from an internal oxidation–reduction reaction. Formally, the intermediate necessary to establish an equilibrium between the starting hydroxy ketone **1** and the desired diosphenol **6** is the enolate anion **5** (or the related dianion formed by removal of the remaining oxygen-bound hydrogen). Certainly, the most stable anionic species in this equilibrium is that related to the enolic α-diketone structure **6**, and, therefore, the practical result of a base-catalyzed enolization of the unsaturated hydroxy ketone **1** should be its ultimate conversion into the diosphenol **6**. Functionally, this same diosphenol **6** is probably intermediate in the oxidative cleavage of the saturated hydroxy ketone **2**, which results in the generation of the required diacid **3**. Thus the diosphenol **6** could serve the ultimate synthetic objective as well through a similar oxidation process.

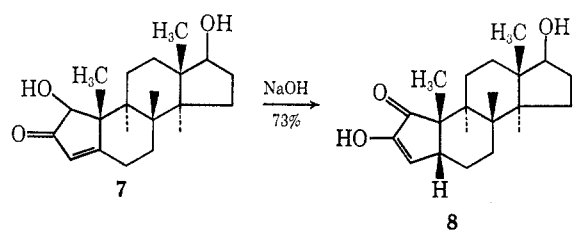


The stereochemical outcome of such a transformation is, of course, crucial if the generated diosphenol is to serve the proposed synthetic use. Only the *cis*-fused isomer is of value in the synthesis of the resin acid derivatives related to deoxypodocarpic acid (**4**). In view of the enolizing conditions suggested for the reaction, it is reasonable to presume that the thermodynamically more stable ring fusion will pertain. Inasmuch as the five-membered ring contains three trigonal carbon atoms and is nearly planar, the *cis* fusion of this ring to the six-membered ring would appear to possess less strain than the *trans* fusion. Inspection of the Dreiding molecular models of both of these possibilities appears to corroborate this conclusion.

The foregoing analysis appeared substantial enough to warrant investigation of the effect of strong base on the hydroxy ketone **1**. When this material was treated with 2 equiv of potassium *t*-butoxide in *t*-butyl alcohol at room temperature and in a nitrogen atmosphere,[6] the solution rapidly developed a deep red coloration which remained until the reaction was quenched with hydrochloric acid after 1 hr. The crystalline product isolated from this treatment in 49% yield was adjudged to be the expected diosphenol **6** on the basis of its chemical and spectral properties. The enolic character of this new substance was demonstrated by its solubility in aqueous base and the purple coloration that it imparted to an aqueous alcoholic ferric chloride solution. The ultraviolet spectrum [$\lambda_{max}^{CH_3OH}$ 262 mμ (ϵ 9040)] was consistent with that expected of an enolic α diketone, and the proton magnetic resonance spectrum showed signals at δ 2.85 (doublet, J = 3 Hz) and 5.65 ppm (doublet, J = 3 Hz) which could be expected to result from the resonances of the C-3a methyne and the C-3 vinylic protons.[7] After further experimentation it was found that this diosphenol could be obtained in essentially quantitative yield when the base-catalyzed rearrangement was carried out at 45° for 1 hr instead of at room temperature. An aqueous methanolic sodium hydroxide medium was also as satisfactory if the solvents were first completely degassed to remove oxygen[6] and the reaction mixture was heated at reflux for 30 min.

As satisfying as these results were, further use of this diosphenol in the synthetic scheme was not possible. Mild oxidative degradation with basic hydrogen peroxide led to a diacid that was *not* identical with the diacid **3**.[5] Cyclization and hydrogenolysis of this new diacid under the same conditions employed for the conversion of the diacid **3** into the tricyclic acid **4** produced a *new* tricyclic acid.[5] The lack of correspondence between the products from the two synthetic schemes cast doubt on our rationalization of the outcome of the rearrangement reaction, and subsequent synthetic efforts were concentrated on the development[5] of the catalytic hydrogenation approach recently reported.[4]

In the interim, the work of Yoshida and Kubota[8] in the A-nor steroid series appeared, wherein a closely analogous rearrangement of the unsaturated hydroxy ketone **7** resulted in the diosphenol **8**. This work not



only fully substantiated the feasibility of the gross functional-group transformations expected, but also supported the contention that the desired *cis* fusion between the five- and six-membered rings should result. It thus became of interest to define the course of the rearrangement of the hydroxy ketone **1** and to determine more exactly the structure of the diosphenol that was generated.

Our first concern was for the stereochemistry at the ring fusion, as the functional character of the diosphenol appeared well established by the chemical and spectral properties cited above. While a *trans* ring fusion

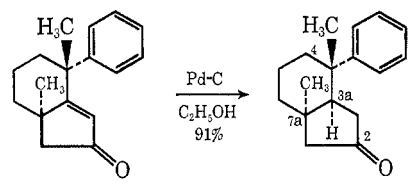
(5) F. Giarrusso, Ph.D. Thesis, University of Michigan, 1966.

(6) An inert atmosphere was found to be exceedingly important, as even small amounts of oxygen led to oxidative cleavage of the hydroxy ketone **1** and resulted in the corresponding unsaturated anhydride.[4]

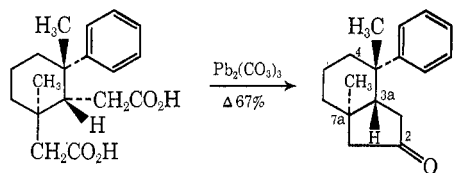
(7) Similar assignments were made for the pmr spectra of the cucurbitacins: C. R. Noller, A. Melera, M. Gut, J. N. Shoolery, and L. F. Johnson, *Tetrahedron Lett.*, 15 (1960); D. Lavie, Y. Shvo, O. R. Gottlieb, and E. Glotter, *J. Org. Chem.*, **27**, 4546 (1962).

(8) K. Yoshida and T. Kubota, *Tetrahedron*, **21**, 759 (1965).

seemed improbable in the face of the Japanese workers' report[8] as well as the analysis of molecular models, the lack of the identity of subsequent transformation products of the diosphenol with those from the saturated hydroxy ketone **2** might arise as a result of this stereochemical variation. This point seemed reasonably amenable to scrutiny, for conversion of the diosphenol into a 4,7a-dimethyl-4-phenylhexahydro-2-indanone would make possible a direct comparison of the degradation product with substances of known stereochemistry that were available from earlier work.[4]



9 **10**



11 **12**

In the C-7aα-methyl series, both of the C-3a epimers of this hexahydro-2-indanone structure—the *cis*-fused (3aα) ketone **10** and the *trans*-fused (3aβ) ketone **12**—had been prepared[4] as indicated above and were thus available for comparison. Firm stereochemical assignments were possible in this series, as the diacid **11** had previously been successfully interrelated[9] with known derivatives of naturally occurring resin acids. Inasmuch as one of these two ketones was the logical result of the degradation of the diosphenol, no initial attempt was made to provide comparison samples of the C-7aβ-methyl epimeric ketones.

The degradation of the diosphenol—represented by structure **13** for visual convenience—to the hexahydro-2-indanone ketone **16** was accomplished as outlined in Scheme I.

After the enolic carbonyl function in the diosphenol **13** was protected as the methyl ether, the C-1 carbonyl was reduced with lithium aluminum hydride. Acid hydrolysis of the resulting hydroxy enol ether then afforded the saturated hydroxy ketone **15** in 95% overall yield. A spectral and melting-point comparison of this hydroxy ketone **15** and its counterpart **2** prepared earlier[4] by hydrogenation of the unsaturated hydroxy ketone **1** revealed their lack of identity and established that the previsously encountered[5] synthetic problems were indeed inherent in the structure of diosphenol **13**.

The conversion of the hydroxy ketone **15** into the desired hexahydro-2-indanone **16** was accomplished in 50% yield by lithium–ammonia reduction of the derived keto acetate and then oxidation of the resulting alcohol. It was a surprise to find that the crystalline ketone **16** was not identical with *either* of the hexahydro-2-indanones **10** or **12** in the C-7aα-methyl series (see Table I).

The nmr spectral comparison between the two C-7aα-methyl ketones **10** and **12** and the ketone **16** is informative. In the spectra of both ketones **10** and **12**, the

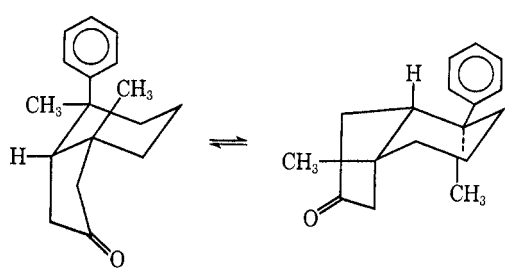
(9) R. E. Ireland and R. G. Kierstead, *J. Org. Chem.*, **31**, 2543 (1966).

TABLE I
PHYSICAL AND SPECTRAL PROPERTIES OF ISOMERIC 4,7a-DIMETHYL-4-PHENYLHEXAHYDRO-2-INDANONES

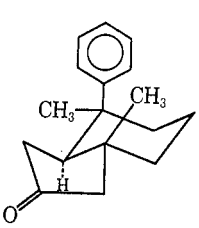
	cis-4β,7aα-$(CH_3)_2$ (**10**)	*trans*-4β,7aα-$(CH_3)_2$ (**12**)
Mp, °C	100.5–101.0	Oil
Semicarbazone mp, °C	241–243	221–223
Ir ($CHCl_3$), cm^{-1}	1738	1735
Nmr (CCl_4), δ		
C-4 methyl	1.06	1.28
C-8 methyl	0.53	0.33
	cis-4β,7aβ-$(CH_3)_2$ (**22**)	*trans*-4β,7aβ-$(CH_3)_2$ (**24**)
Mp, °C	100.5–101.0	81.5–82.5
Semicarbazone mp, °C	220.5–222.0	203.5–205
Ir ($CHCl_3$), cm^{-1}	1738	1735
Nmr (CCl_4), δ		
C-4 methyl	1.40	1.39
C-8 methyl	1.33	1.09

C-7aα-methyl signal occurs at significantly higher field (δ 0.33–0.53 ppm) than does the signal which is due to the same methyl group in the ketone **16** (δ 1.33 ppm). The shielding of the C-7aα-methyl group of the ketones **10** and **12** can be reasonably attributed to the C-4 phenyl group, which in both compounds is situated so as to include the C-7aα-methyl group in the shielding cone of the ring.

As can be seen in the conformational representations **10a** and **12a**, the C-4-phenyl group bears a 1,3-diaxial relationship[10] to the C-7aα-methyl group in the *trans* ketone **12a** and in one of the two conformations of the *cis* ketone **10a**. This interaction would adequately



10a



12a

explain the occurrence of the C-7aα-methyl resonance at such high field. An analogous treatment was used by Wenkert and coworkers[11] to rationalize the similar phenomenon observed in tricyclic resin acid derivatives. This interpretation also makes it apparent that the ketone **16** *cannot* have a similar *cis* relationship between the C-4-phenyl and C-7a-methyl groups, for the C-7a-methyl resonance occurs significantly farther downfield (δ 1.33 ppm). Inasmuch as the phenyl and methyl groups of the ketone **16** *cannot* be *cis* to one another, the

(10) While there may be some distortion of the six-membered ring out of the chair conformation in the ketones **10** and **12** owing to this severe 1,3-diaxial phenyl–methyl interaction, the high-field shift of the methyl resonance and the structures of the related hydroxy ketones **1** and **18** and the diosphenol **19**, as determined by single-crystal X-ray analysis, argue against any significant modification of the conformations.

(11) E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *ibid.*, **30**, 713 (1965).

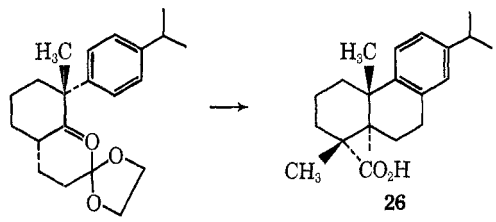
ketone **16** *cannot* be a member of the C-7aα-methyl series.

One interpretation that will satisfy the above spectral requirements, as well as the nonidentity of the ketone **16** with either ketone **10** or **12**, is the assumption that the ketone **10**—and hence the diosphenol **13** as well—belongs to the 7aβ-methyl series. If such were the case, the C-7a methyl would bear a 1,3-diaxial relationship to the C-4 methyl and would quite logically give rise to a signal in the observed range in the nmr spectrum. Of course, neither the *cis*- nor the *trans*- C-7aβ-methyl hexahydro-2-indanones would be identical with the ketones **10** or **12**.

While it appeared unlikely at the outset that epimerization at the quaternary C-7a carbon atom was probable during the generation of the diosphenol **13** from the hydroxy ketone **1**, the foregoing circumstances made the outcome of such a process an attractive solution to the structural problem at hand.

In order to test this possibility, it was necessary to prepare samples of the authentic *cis*-7aβ-methyl ketone **22** and *trans*-7aβ-methyl ketone **24**. The *trans* ketone **24** was readily obtained from the diacid **23**—the structure of which had been firmly established earlier[9]—by pyrolysis of the lead salt (Scheme II). As expected, this ketone **24** was also *not* identical with the ketone **16** from the diosphenol **13**.

The remaining hexahydro-2-indanone in the series—the *cis*-7aβ-methyl ketone **22**—was more difficult to prepare. As none of the previous work in this laboratory had led to intermediates that might easily be converted into the ketone **22**, a complete synthetic scheme was necessary. The essence of such a scheme is provided by the approach used earlier[9] for the synthesis of dehydroabietic acid (**26**) from the ketone ketal **25**. The



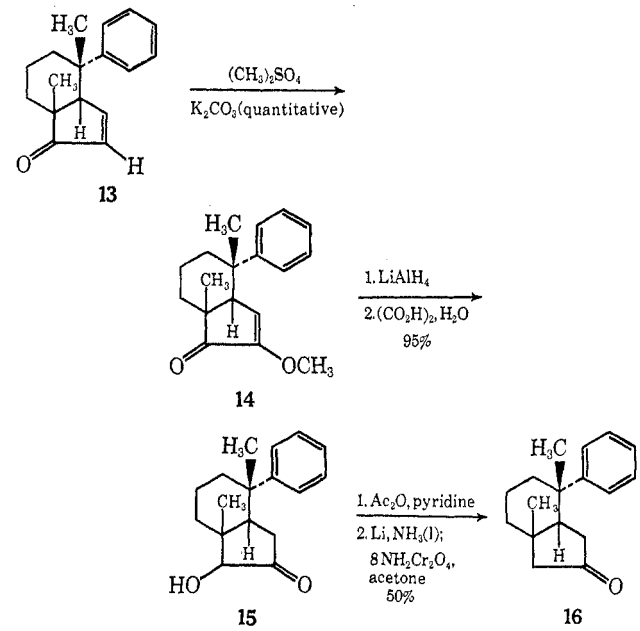
25 **26**

required *cis* relationship between the two methyl groups resulted when the ketone ketal **25** was methylated with methyl iodide in the presence of potassium *t*-butoxide. Application of the same method for the control of the stereochemical relationship of the two methyl groups to the synthesis at hand required the methallylated ketone **19**. This ketone **19** was prepared in 62% overall yield from 2-methyl-2-phenylcyclohexanone (**17**) through the Claisen rearrangement[12] of the methallyloxymethylene derivative **18**. Methylation of the ketone **19** was executed in virtually quantitative yield, but the product proved to be a mixture of isomeric methylated ketones. Analysis of the nmr spectrum of the crude product indicated that both the *cis*-dimethyl ketone **20** and the *trans*-dimethyl ketone **27** were present in a ratio of 5:1. This result was also confirmed by gas–liquid chromatography. While quantitative separation of these

(12) L. Claisen, *Ber. Deut. Chem. Ges.*, **45**, 3157 (1912); A. W. Burgstahler and I. C. Nordin, *J. Amer. Chem. Soc.*, **83**, 198 (1961).

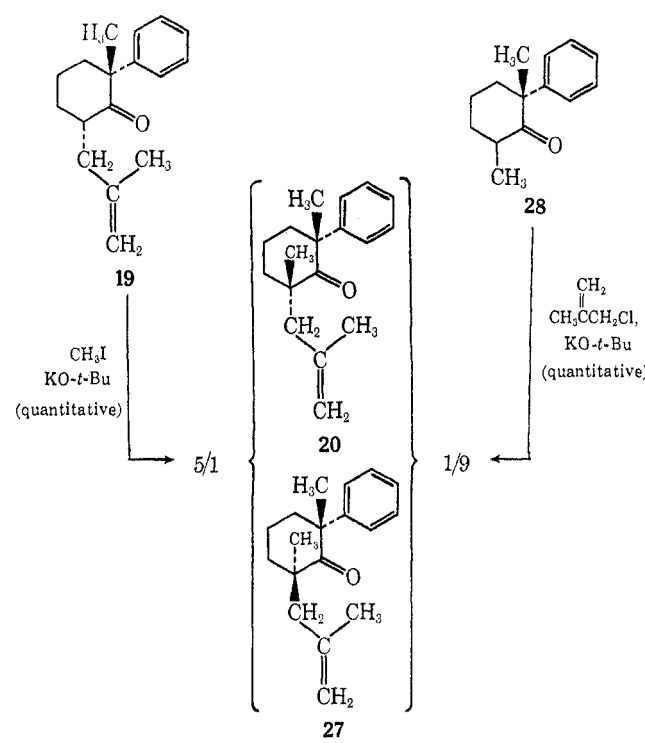
SCHEME I

DEGRADATION OF DIOSPHENOL **13**



13 **14** **15** **16**

isomers on a preparative scale was not possible, the 94% isomerically pure *cis*-dimethyl ketone **20** was obtained in a 72% yield by column chromatography on silicic acid. The early fractions of this chromatographic separation were rich (9:1 by nmr analysis) in the *trans*-dimethyl ketone **27** and were used to confirm

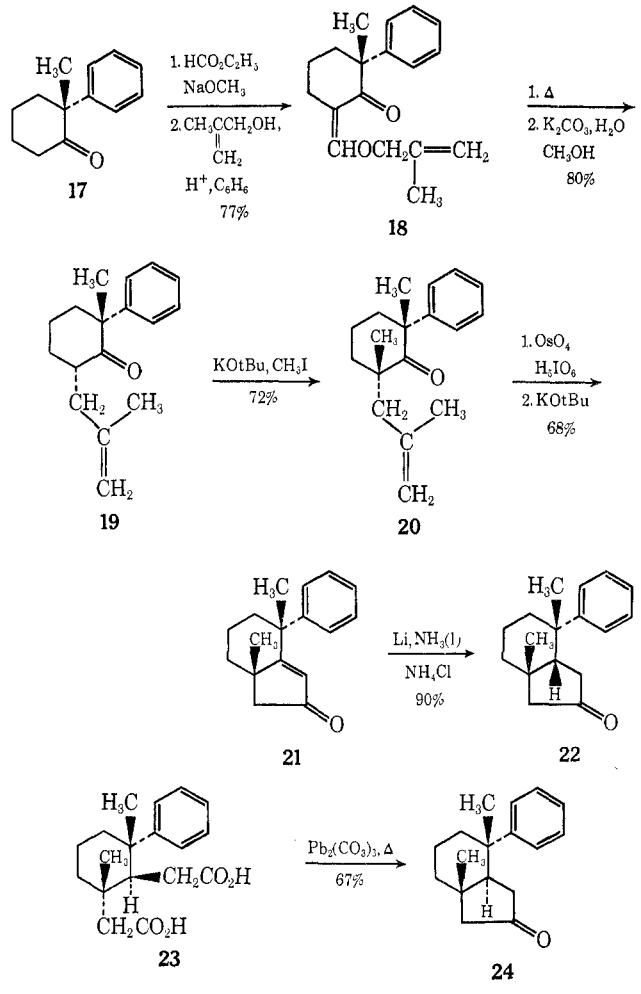


its identity. Thus osmium tetroxide–periodate oxidation[9,13] of these fractions afforded a 63% yield of the *trans*-dimethyl diketone, which was shown to be identical with the material prepared earlier[4] and was converted into deoxypodocarpic acid (**4**). Similar oxidation of the 94% pure *cis*-dimethyl ketone **20** afforded the corresponding crystalline *cis*-dimethyl diketone,

(13) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

SCHEME II

SYNTHESIS OF *cis*- AND *trans*-7aβ-METHYL KETONES **22** AND **24**



which, on cyclization in the presence of potassium *t*-butoxide, afforded the expected unsaturated ketone **21** in 68% overall yield.

Inasmuch as the methylation of the ketone **19** had resulted in a mixture of isomeric methylated ketones **20** and **27**, the previously reported[4] methallylation of 2,6-dimethyl-2-phenylcyclohexanone (**28**) was reinvestigated. In the earlier work,[4] the *trans*-dimethyl ketone **27** had resulted from this reaction in 84% yield, and there was no evidence found for the formation of the isomeric *cis*-dimethyl ketone **20**. However, on careful gas–liquid chromatographic and nmr spectral analyses of the crude methallylation product, both *cis* (**20**) and *trans* (**27**) ketones were, indeed, found to be present in a ratio of 1:9. The lower concentration of the *cis*-dimethyl ketone **20** in this mixture made the isolation of the pure *trans*-dimethyl ketone **27** in high yield an easier task. When large-scale reactions are carried out, the *cis*-dimethyl ketone **20** is easily missed on distillation.

While these alkylation reactions do not form exclusively the axially alkylated product, the highly stereoselective axial attack observed (regardless of the entering alkyl residue) is in contrast to the results found by House and coworkers[14] in the 4-*t*-butylcyclohexanone system. These workers found that the alkylation of this system was not stereoselective and concluded that there is no inherent factor which strongly favors the alkylation of a cyclohexanone enolate anion from that direction which will form a product with an axial alkyl substituent. That the situation that pertains in the 4-monosubstituted cyclohexanone enolate anion is *not* the generally applicable one is pointed up by the case at hand.[15] Exactly how the structural differences between these two systems affect the stereochemical outcome of the alkylation reactions is not clear and will require further investigation.

The ultimate objective of the present synthetic effort—the *cis*-7aβ-methyl ketone **22**—was finally obtained by lithium–ammonia reduction of the unsaturated ketone **21**. In contrast to the lithium–ammonia reduction of the 7aα-methyl unsaturated ketone **9**,[4] which led to a 2:3 mixture of the *cis*- and *trans*-7aα-methyl ketones **10** and **12**, the present reduction afforded only the *cis*-7aβ-methyl ketone **22** in 90% yield. Again, the different steric characteristics of the compounds in the two series is manifested in the outcome of the reactions used. All four of the isomeric 4,7a-dimethyl-4-phenylhexahydro-2-indanones have now been prepared, and their pertinent physical and spectral properties are recorded in Table I.

The *cis*-7aβ-methyl ketone **22** was shown to be identical with the ketone **16** by spectral, as well as mixture melting point, determinations. While the identity of these two ketones settles the problem of the structure of the degradation ketone **16**, the generation of a reasonable rationale for the formation of the C-7a epimer from the starting unsaturated hydroxy ketone **1** loomed as a further task.

Certainly, since the saturated ketone **16** is a member of the 7aβ-methyl series, the diosphenol **13**, from whence it was derived, must also be of the 7aβ-methyl series. There is no valid reason to expect epimerization of the C-7a position during this degradation process. Therefore, epimerization must have taken place during the base-catalyzed rearrangement of the hydroxy ketone **1**, and the resulting product is the diosphenol **31** (Scheme III).

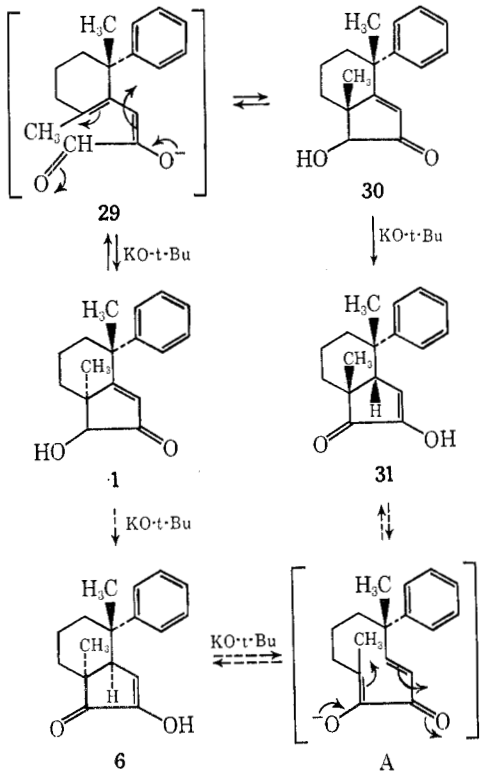
The epimerization of a quaternary carbon, such as the C-7a carbon of the unsaturated hydroxy ketone **1**, is not a general phenomenon and was *not* observed[8] in the A-nor steroid series, which bears a close similarity to the case at hand. However, there are at least two reasonable pathways that might serve to rationalize the transformation. The first devolves from the fact that the unsaturated hydroxy ketone **1** is a vinylogous β-hydroxy ketone and may undergoe a reverse aldol-type condensation in a basic medium. Such a cleavage reaction will formally generate the enolate of the α-keto aldehyde **29** and thereby destroy the asymmetry about the C-7a position of the ring system. Recyclization of this enolate **29** can then lead to either the starting unsaturated hydroxy ketone structure **1** or the epimeric unsaturated hydroxy ketone structure **30**. If the ketone **30** is more stable than the starting ketone **1** and subsequent rearrangement to the diosphenol structure **31** is fast and (under these reaction conditions) irreversible, then this process would explain the observed results of the reaction.

Another plausible explanation for the epimerization is the postulate that there is a direct equilibrium possible

(14) H. O. House, B. A. Tefertiller, and H. O. Olmstead, *J. Org. Chem.*, **33**, 935 (1968).

(15) See also G. Stork and J. E. McMurry, *J. Amer. Chem. Soc.*, **89**, 5464 (1967).

SCHEME III



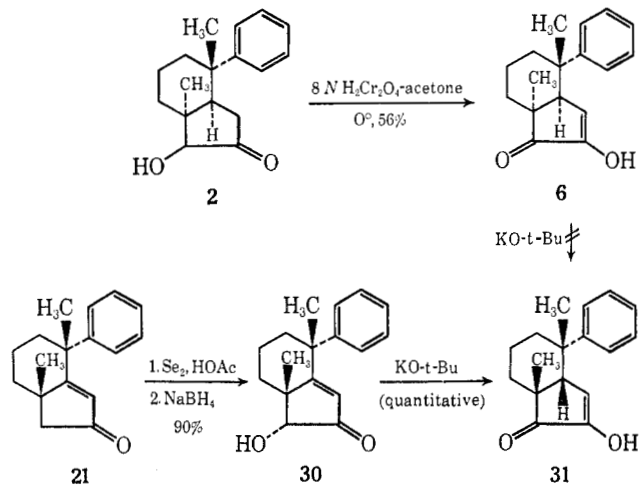
between the expected diosphenol **6** and the epimeric diosphenol structure **31**. The intermediate state between these two diosphenol structures that would account for the racemization of the C-7a position is the nine-membered-ring enolate A. Thus, should the initially formed diosphenol **6** be less stable than its epimeric counterpart **31** and an equilibrium between the two structures be possible through the enolate A, the result of the base-catalyzed rearrangement of the unsaturated hydroxy ketone **1** would be the generation of the observed diosphenol **31**. Certain phases of these mechanistic postulates were amenable to test with derivatives of compounds that were on hand.

If the explanation for the epimerization of the C-7a position was the instability of the initially generated diosphenol **6** to the basic reaction conditions, this could readily be tested by the independent synthesis of this isomer and then the subjection of it to the same reaction conditions. The synthesis of the required diosphenol **6** was accomplished by the oxidation of the saturated hydroxy ketone **2** with Jones reagent[16] at 0° (Scheme IV). As described earlier,[4] more vigorous oxidation of this same ketone **2** affords the diacid **3**, and it was not surprising to find that strict attention to experimental detail was necessary in order to realize even a 56% yield of the diosphenol **6**. Indeed, even at 0° with exactly 1 equiv of oxidant, a 14% yield of the diacid **3** was also obtained; at −10° the oxidation was ineffective and mainly starting ketone **2** was recovered; and at 10° the process afforded the diacid **3** and its anhydride as the sole reaction products.

The new diosphenol **6** had properties similar to those of its counterpart **31**. It imparted a purple coloration to aqueous alcoholic ferric chloride solution, formed an

(16) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Wiedon, *J. Chem. Soc.*, 39 (1946); see also C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

SCHEME IV



O-methyl ether with dimethyl sulfate in the presence of potassium carbonate, and its ultraviolet spectrum showed a maximum at 259 mμ (ε 9620).[8] Both the infrared and nmr spectra were equally consistent with the assigned structure. After treatment with potassium *t*-butoxide in *t*-butyl alcohol under the same conditions that cause rearrangement of the unsaturated hydroxy ketone **1**, the diosphenol **6** was quantitatively recovered unchanged, and no evidence for the presence of the isomeric diosphenol **31** could be found. Thus the observed epimerization of the C-7a carbon cannot be due to the rearrangement of the initially formed diosphenol **6**.

In order to test the alternate mechanism above, the 7aβ-methyl epimer **30** was synthesized from the recently available unsaturated ketone **21**. The procedures used for this preparation mimic exactly those used earlier[4] for the preparation of the unsaturated hydroxy ketone **1**, and the results were equally as satisfying. When the new unsaturated hydroxy ketone **30** was treated with either potassium *t*-butoxide in *t*-butyl alcohol or aqueous alcoholic sodium hydroxide under the same conditions employed earlier for the rearrangement of its epimer **1**, the diosphenol **31** resulted in virtually quantitative yield. In fact, crude rate measurements based on the gas–liquid chromatographic analysis of aliquots of the potassium *t*-butoxide reaction indicated that the diosphenol **31** was generated from the unsaturated hydroxy ketone **30** about five times faster than from the epimeric unsaturated hydroxy ketone **1**. While the rate measurements were not pursued in detail, the facile rearrangement of the unsaturated hydroxy ketone **30** does make a satisfying contribution to the postulated reverse aldol concept of the rearrangement reaction.

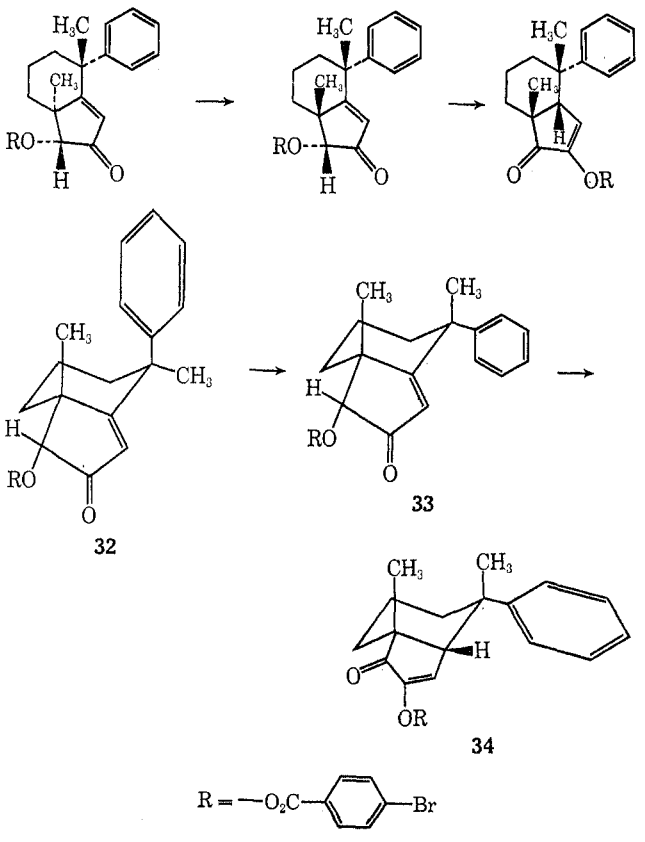
The driving force of the epimerization reaction was the next concern. The obvious difference between the unsaturated hydroxy ketones **1** and **30** under investigation here and the A-norandrostenone **7** examined by the Japanese workers[8] is the presence of the two geminal substituents in a 1,3 relationship to the angular methyl group in the former series. The steric strain that is associated with a 1,3-diaxial interaction between the axial C-7a-methyl group and the axial one of the C-4 substituents in the hexahydro-2-indanone series might provide the energy that is lacking in the A-nor steroid series. This steric congestion is not so great that the unsaturated hydroxy ketones **1** and **30** simply undergo

the reverse aldol-type cleavage and, without recyclization, generate products related to the enolate **29**. The steric strain is, however, sufficiently great in the case of the unsaturated hydroxy ketone **1** (1,3-diaxial methyl–phenyl interaction) that the cleavage–recyclization sequence through the enolate **29** takes precedence to the exclusion of the rearrangement to the diosphenol **6**. The strain must certainly be less in the case of the unsaturated hydroxy ketone **30** (1,3-diaxial methyl–methyl interaction), since formation of the diosphenol **31** is a facile process. An estimation of the strain energies involved in these two systems might be obtained by a study of the equilibrium between the two unsaturated hydroxy ketones **1** and **30**. However, whether there is a measurable equilibrium between these ketones was not possible to determine, as the unique formation of the diosphenol **31** from both ketones precluded meaningful analysis.

An alternative approach to the intimate details of these structures was found in the single-crystal X-ray analysis of the derived *p*-bromobenzoates (Scheme V).

SCHEME V

GRAPHIC REPRESENTATION OF REARRANGEMENT IN LIGHT OF X-RAY RESULTS

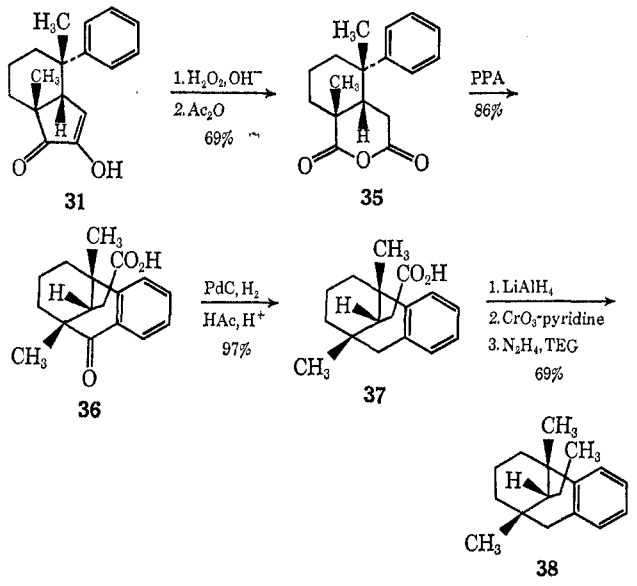


Surprisingly, the crystal structures of both of these derivatives **32** and **33** of the unsaturated hydroxy ketones **1** and **30** reveal little or no distortion of the six-membered ring away from the chair conformation as a result of the 1,3-diaxial interactions present. The nonbonded distance from the carbon atom of the methyl group and the closest carbon atom of the benzene ring in the structure **32** is 3.35 Å. In the structure **33**, the corresponding carbon–carbon distance between the two 1,3-diaxial methyl groups is a similar 3.33 Å. In view of the trigonal character of the benzene-ring carbon atoms, there might, then, seem to be less steric congestion present in the unsaturated hydroxy ketone **1** than in its epimer **30**. However, these nonbonded distances refer to the static crystalline state in which the plane of the benzene ring in structure **32** is "frozen" such that it is spatially as far removed from the methyl group as possible. Freer rotation of the phenyl group that is possible in the solution state, which is less ordered than the crystalline state, would impose a more serious steric interaction in the case of the unsaturated hydroxy ketone **1** than is indicated by these nonbonded crystalline interactions. Such would not be expected in the case of the epimer **30**, where the two methyl groups are spatially symmetrical, and the crystalline representation should closely approximate that in solution. A possible driving force, then, for the initial retroaldolization of the unsaturated hydroxy ketone **1** may indeed be the relief of the steric strain imposed on the molecule by the 1,3-diaxial phenyl–methyl interaction.

With the definition of the structure of the diosphenol **31** complete, concern was shifted to its oxidative cleavage to a diacid, and the subsequent cyclization of the related anhydride **35** that formed tricyclic material (see Scheme VI). This overall transformation was initially thought to generate an isomer of demethoxypodocarpic acid or deisopropyldehydroabietic acid in concert with previous experience.[4,9] However, the lack of similarity between the observed physical and spectral properties of the resulting tricyclic acid **37** and those recorded[4,9,17] for the isomeric, tricyclic resin-type acids shattered this expectation. Inasmuch as all of the possible stereoisomers of these 1,4a-dimethyloctahydrophenanthrene-1-carboxylic acids are known,[17] the acid **37** produced by this sequence must be a structural variant.

SCHEME VI

SYNTHESIS OF *syn*-9-ETHYL-1,5-DIMETHYL-2,3-BENZOBICYCLO[3.3.1]NONANE (**38**)

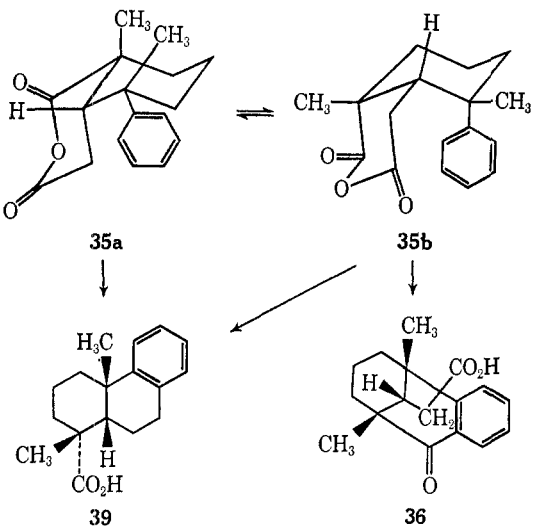


Consideration of the modes of cyclization available to the anhydride **35** led to a plausible structural variant for the acid **37**. By virtue of the *cis* ring fusion in the

(17) V. R. Ghatak, D. K. Datta, and S. C. Ray, *J. Amer. Chem. Soc.*, **82**, 1728 (1960).

anhydride **35**, two conformations are possible. In one, **35a**, the phenyl group is equatorial and, if the cyclization transition state approached this arrangement, the previously expected 5-isodeisopropyldehydroabietic acid (**39**) should result (Scheme VII). In the other,

SCHEME VII



35b, the phenyl group is axial, and cyclization through a transition state that resembled this conformation could lead to the acid **39** as well as the bicyclo[3.3.1]nonane structure **36** through acylation of the ring by the tertiary axial carboxyl group. This latter structure offered an explanation for the occurrence of a new tricyclic acid **37** formed after hydrogenolysis of the benzylic ketone group of the keto acid **36**.

Direct evidence for the occurrence of the bicyclic structure was obtained through nmr spectroscopy and chemical degradation of the carboxyl group to a methyl group. In the nmr spectrum of the keto acid **36** there appeared a doublet at δ 2.25 ppm (J = 1.5 Hz) that integrated for two protons. Such a signal is best assigned to the methylene group adjacent to the carboxyl group and shielded by the benzene ring. The alternate assignment of this signal to the C-6-methylene group of the 5-isodeisopropyldehydroabietic acid structure (**39**) is less satisfactory, for the position of the resonance which is due to such a methylene group is known[4,9,11] to occur at *ca.* δ 3.00 ppm.

Reduction of the acid **36** over palladium on carbon in a hydrogen atmosphere and then with lithium aluminum hydride afforded an alcohol, which on oxidation with chromic oxide–dipyridine complex[18] was transformed into the corresponding aldehyde. The nmr spectrum of this aldehyde substantiated the presence of an acetaldehyde side chain that would result from the acid **36** in contrast with the tertiary carboxaldehyde expected of a derivative of the acid **39**. The signal which is due to the aldehyde proton occurred as a triplet (J = 1 Hz) at δ 9.83 ppm and can only be ascribed to an aldehyde function joined to a methylene group.

Final confirmation of these conclusions was obtained on Wolff–Kishner reduction of the bicyclic aldehyde. The 100-MHz nmr spectrum of the hydrocarbon that resulted from this reaction contains signals which are due to only two quaternary methyl groups, as expected for the bicyclo[3.3.1]nonane structure **38** but not for the hydrocarbon derived from the keto acid **39**. As well, the signal which is due to the benzylic methylene group appeared as an AB quartet centered at δ 2.63 ppm (J_{AB} = 9 Hz) in agreement with the arrangement present in the hydrocarbon **38**.

The reason for the exclusive formation of the bicyclo[3.3.1]nonane structure **36** on cyclization of the anhydride **35** in polyphosphoric acid is not clear, and indeed some preliminary evidence[19] indicates that the conditions and catalyst are important to the outcome. Further investigation of the reaction sequence is in progress.

Experimental Section[20]

4β,7a$\alpha\beta$-Dimethyl-2-hydroxy-4α-phenyl-3a$\alpha\beta$,4,5,6,7a-hexahydroindone (31). A. Potassium *t*-Butoxide Rearrangement of the Unsaturated Hydroxy Ketone 1.—To a stirred solution of 1.31 g (11.7 mmol) of potassium *t*-butoxide in 60 ml of dry *t*-butyl alcohol contained in a nitrogen-protected flame-dried flask was added dropwise a solution of 1.50 g (5.85 mmol) of unsaturated hydroxyl ketone 1[4] in 60 ml of dry *t*-butyl alcohol. The blood-red solution was stirred for an additional 1 hr at *ca.* 45°, acidified with iced, concentrated hydrochloric acid, and diluted with 100 ml of water. The mixture was extracted three times with 100-ml portions of an ether–benzene solution (4:1). The combined organic layers were washed three times with 40-ml portions of water and twice with 25-ml portions of a saturated salt solution and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 1.50 g of solid diosphenol **31** [glpc (285°) 95% with a retention time of 25 sec]. Chromatography on silicic acid afforded 1.37 g (91%) of diosphenol **31**, mp 161–163°, on elution with 3 l. of a 10% ether–petroleum ether solution. The analytical sample was obtained after two crystallizations of a portion of this material from ether–petroleum ether: mp 162–164°; ir ($CHCl_3$) 3500, 3350 (OH), 1700, and 1650 cm^{-1} (enolic dione); uv max (MeOH) 262 mμ (ϵ 9040); nmr ($CDCl_3$) δ 1.32 (s, 3, C-7aβ CH_3), 1.48 (s, 3, C-4β CH_3), 2.85 (d, 1, J = 3 Hz, C-3aβ H), 5.65 (d, 1, J = 3 Hz, C-3 H), and 6.22 (br s, 1, OH).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.61; H, 7.84.

The *p*-bromobenzoate **32** was prepared for single-crystal X-ray analysis from 600 mg (2.31 mmol) of the unsaturated hydroxy ketone 1[4] by treatment with 618 mg (2.81 mmol) of *p*-bromobenzoyl chloride in 20 ml of dry pyridine. After the mixture was stirred at room temperature under a nitrogen atmosphere for 18 hr, most of the pyridine was removed in a nitrogen jet at slightly reduced pressure, and the ester was isolated by ether extraction. The crude product (1.02 g) was purified by thick layer chromatography on two silicic acid plates (0.2 × 20 × 20 cm) developed in 45% ether–petroleum ether. The major band (R_f 0.60) on each plate was eluted with ether, and the combined ether extracts were evaporated to dryness at reduced pressure. In this manner, there was obtained 712 mg (70%) of the ester **32**, mp 177–179°, that was eluted as a single peak after 340 sec at 303° on gas chromatography. Analytically pure material was prepared for the X-ray analysis after one crystallization from ether–methanol and a second crystallization from acetone–petroleum

(18) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

(19) P. S. Grand, Ph.D. Thesis, California Institute of Technology, 1968; see also R. Ghatak and J. Chakravarty, *Tetrahedron Lett.*, 2449 (1966).

(20) Melting points, unless otherwise noted, were taken on a Kofler hot stage and are uncorrected. Boiling points are also uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 237B infrared spectrometer, and ultraviolet spectra were recorded on a Cary Model 11M recording spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A-60A nuclear magnetic resonance spectrometer. All gas chromatographic analyses were taken on an F & M Model 810 gas chromatograph using a 6-ft silicone gum rubber (SE-30) column. The pressures of the gases employed during vapor phase chromatographic analysis follow: helium, 50 psi; hydrogen, 22 psi; and compressed air, 24 psi. Petroleum ether, unless otherwise noted, refers to the fraction boiling in the range of 30–60°. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and Elek Microanalytical Laboratories, Torrance, Calif.

ether: mp 177.5–179°; ir ($CHCl_3$) 1720, 1715 (C=O), 1592 (aromatics), and 1270 cm^{-1} (COC); uv max (MeOH) 246 mμ (ε 31,000); nmr ($CDCl_3$) δ 0.62 (s, 3, C-7aα CH_3), 1.44 (s, 3, C-4aβ CH_3), 5.37 (s, 1, C-1β H), 6.39 (s, 1, C-3 H), and 7.48, 7.52, 7.87, and 8.02 (A_2B_2 q, 4, *para*-substituted aromatics).

Anal. Calcd for $C_{24}H_{23}BrO_3$: C, 65.61; H, 5.28; Br, 18.19. Found: C, 65.66; H, 5.21; Br, 18.07.

The *p*-bromobenzoate **34**, mp 138–140°, was prepared in 90% yield for single-crystal X-ray analysis from 400 mg (1.56 mmol) of the diosphenol **31** and 1.26 g (4.5 mmol) of *p*-bromobenzoyl chloride in 20 ml of dry pyridine by exactly the same procedure described below for the formation of the corresponding derivative of the unsaturated hydroxy ketone **1**. Material of analytical purity for the X-ray analysis was obtained after one crystallization from acetone–petroleum ether: mp 139.5–140.5°; ir ($CHCl_3$) 1743, 1723 (C=O), 1643 (C=O), 1590 (aromatic), and 1262 cm^{-1} (COC); uv max (MeOH) 238 mμ (ε 34,900); nmr ($CDCl_3$) δ 1.42, 1.53 (two s, C-7aβ and C-4aβ CH_3), 3.02 (d, 1, J = 2.4 Hz, C-3aβ H), 6.48 (d, 1, J = 2.4 Hz, C-3 H), and 7.50, 7.64, 7.85, and 8.00 (A_2B_2 q, 4, *para*-substituted aromatics).

Anal. Calcd for $C_{24}H_{23}BrO_3$: C, 65.61; H, 5.28; Br, 18.19. Found: C, 65.69; H, 5.35; Br, 18.25.

Potassium *t*-Butoxide Rearrangement from Unsaturated Hydroxy Ketone 30.—To a stirred solution of 106 mg (0.934 mmol) of potassium *t*-butoxide in 6 ml of dry *t*-butyl alcohol contained in a nitrogen-protected, flame-dried flask was added dropwise a solution of 120 mg (0.467 mmol) of unsaturated hydroxy ketone **30** in 6 ml of *t*-butyl alcohol. The blood-red solution was stirred at room temperature. Four equal aliquots, removed and quenched with iced, concentrated hydrochloric acid, were worked up as described above. The progress of the reaction was followed by vapor phase chromatography—the retention time of diosphenol **31** was 40 sec and the retention time of hydroxy ketone **30** was 46 sec at an oven temperature of 275°. The diosphenol/hydroxy ketone ratio of the 30 mg of oil isolated after 10 min was 1:4. The ratio of the partially crystalline oil was 3.5:5.0 after 20 min, 4:1 after 43 min, and 6.5:1.0 after 80 min.

Sodium Hydroxide Rearrangement from Unsaturated Hydroxy Ketones 1 and 30.—To a solution of 2.4 ml of 40% aqueous sodium hydroxide solution in 10 ml of methanol in a nitrogen atmosphere, repeatedly degassed at 0.03 mm with the aid of liquid nitrogen, was added dropwise 400 mg (1.58 mmol) of hydroxy ketone **1** in 10 ml of methanol. The red-colored solution, which turned pale yellow in 15 min, was heated under reflux for 30 min, cooled, quenched with iced, concentrated hydrochloric acid, and then diluted with 100 ml of water. The mixture was extracted three times with 25-ml portions of ether–benzene (4:1), and the combined ethereal extracts were washed three times with 10-ml portions of a saturated brine solution and dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 400 mg of a white solid [glpc (285°) 100% with a retention time of 23 sec]. The infrared spectrum, melting point, and mixture melting point with diosphenol **31**, prepared from the potassium *t*-butoxide rearrangement described above, indicated that the isolated product and diosphenol **31** were identical.

By the same procedure as described above, 40 mg (0.16 mmol) of the unsaturated hydroxy ketone **30** underwent rearrangement to the diosphenol **31** in a degassed solution of 0.25 ml of 40% aqueous sodium hydroxide in 2 ml. of methyl alcohol. There resulted 40 mg of an off-white, crystalline solid which produced a single peak on gas chromatographic analysis at 270° with a retention time of 33 sec. The infrared spectrum, melting point, and mixture melting point with authentic diosphenol **31** indicated that the isolated product was identical with diosphenol **31**.

4β,7aβ-Dimethyl-2-methoxy-4α-phenyl-3aβ,4,5,6,7,7a-hexahydroindone (14).—A stirred mixture of 1.40 g (5.46 mmol) of diosphenol **31**, 5.96 ml (0.06 mol) of dimethyl sulfate, 19.95 g (0.14 mol) of anhydrous potassium carbonate, and 100 ml of anhydrous acetone were heated under reflux in a nitrogen atmosphere for 22 hr. The two-phase system was cooled, concentrated, and diluted with 400 ml of water. After cooling for 2 hr in the refrigerator, the precipitated pale yellow solid that separated was collected by filtration, washed four times with 20-ml portions of water, and heated at 56° (0.1 mm) until a constant weight of 1.470 g, mp 109–111° [100%, glpc (285°) a single component a with retention time of 28 sec] was maintained. The analytical sample, prepared by two recrystallizations of a portion of this material from ether–petroleum ether (bp 60–75°), consisted of thick, colorless platelets: mp 110.5–111.5°; ir ($CHCl_3$) 1710 (C=O), 1628 (conjugated C=C), 1250, and 1075 cm^{-1} (vinyl ether); uv max (MeOH) 257 mμ (ε 8400); nmr ($CDCl_3$) δ 1.34 (s, 3, C-7aβ CH_3), 1.50 (s, 3, C-4β CH_3), 2.97 (d, 1, J = 3 Hz, C-3aβ H), 3.46 (s, 3, OCH_3), and 5.38 (d, 1, J = 3 Hz, C-3 H).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.03; H, 8.28.

4β,7aβ-Dimethyl-1-hydroxy-4α-phenyl-*cis*-hexahydro-2-indanone (15).—To a suspension of 577 mg (15.2 mmol) of lithium aluminum hydride in 35 ml of dry tetrahydrofuran was added a solution of 412 mg (1.52 mmol) of the unsaturated ketone **14** in 35 ml of dry tetrahydrofuran, and the reaction was heated under reflux in a nitrogen atmosphere for 1.5 hr. After the solution was cooled, it was treated with 0.15 ml of 10% aqueous sodium hydroxide solution, and the precipitated salts were removed by filtration. The filtrate was diluted with 100 ml of ether, and the ethereal solution was washed three times with 15-ml portions of water and two times with 10-ml quantities of saturated salt solution, dried (Na_2SO_4), and evaporated to dryness at reduced pressure.

Without further purification, the residue (407 mg) was dissolved in 60 ml of acetone and treated with a solution of 1.00 g (11.1 mmol) of oxalic acid in 10 ml of water. The mixture was stirred at room temperature for 48 hr. The solution was then concentrated at reduced pressure to *ca.* 10 ml, and 100 ml of ether–benzene (9:1) was added. The system was washed three times with 10-ml portions of 10% aqueous sodium bicarbonate, twice with 10-ml quantities of water, and twice with 10-ml quantities of saturated salt solution and dried (Na_2SO_4). After removal of the solvent at reduced pressure, there remained 390 mg (95% overall yield) of an off-white solid [glpc (278°) a single component with a retention time of 26 sec], mp 120–124°. The analytical sample, obtained after four recrystallizations of a portion from ether–petroleum ether, consisted of small, colorless plates: mp 122–124°; ir ($CHCl_3$) 3550, 3450 (OH), and 1698 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.43, 1.46 (two s, 6, C-7aβ and C-4aβ CH_3), 3.15 (br 2, 1, OH), and 3.83 (s, 1, C-1 H).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.85; H, 8.44.

4β,7aβ-Dimethyl-1-acetoxy-4α-phenyl-*cis*-hexahydro-2-indanone.—A solution of 412 mg (1.60 mmol) of hydroxy ketone **15** in 8.6 ml (107 mmol) of anhydrous pyridine was treated with 10 ml (107 mmol) of acetic anhydride and stirred at room temperature for 15 hr. Most of the pyridine was removed with the aid of a nitrogen jet, and the residue was taken up in 100 ml of ether–benzene (4:1). The organic solution was washed successively with three 8-ml portions of 5 *N* sulfuric acid, three 10-ml portions of water, three 10-ml quantities of saturated aqueous sodium bicarbonate, two 10-ml portions of water, and two 10-ml portions of saturated salt solution, and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 446 mg of a pale yellow solid. Crystallization of this material from acetone–hexane afforded 319 mg of a white, crystalline solid, mp 172–176°. Chromatography of the mother liquor from this crystallization on 15 g of Florisil afforded an additional 55 mg (83% combined yield) of crystalline material, mp 174–177°, on elution with 350 ml of ether. The analytical sample was prepared by three additional recrystallizations of a portion of this material from acetone–hexane: mp 175–176.5°; ir ($CHCl_3$) 1763 (ester C=O), 1738 (C=O), and 1215 cm^{-1} (ester); nmr ($CDCl_3$) δ 1.38, 1.46 (two s, 6, C-7aβ and C-4β CH_3), 2.13 (s, 3, $OCOCH_3$), and 5.13 (s, 1, C-1 H).

Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.98; H, 8.13.

4β,7aβ-Dimethyl-4α-phenyl-*cis*-hexahydro-2-indanone (22).—A. From Degradation of the Diosphenol 31.—After 155 mg (22.3 g-atoms) of lithium wire had been allowed to dissolve in *ca.* 100 ml of liquid ammonia, a solution of 270 mg (1.100 mmol) of the above acetoxy ketone in 10 ml of tetrahydrofuran was added dropwise. The reaction mixture was stirred for 1 hr, and then sufficient solid ammonium chloride was added to discharge the blue color. The ammonia was allowed to evaporate, and the resulting solid, white residue was partitioned between 50 ml of water and 100 ml of ether–benzene (4:1). The ethereal solution was separated, washed with 10 ml of 3 *N* hydrochloric acid, three 10-ml portions of water, and two 10-ml portions of saturated salt solution, and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 232 mg of a yellow oil, the infrared spectrum of which indicated that partial reduction of ketone had also taken place. Consequently, an ice-cooled

mixture of the crude product in 5 ml of acetone was oxidized with 0.23 ml of 8 *N* aqueous chromic acid solution.[16] After the excess oxidant was destroyed with isopropyl alcohol, the product was isolated by ether extraction. Removal of the solvent at reduced pressure yielded 205 mg of an orange oil which crystallized on standing overnight. The crude product was purified by preparative thin layer chromatography on a silicic acid plate (0.2 × 20 × 20 cm). After development in 30% ether–petroleum ether, a band of R_f 0.60 that contained 129 mg (59%) of the crystalline ketone **22** [glpc (300°) a single component with a retention time of 24 sec] was isolated by ether elution. A sample of analytical purity, obtained as thin plates after two recrystallizations of a portion from hexane, melted at 100.5–101°. A mixture of this material and the isomeric ketone **10**, mp 100.5–101°, melted at 70–102°.

The ketone **22** afforded a semicarbazone, mp 220.5–222°, as a light yellow, crystalline solid after two recrystallizations from methyl alcohol–ethyl alcohol. A mixture of this material and the semicarbazone from the isomeric ketone **12**, mp 221–223°, melted at 203–243°.

B. By Reduction of the Unsaturated Ketone 21.—After 852 mg (12.2 g-atoms) of lithium wire had been allowed to dissolve in *ca.* 250 ml of liquid ammonia, a solution of 600 mg (2.50 mmol) of unsaturated ketone **21** in 90 ml of dry ether was added dropwise. The reaction mixture was stirred for 1 hr; sufficient solid ammonium chloride was then added to discharge the blue color, and the ammonia was allowed to evaporate at room temperature. The resulting solid residue was partitioned between 200 ml of ether–benzene (4:1) and 40 ml of water. The organic layer was separated, washed successively with three 20-ml portions of water and two 10-ml portions of a saturated salt solution, and dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 588 mg of an off-white solid. As a portion of the carbonyl had been reached, this mixture was dissolved in 15 ml of acetone and oxidized with 1.5 ml of 8 *N* aqueous chromic acid solution.[16] After the solution had been stirred in the cold for 10 min, isopropyl alcohol was added to destroy the excess oxidant and the product was isolated by ether extraction. Removal of the solvent at reduced pressure afforded 567 mg of an off-white, crystalline solid. Analysis by vapor phase chromatography of this crude product at 264° indicated the presence of 97% ketone **22** (retention time of 82 sec) and 3% unreacted unsaturated ketone **21** (retention time of 91 sec). Separation of the mixture was achieved by preparative thin layer chromatography on three silica gel plates (0.2 × 20 × 20 cm) developed with 40% ether–petroleum ether. Isolation of the bands with R_f 0.56 by ether extraction afforded 526 mg (90%) of the crystalline ketone **22**, mp 99–100° (capillary). The analytical sample, obtained as thin platelets after two crystallizations of a portion of this material from hexane, melted at 99.5–100° (capillary). The melting point of ketone **22**, obtained by degradation from diosphenol **31**, was also 99–100° (capillary) and the melting point of a mixture of the two samples was 99–100°. Both the infrared and nmr spectra of the two samples were identical. On thin layer chromatography on silicic acid, both samples exhibited the identical R_f value of 0.56 after development of the plates in 40% ether–petroleum ether; peak enhancement on gas chromatography also indicated that the two samples were identical. The melting range of a mixture of either sample of the ketone **22** and the isomeric ketone **24**, mp 81.5–82.5° (capillary), was 72–93°. The spectral properties of the ketone **22**, mp 99.5–100° (capillary), follow: ir ($CHCl_3$) 1738 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.33 and 1.40 (two s, 6, C-7aβ and C-4β CH_3).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.33; H, 9.21.

4β,7aβ-Dimethyl-4α-phenyl-*trans*-hexahydro-2-indanone (24).—An intimate mixture of 200 mg (0.658 mmol) of the diacid **23**[9] and 214 mg (0.798 mmol) of lead carbonate was heated at 285° (5 mm) for 2 hr. The distillate was taken up in 100 ml of ether–petroleum ether (4:1), and the solution was washed three times with 5-ml portions of 5% potassium hydroxide solution and two times with 5-ml portions of saturated salt solution and then dried (Na_2SO_4). Evaporation of the solvents at reduced pressure afforded 133 mg of an off-white, solid residue. The crude product was purified by thin layer chromatography on a silicic acid plate (0.2 × 20 × 20 cm) and developed in 40% ether–petroleum ether. Ether extraction of the major band (R_f 0.44) afforded 107 mg (67%) of the crystalline ketone **24**, mp 80–81°. The analytical sample was obtained as thick plates after two crystallizations of a portion of this material from hexane: mp 81.5–82.5° (capillary); ir ($CHCl_3$) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 1.09 (s, 3, C-7aβ CH_3) and 1.39 (s, 3, C-4β CH_3).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.25; H, 9.22.

The *cis* ketone **22** could not be resolved from this *trans* ketone **24** on vapor phase chromatography, but resolution was achieved on analytical, silicic acid, thin layer chromatography in 50% ether–petroleum ether. Under these conditions the *cis* ketone **22** had an R_f value of 0.49, while this *trans* ketone **24** had an R_f value of 0.51.

The semicarbazone of this *trans* ketone **24**, prepared in aqueous methanol in the presence of a catalytic amount of pyridine, melted at 203.5–205.5° after two crystallizations from methyl alcohol–ethyl alcohol.

Anal. Calcd for $C_{18}H_{25}N_3O$: C, 72.20; H, 8.42; N, 14.04. Found: C, 72.18; H, 8.56; N, 13.94.

6-Methyl-2-(2′-methylallyloxy)methylene-6-phenylcyclohexanone (18).—A solution of 21.6 g (0.1 mol) of 2-hydroxymethylene-6-methyl-6-phenylcyclohexanone,[9] 8.30 g (0.12 mol) of β-methallyl alcohol, and a trace of *p*-toluenesulfonic acid in 100 ml of benzene was heated at reflux in a nitrogen atmosphere under a Dean–Stark water separator for 10 hr, and then cooled and diluted with 100 ml of ether. The organic solution was washed four times with 10-ml portions of 10% potassium hydroxide solution and four times with 10-ml portions of saturated salt solution and dried (Na_2SO_4). Removal of the solvent at reduced pressure and chromatography of the crude product (25.0 g) on 300 g of silicic acid afforded 21.9 g (81%) of the desired allyl vinyl ether **18**, which was eluted with 15 l. of a 12.5% ether–petroleum ether. This material crystallized after standing at room temperature for several weeks, and the analytical sample, obtained as platelets, was prepared by two recrystallizations of a portion from ether–isopentane: mp 66.5–67.5°; ir (neat) 1675 (C=O), 1582 (C=C), and 1073 cm^{-1} (COC); uv max (MeOH) 278 mμ (ϵ 11,960); nmr ($CDCl_3$) δ 1.43 (s, 1, C-2 CH_3), 1.70 (m, 3, C-2′ CH_3), 4.37 (br s, 2, OCH_2), 4.96 (m, 2, C=CH_2), 7.41 (two d, 1, C=CHO).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.69; H, 8.24.

6-Methyl-2-(2′-methylallyl)-6-phenylcyclohexanone (19).—After 15.1 g (0.056 mol) of the allyl vinyl ether **18** were heated under nitrogen at 190° for 1 hr, the resulting yellow-orange oil was dissolved in 450 ml of methyl alcohol and treated with a solution of 30 g of potassium carbonate in 30 ml of water. The mixture was stirred for 9 hr at room temperature, and then concentrated to *ca.* 150 ml under reduced pressure. This mixture was diluted with 400 ml of water and then extracted with three 100-ml portions of ether–benzene (1:1). The combined ethereal layers were separated, washed three times with 25-ml portions of saturated salt solution, and then dried (Na_2SO_4). Removal of the solvent at reduced pressure and chromatography of the residue (13.5 g) on 200 g of silicic acid afforded 10.8 g (80%) of the ketone **19**, as a clear, colorless oil [glpc (237°) a single component with a retention time of 66 sec] on elution with 3 l. of 10% ether–petroleum ether. The analytical sample was obtained by evaporative distillation of a portion at 54–57° (0.05 mmol): ir (neat) 1718 (C=O), 1651, and 889 cm^{-1} (C=CH_2); nmr ($CDCl_3$) δ 1.23 (s, 3, C-2 CH_3), 1.56 (s, 3, C-2′ CH_3), 4.52, and 4.63 (m, 2, C=CH_2).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.35; H, 9.25.

2β,6β-Dimethyl-2α-(2′-methylallyl)-6α-phenylcyclohexanone (20).—To a suspension of 23.6 g (0.21 mol) of potassium *t*-butoxide in 700 ml of dry benzene under a nitrogen atmosphere was added with stirring at room temperature a solution of 10.0 g (0.041 mol) of methallyl ketone **19** in 300 ml of dry benzene. After the reaction mixture had stirred for 15 min, it was cooled in an ice–water bath for 3 min and then 25.0 ml (56.8 g, 0.4 mol) of methyl iodide was added all at once. The reaction mixture was then allowed to stir overnight while the cooling bath came to room temperature. An additional 75 ml of methyl iodide was then added, and the reaction mixture was stirred and maintained at reflux for 2.5 hr. The cooled mixture was concentrated under reduced pressure to *ca.* 30% of its original volume, and 200 ml of water and 100 ml of ether were added. The aqueous layer was separated and washed two times with 70-ml portions of ether–benzene (4:1). The combined ethereal extracts were washed two times with 40-ml portions of a saturated salt solution and dried (Na_2SO_4). After the solvent was removed under reduced pressure, gas chromatographic analysis of the product (10.5 g)

at 238° indicated the lack of any starting ketone **19** and its complete conversion into the methylated ketones **20** and **27**; nmr spectral analysis of this crude product indicated that the ratio of C-2 β-methylated ketone **20** to its C-2 α-methylated epimer **27** (*e.g.*, C-2-methyl resonance at 1.10 ppm *vs.* 0.68 ppm, respectively) was 5:1. On chromatography of this material on 300 g of silicic acid, fractions rich in the C-2 α-methylated isomer **27** were eluted first as the solvent polarity was increased from 70% to 99% benzene–petroleum ether. Thus the purest sample of the C-2 α-methylated ketone **27** (1.02 g, 90% ketone **27** by nmr analysis) was obtained from early fractions amounting to 500 ml of 70–75% benzene–petroleum ether. Fractions that increased in the concentration of the C-2 β-methylated ketone **20** accounted for another 1.7 g of the ketone mixture (1000 ml of 75–90% benzene–petroleum ether) and then the bulk of the material was eluted with 3500 ml of 90–99% benzene–petroleum ether. This latter material amounted to 7.50 g (72%) of the C-2 β-methylated ketone **20** of 94% isomeric purity by nmr analysis. A portion of this latter material was used to prepare the analytical sample by evaporative distillation at 84–87° (0.05 mmol): ir heat 1968 (C=O), 1643, and 890 cm^{-1} (C=CH_2); nmr ($CDCl_3$) δ 1.10 (s, 3, C-2 β CH_3), 1.33 (s, 3, C-6β CH_3), 1.54 (d, 3, J = 1 Hz, C-2′ CH_3), 4.48, and 4.77 (m, 2, C=CH_2).

Anal. Calcd for $C_{15}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.57; H, 9.66.

2α,6β-Dimethyl-2β-(2′-methylallyl)-6α-phenylcyclohexanone (27).—By a procedure identical with that described previously,[4] 300 mg (1.48 mmol) of the ketone **28**[9] and 252 mg (2.24 mmol) of potassium *t*-butoxide in 4 ml of dry benzene was treated with 0.435 ml (402 mg, 4.34 mmol) of freshly distilled methallyl chloride. Gas chromatographic analysis of the crude product at 238° indicated the lack of any starting ketone **28** and the complete formation of the ketones **20** and **27**. The ratio of the C-2 epimeric ketones **20** and **27** was determined to be 1:9 by nmr spectral analysis of, this mixture in the same manner as described above. This ratio was also confirmed by careful gas chromatographic analysis of this mixture at 152° (injection port 317°). Under these conditions, the C-2 β-methylated ketone **20** is eluted in 675 sec, and the C-2 α-methylated ketone **27** is eluted in 735 sec. Peak-enhancement studies with authentic materials isolated from the above experiment verified these assignments.

2α-Acetonyl-2β,6β-dimethyl-6α-phenylcyclohexanone.—A solution of 6.45 g (0.025 mol) of the ketone **20** (94% isomerically pure) in 650 ml of dioxane, 64.5 ml of glacial acetic acid, and 129 ml of water was treated with 65 mg of osmium tetroxide, and the resulting solution was allowed to stir for 10 min at room temperature. Crystalline paraperiodic acid (22.8 g, 0.10 mol) was added in small portions over the ensuing 25-min period, and the mixture was then allowed to stir for an additional 24 hr. The reaction mixture was diluted with 100 ml of water, and the system was extracted four times with 500-ml portions of chloroform. The combined organic extracts were then washed successively three times with 300-ml portions of water, three times with 70-ml portions of 10% aqueous potassium hydroxide solution, 200 ml of water, and saturated salt solution, and then dried (Na_2SO_4). The solution, concentrated to dryness under reduced pressure, yielded 6.50 g of a yellow oil. Chromatography of the crude product (6.50 g) obtained after evaporation of the solvent on 200 g of silicic acid afforded 5.52 g (85% yield) of the diketone as a pale yellow, crystalline solid, mp 82–86° (elution, 12 l. of 30% ether–petroleum ether). Two successive crystallizations of a portion of this material from petroleum ether afforded colorless platelets that served as the analytical sample: mp 88.5–89.5° (capillary); ir ($CHCl_3$) 1712 and 1692 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.22 (s, 3, C-2β CH_2), 1.44 (s, 3, C-6β CH_3), 1.90 (s, 3, $COCH_3$), 2.42, and 2.58 (two s, 2, CH_2COCH_3).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.13; H, 8.60.

2β-Acetonyl-2α,6β-dimethyl-6α-phenylcyclohexanone.—By a similar procedure, the early fractions from the chromatogram of the product of methylation of the methallyl ketone **19** were converted as well into the corresponding diketone.[4] Thus 1.02 g (3.6 mmol) of a sample of the methylated ketone **27**, judged by nmr analysis to be 90% isomeric homogeneous, was oxidized with 10 mg of osmium tetroxide and 3.65 g (0.016 mol) of paraperiodic acid in 100 ml of dioxane, 10 ml of glacial acetic acid, and 20 ml of water. After the same procedure was followed as described above, there was obtained 775 mg (83% based on the isomeric purity of the starting sample) of the diketone, mp 92–94°, as a pale yellow, crystalline solid. The melting range of a mixture of this material and the authentic diketone,[4] mp 92–93.5°, was also 92–94°.

4β,7aβ-Dimethyl-4α-phenyl-4,5,6,7-tetrahydro-2-indanone (21).—A solution of 2.00 g (7.75 mmol) of the above diketone in 17 ml of benzene was added dropwise to a stirred suspension of 2.62 g (23.2 mmol) of potassium *t*-butoxide in 25 ml of *t*-butyl alcohol under a nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 24 hr. The orange mixture was acidified with 2.5 ml of 3 *N* hydrochloric acid, and most of the *t*-butyl alcohol was removed at reduced pressure. The residue was partitioned between 100 ml of ether–benzene (4:1) and 20 ml of water, and the organic layer was separated, washed three times with 10-ml portions of water and once with 10 ml of saturated salt solution, and then dried (Na_2SO_4). Removal of the solvents under reduced pressure left 1.90 g [98%, glpc (275°) a single component with a retention time of 90 sec, R_f 0.42 by silicic acid tlc in 50% ether–petroleum ether] of a white crystalline solid. The analytical sample was obtained as colorless, thick platelets after three recrystallizations of a portion of this material from ether–hexane: mp 90–91°; ir ($CHCl_3$) 1690 (C=O) and 1593 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.47 (s, 3, C-7aβ CH_3), 1.71 (s, 3, C-4β CH_3), 2.33 (s, 2, C-1 CH_2), and 5.13 (s, 1, C-3 H).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.95; H, 8.49.

4β,7aα-Dimethyl-2-hydroxy-4α-phenyl-3aα,4,5,6,7,7a-hexahydroindone (6).—An ice-cooled mixture of 980 mg (3.78 mmol) of the hydroxy ketone **2**[4] in 100 ml of acetone was oxidized with 4 ml of 8 *N* aqueous chromic acid solution.[16] After the mixture had stirred at 0° under a nitrogen atmosphere for 45 min, sufficient isopropyl alcohol was added to destroy the excess oxidant. The reaction mixture was then filtered, and after 5 ml of saturated sodium bicarbonate had been added to ensure the alkalinity of the solution, the filtrate was concentrated to *ca.* 20 ml at reduced pressure and 40°.

The chromium salts that were removed by filtration above were then washed twice with 250-ml portions of water, and the combined aqueous washings were extracted three times with 50-ml portions of ether–benzene (4:1). These ethereal extracts were then combined with the aqueous residue obtained above from the filtrate and the resultant system was washed three times with 15-ml portions of water and two times with 10-ml portions of saturated salt solution and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 860 mg of an off-white, oily solid. Chromatography of this material on 40 g of silicic acid afforded 545 mg (56%) of the diosphenol **6**, mp 120–122°, after elution with 900 ml of 12% ether–petroleum ether. The analytical sample was obtained as platelets after two crystallizations of a portion of this material from ether–petroleum ether: mp 121–123°; ir ($CHCl_3$) 3480 and 3240 (OH) and 1695 and 1652 cm^{-1} (enolic α diketone); uv max (MeOH) 259 mμ (ε 9600); nmr ($CDCl_3$) δ 0.93 (s, 3, C-7aα CH_3), 1.20 (s, 3, C-4β CH_3), 3.25 (m, 1, C-3aα H), and 6.68 (d, 1, J = 3.4 Hz, C-3 H).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.77; H, 7.86.

The diosphenol **6** imparted a purple color to an aqueous alcoholic ferric chloride test solution, and the melting range of a mixture of this diosphenol **6**, mp 121–123°, and the diosphenol **31**, mp 152–164°, was 105–145°. On gas chromatography of a mixture of the two diosphenols **6** and **31** at 268° the diosphenol **6** was eluted after 112.5 sec and the diosphenol **31** was eluted after 121.5 sec. The diosphenol **6** was quantitatively recovered unchanged after treatment with potassium *t*-butoxide in *t*-butyl alcohol under identical conditions reported above for the conversion of the unsaturated hydroxy ketone **1** into the diosphenol **31**.

Acidification of the combined aqueous extracts from this oxidation with concentrated hydrochloric acid afforded 153 mg (14%) of crude diacid **3**, mp 201–206°, as a curdy, off-white solid. After three crystallizations of this material from ether–petroleum ether, the melting range was 206–208°, alone or after admixture with an authentic sample[4] of the diacid **3**, mp 207–209°. The solution ($CHCl_3$) infrared spectra[4] of the two samples were also identical.

For further characterization of the diosphenol **6**, a 205-mg (0.80 mmol) sample was converted into its methyl ether in quantitative yield by treatment with 0.75 ml of dimethyl sulfate and 2.5 g of anhydrous potassium carbonate in 50 ml of dry acetone by the same procedure described above for the formation of the methyl ether **14** of the diosphenol **31**. The analytical sample was obtained after one crystallization from ether–petroleum ether: mp 73–75°; ir ($CHCl_3$) 1710 (C=O), 1628 (C=C),

and 1258 and 1080 cm^{-1} (COC); uv max (MeOH) 256 mμ (ε 8200); nmr ($CDCl_3$) δ 0.83 (s, 3, C-7aα CH_3), 1.09 (s, 3, C-4β CH_3), 3.16 (d, 1, J = 3 Hz, C-3aα H), 3.68 (s, 3, OCH_3), and 6.36 (d, 1, J = 3 Hz, C-3 H).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.87; H, 8.13.

4β,7aβ-Dimethyl-4α-phenyl-4,5,6,7-tetrahydroindan-1,2-dione.—A solution of 800 mg (3.36 mmol) of unsaturated ketone **21**, 1.16 g (10.4 mmol) of selenium dioxide, and 0.188 ml (10.4 mmol) of water in 40 ml of glacial acetic acid was heated under reflux for 4 hr. Filtration of the cooled reaction mixture and removal of the acetic acid from the filtrate at reduced pressure left an orange-colored oil. A solution of this oily residue in 200 ml of ether–benzene (4:1) was washed five times with 20-ml portions of water, three times with 20-ml portions of 5% aqueous sodium bicarbonate, and three times with 15-ml portions of saturated salt solution and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 843 mg (98%) of the diketone, mp 109–111°, as a yellow, crystalline solid. Two successive crystallizations of a portion of this material from ether–petroleum ether afforded material of analytical purity as thin yellow platelets: mp 111.5–112.5°; ir ($CHCl_3$) 1765 (C=O), 1717 (conjugated C=O), and 1622 cm^{-1} (C=C); uv max (MeOH) 278 mμ (ε 5720); nmr ($CDCl_3$) δ 1.53, 1.80 (two s, 6, C-7aβ and C-4β CH_3), and 5.97 (s, 1, C-3 H).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.25; H, 7.13. Found: C, 80.38; H, 7.25.

4β,7aβ-Dimethyl-1α-hydroxy-4α-phenyl-4,5,6,7-tetrahydro-2-indanone (30).—An ice–water-cooled solution of 889 mg (3.49 mmol) of the above diketone in 25 ml of methanol was treated with 33 mg (0.873 mmol) of sodium borohydride in 4 ml of water, and the mixture was stirred at room temperature under a nitrogen atmosphere for 3.5 hr. The reaction mixture was diluted with 150 ml of water and extracted with three 50-ml portions of ether–benzene (4:1). The combined organic extracts were washed with three 15-ml portions of a saturated salt solution, dried (Na_2SO_4), and evaporated to dryness under reduced pressure. The resulting pale yellow solid (887 mg) was chromatographed on 50 g of silicic acid, and 823 mg (90%) of the unsaturated hydroxy ketone **30**, mp 114–117°, was eluted with 1300 ml of 50% ether–petroleum ether. The analytical sample was obtained as fine, thin platelets after one crystallization of a portion of this material from ether–petroleum ether: mp 116.5–118.5°; ir ($CHCl_3$) 3514, 3370 (OH), 1710 (C=O), and 1585 cm^{-1} (C=C); uv max (MeOH) 235 mμ (ε 10,790); nmr ($CDCl_3$) δ 1.37, 175 (two s, 6, C-7aβ and C-4β CH_3), 3.16 (br s, 1, OH), 4.04 (d, 1, J = 1 Hz, C-1β H), and 5.29 (s, 1, C-3 H).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.69; H, 7.87.

The *p*-bromobenzoate **33**, mp 106–108° with sintering at 50°, was prepared in 67% yield for single-crystal X-ray analysis from 150 mg (0.59 mmol) of the unsaturated hydroxy ketone **30** and 230 mg (1.05 mmol) of *p*-bromobenzoyl chloride in 5 ml of dry pyridine by exactly the same procedure described below for the formation of the corresponding derivative of the unsaturated hydroxy ketone **1**. Material of analytical purity for X-ray analysis was prepared after two crystallizations from ether–methanol and melted at 107.5–108.5° after drying at 143° (0.03 mm) for 1.5 hr to remove occluded ether: ir ($CHCl_3$) 1725, 1715 (C=O), 1592 (aromatics), and 1270 cm^{-1} (COC); uv max (MeOH) 246 mμ (ε 29,600); nmr ($CDCl_3$) δ 1.41, 1.77 (two s, 6, C-7aβ and C-4β CH_3), 5.36 (s, 1, C-1β H), 5.47 (s, 1, C-3 H), and 7.54, 7.68, 7.93, and 8.09 (A_2B_2 q, 4, *para*-substituted aromatics).

Anal. Calcd for $C_{24}H_{23}BrO_3$: C, 65.61; H, 5.28; Br, 18.19. Found: C, 65.81; H, 5.33; Br, 18.15.

2α-Carboxymethyl-1β,3β-dimethyl-3α-phenylcyclohexanecarboxylic Acid Anhydride (35).—To a stirred solution of 942 mg (3.66 mmol) of diosphenol **31** in 40 ml of methyl alcohol was added 1.5 ml of 10% aqueous sodium hydroxide solution and 4 ml of 30% hydrogen peroxide, and the solution was heated at reflux for 3 hr; during this period, two additional charges of 1.5 ml of 10% aqueous sodium hydroxide solution and 4 ml of 30% hydrogen peroxide each were added at 1-hr intervals. To the cooled solution was added 100 ml of ether–benzene (4:1); the ethereal solution was separated and extracted twice with 50-ml portions of 3% aqueous sodium hydroxide solution. The combined aqueous layer was acidified with iced, concentrated hydrochloric acid, and the resulting precipitate was extracted with three 30-ml portions of ether–benzene (4:1). The combined ethereal layers were washed four times with 10-ml portions of saturated salt solution and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 1.10 g of a pale yellow, crystalline solid: ir ($CHCl_3$) 3530–2326 (acid OH), 1775 (acid C=O, monomer), and 1725–1700 cm^{-1} (acid C=O dimer); glpc (300°) 94% with a retention time of 106 sec. This crude material was combined with 30 ml of acetic anhydride and heated at reflux under nitrogen for 2 hr. Evaporation of the solution to dryness at reduced pressure afforded 1.030 g of an orange, oily residue which readily crystallized upon being triturated with ether. Crystallization of the crude product from ether–petroleum ether afforded 675 mg (69%) of the anhydride **35**, mp 121–124°, in two equal crops [glpc (300°) 99% with a retention time of 66 sec]. A single crystallization of a portion of the solid material from ether–petroleum ether afforded a white, crystalline solid: mp 124–125° (lit.[5] mp 124–125°); ir ($CHCl_3$) 1804 and 1759 cm^{-1} (anhydride C=O); nmr ($CDCl_3$) δ 1.42 and 1.53 (two s, 6, C-1 and C-3 CH_3).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.01; H, 7.26.

***syn*-9-(1,5-Dimethyl-4-oxo-2,3-benzobicyclo[3.3.1]nonanyl)-acetic Acid (36).**—To 38.4 ml of 85% phosphoric acid under nitrogen was added 48 g of phosphorus pentoxide. After stirring for 1 hr, 320 mg (1.1 mmol) of anhydride **35** was added, and the mixture was heated with stirring at 90° for 1 hr. While still warm, the brown-colored reaction mixture was poured over *ca.* 100 g of crushed ice and the precipitate was isolated by multiple ether extraction. The combined ethereal layers were washed twice with 15-ml portions of water and four times with a saturated salt solution, and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 310 mg of a yellow solid. Crystallization of the crude product from ethyl acetate–hexane afforded 275 mg (86%) of a white, crystalline solid, mp 171–174°. The analytical sample, obtained as white platelets melting at 172–173.5°, was prepared by two further crystallizations from ethyl acetate–hexane: ir ($CHCl_3$) 3560–2224 (acid OH), 1710 (acid C=O), 1675 (ketone C=O), and 1599 cm^{-1} (C=C); uv max (MeOH) 253 mμ (ε 10,750), and 292 (1620); nmr ($CDCl_3$) δ 1.23 (s, 3, C-5 CH_3), 1.49 (s, 3, C-1 CH_3), 2.25 (d, 2, J = 1.5 Hz, CH_2CO_2H), and 10.65 (s, 1, CO_2H).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 74.97; H, 7.40. Found: C, 74.91; H, 7.28.

***syn*-9-(1,5-Dimethyl-2,3-benzobicyclo[3.3.1]nonanyl)acetic Acid (37).**—To a suspension of 100 mg of 10% palladium on carbon in 5 ml of glacial acetic acid was added a solution of 197 mg (0.72 mmol) of keto acid **36** and 4 drops of 60% aqueous perchloric acid in 10 ml of glacial acetic acid, and the mixture was stirred in a hydrogen atmosphere until the uptake of hydrogen gas ceased (36.5 ml of H_2 in 2 hr). The catalyst was removed by filtration and washed with 50 ml of benzene. The filtrate was diluted with 100 ml of water, and the benzene layer was separated. The aqueous layer was extracted three times with 30-ml portions of ether–benzene (1:1). The combined organic layers were washed successively with three 15-ml portions of water and three 15-ml portions of a saturated brine solution, and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 189 mg (98%) of an off-white, crystalline solid, mp 159–163°. The analytical sample, obtained as white platelets melting at 162–164°, was prepared by two further crystallizations from ethyl acetate–hexane: ir ($CHCl_3$) 3540–2320 (acid OH) and 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.01 (s, 3, C-5 CH_3), 1.39 (s, 3, C-1 CH_3), 2.22 (m, 2, CH_2CO_2H), 2.56 (q, 2, J_{AB} = 0.8 Hz, C-4 CH_2), and 11.23 (s, 1, CO_2H).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.94; H, 8.48.

***syn*-9-(1,5-Dimethyl-2,3-benzobicyclo[3.3.1]nonanyl)-2-ethyl Alcohol.**—A solution of 300 mg (1.16 mmol) of acid **37** in 20 ml of tetrahydrofuran was added dropwise to 228 mg (6.00 mmol) of lithium aluminum hydride in 80 ml of tetrahydrofuran. The stirred mixture was heated at reflux in a nitrogen atmosphere for 3 hr, cooled, and cautiously decomposed with 5 ml of 10% aqueous sodium hydroxide. The filtrate obtained after the removal of the precipitated salts was concentrated at reduced pressure, and the residue was taken up in 100 ml of ether–benzene (1:1), washed successively with two 10-ml portions of water and three 10-ml portions of a saturated salt solution, and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 260 mg of a yellow oil [83%, glpc (260°) 90% with a retention time of 58 sec]. The analytical sample was obtained as a colorless oil after preparative thin layer chromatography of a

60-mg sample of this material on a 20 × 20 × 0.2 cm silicic acid plate developed with 50% ether–petroleum ether and then evaporative distillation of the band centered at R_f 0.65 at 100–102° (0.2 mm): ir ($CHCl_3$) 3606 (sharp) and 3420 cm^{-1} (shoulder, OH); nmr ($CDCl_3$) δ 0.99 (s, 3, C-5 CH_3), 1.18 (br s, 1, OH), 1.39 (s, 3, C-1 CH_3), and 3.60 (t, 2, J = 8 Hz, CH_2OH).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.64; H, 9.98.

***syn*-9-(1,5-Dimethyl-2,3-benzobicyclo[3.3.1]nonanyl)acetaldehyde.**—To 207 mg (90% pure, 0.760 mmol) of the above crude alcohol dissolved in 24 ml of methylene chloride was added 1.31 g (5.06 mmol) of solid chromic oxide–dipyridine complex.[18] The dark brown mixture was stirred at room temperature for 15 min, and then filtered through 25 g of Merck acid-washed alumina with 100 ml of methylene chloride. The clear, colorless eluent was concentrated at reduced pressure and taken up in 150 ml of ether–benzene (1:1). The ethereal solution was washed successively with two 5-ml portions of 1 N hydrochloric acid, two 10-ml portions of water, and three 10-ml portions of a saturated salt solution and then dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 197 mg of a yellow oil [88%, glpc (270°) 88% with a retention time of 41 sec]: ir ($CHCl_3$) 1722 cm^{-1} (C=O); nmr ($CDCl_3$), δ 0.94 (s, 3, C-5 CH_3), 1.32 (s, 3, C-1 CH_3), and 9.83 (t, 1, J = 1 Hz, CHO). The aldehyde was converted into its semicarbazone derivative, and an analytical sample of the derivative was obtained after two crystallizations from methyl alcohol–ether: mp 159–160°; ir ($CHCl_3$) 3530, 3474, 3402, 3350 (NH), 1690, 1635, and 1567 cm^{-1} (amide bands).

Anal. Calcd for $C_{18}H_{25}N_3O$: C, 72.21; H, 8.42; N, 14.03. Found: C, 72.05; H, 8.54; N, 13.58.

***syn*-9-Ethyl-1,5-dimethyl-2,3-benzobicyclo[3.3.1]nonane (38).**—To 90 mg (88% pure, 0.326 mmol) of the above crude aldehyde was added 224 mg (3.40 mmol) of potassium hydroxide and 192 mg (5.70 mmol) of 95% hydrazine in 10 ml of triethylene glycol. The stirred solution was first heated at 105° for 2.5 hr in a nitrogen atmosphere, and then at 205° for 4 hr. The solution was cooled and 100 ml of petroleum ether–ether (4:1) was added. The ethereal mixture was separated, washed successively with three 50-ml portions of water and one 10-ml portion of a saturated salt solution, and dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded 85 mg of a yellow oil [glpc (280°) 80% with a retention time of 26 sec]. Purification was effected by preparative thin layer chromatography on a 20 × 20 × 0.2 cm silicic acid plate developed with 10% benzene–petroleum ether. Extraction of the band with R_f 0.69 with ether afforded 58 mg (94%) of a colorless oil [glpc (280°) 98% with a retention time of 26 sec]. The analytical sample was obtained by evaporative distillation of this material at 55–57° (0.06 mm): ir ($CHCl_3$) 1373 cm^{-1} (singlet, CH_3); nmr (60 MHz, $CDCl_3$) δ 1.00 (m, 6, CH_2CH_3 and C-5 CH_3) and 1.40 (s, 3, C-1, CH_3); nmr (100 MHz, $CDCl_3$) δ 2.63 (q, 2, J_{AB} = 9 Hz, C-4 CH_2).

Anal. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.37; H, 10.68.

X-Ray Crystallographic Structure Analysis.—Crystals of the *p*-bromobenzoates **32**, **33**, and **34** suitable for an X-ray analysis were grown utilizing the slow evaporation technique with suitable solvents (Table II). The choice of ether for compound **33** was unfortunate, since the nmr spectrum of the crystalline material obtained revealed that ether was trapped in the crystals (*ca.* one molecule of ether for every four molecules of the *p*-bromobenzoate **33**). Ether, however, was the only solvent system investigated that gave crystallographically suitable crystals.

The resulting crystals were surveyed on a precession camera; the results of the surveys are given in Table II.

One-ångström intensity data were collected for the three compounds on the General Electric–Datex diffractometer using nickel-filtered copper radiation. A θ–2θ scan technique was employed, background was counted for 10 sec at each end of the scan, and a scan rate of 2°/min in 2θ was utilized. A single-check reflection was monitored every 30 reflections. The check reflection in every case indicated no crystal damage and was reproducible well within counting statistics.

The diffractometer output was processed using subprograms of the CRYRM crystallographic computer system.[21] The processing included corrections for background and for Lorentz and polarization effects. It also included calculation of the F^2 value and its standard deviation for each of the reflections. The standard deviations were assigned on the basis of eq 1, where S

$$\sigma^2(I) = S + (B_1 + B_2)\alpha^2 + (dS)^2 \quad (1)$$

is the scan count, B_1 and B_2 are the background counts, d is an empirical constant equal to 0.02, and $\alpha = n/2mt$ where n = scan range, m = scanning speed, and t = time for background count in seconds. Finally, the data were placed on an absolute scale by means of Wilson[22] statistics.

Trial structures for all three compounds were derived using the usual Patterson and Fourier techniques in three dimensions. Hydrogen positions were located by difference Fourier techniques. All trial structures were refined using full-matrix least-squares techniques. In every case, the final refinement cycles included the following parameters: atomic coordinates, anisotropic temperature factors, and scale factor. While the hydrogen positions were added to the structure-factor calculations, they were not subjected to refinement. The final criteria of data fit for all compounds are listed in Table III. A difference Fourier of each final structure revealed no misplaced or missing atoms.

Both compounds **32** and **34** refined in a routine manner. However, since compound **33** contained an ether of crystallization, its refinement deserves special comment.

Refinement of *p*-Bromobenzoate 33.—Full-matrix least-squares refinement of coordinates, isotropic temperature factors, and scale factor reduced the R index to 26.7%. At this point, a difference Fourier was produced to locate the ether molecule

TABLE II
DETAILS OF CRYSTAL SURVEYS

	32	33	34
Solvent system	Methanol–ether	Ether	Methanol–chloroform
a, Å	24.80	6.567	7.174
b, Å	12.62	32.61	35.78
c, Å	13.09	20.75	7.929
α, deg	90.00	90.00	90.00
β, deg	93.64	90.00	93.20
γ, deg	90.00	90.00	90.00
Systematic extinctions	hkl: $h + k$ odd $h0l$: l odd	$0kl$: k odd $h0l$: l odd $hk0$: h odd	$h0l$: l odd $0k0$: k odd
Space group	$C2/c$[a]	$Pbca$	$P2_1/c$
Molecules per unit cell	8	8	4
ρ_{calcd} g/cm³	1.426	1.312	1.435
ρ_{obsd} g/cm³	1.43	1.30	1.43
No. of reflections	2146	2284	2146
No. of nonzero reflections	2071	1875	2042

[a] Systematic extinction data established the space group of this compound as either Cc or C2/c. The choice between the acentric space group (Cc) and the centric space group (C2/c) was made on the basis of the data of Howells, Phillips, and Rogers [E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950)], which suggested the centric space group. The final refinement data confirmed that a center of symmetry was indeed present.

TABLE III
DATA FIT AND STANDARD DEVIATIONS

	32	33	34
Final R index	0.072	0.161	0.110
Final goodness-of-fit[a] index	2.95	1.64	1.86
Std deviations[b] of coordinates, Å			
Br	0.0009	0.0016	0.0010
C, O	0.005	0.01	0.007
Uncertainties in C, O, Br bond lengths, Å	±0.007	±0.02	±0.01
Uncertainties in C, O, Br bond angles, deg	±1.5	±1.0	±0.5

[a] Goodness of fit = $\{\Sigma (1/m - n) = [(F_o^2 - F_c^2)^2/\sigma^2(F_o^2)]\}^{1/2}$, where $\sigma(F_o^2)$ is the standard deviation of the data determined during the data collection, m is the number of observations, and n is the number of parameters. The goodness-of-fit index [S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957)] for perfect fit is 1.0; acceptable goodness-of-fit values range in the neighborhood of 3.0. [b] Standard deviations in the coordinates were derived from the residuals and the diagonal elements of the inverse matrix of the final least-square cycle.

(21) D. J. Duchamp, American Crystallographic Association Meeting, Bozeman, Mont., 1964, Paper B-14, p 29.

(22) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

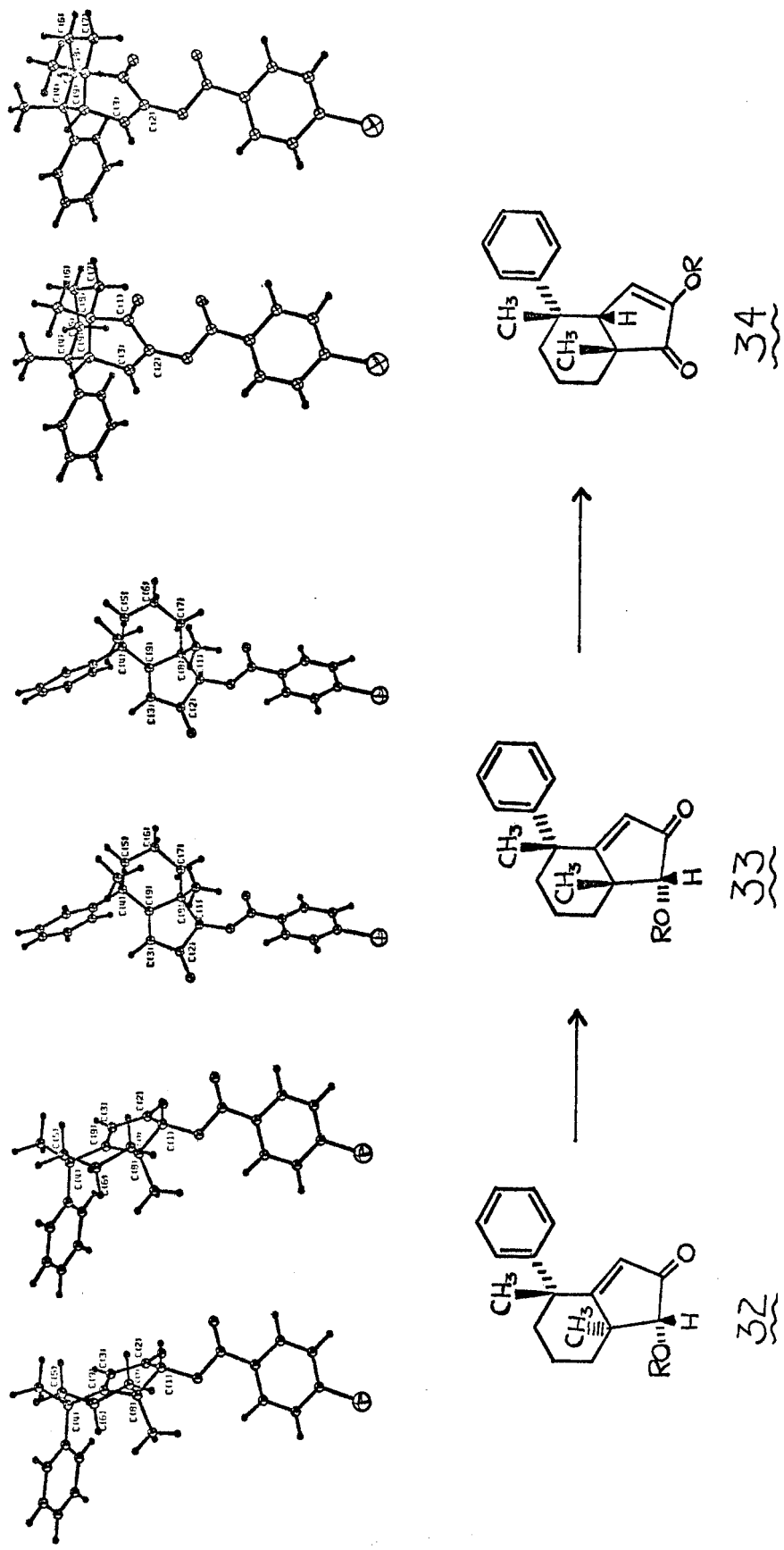


Figure 1.—Stereo drawings of the rearrangement.

which had been observed in the nmr spectrum. This difference Fourier revealed a channel of electron density almost parallel to the *a* axis and indicated that the ether was not highly ordered in the crystal. Since the main interest of the analysis was the structure of **33** and not the structure of disordered ether molecules, no significant attempt was made to fit approximate ether coordinates. Because the disordered ether molecules occupied positions almost parallel to the *a* axis, the intensities most affected by these ether molecules are contained in the 0*kl* set. Therefore, these intensities were removed from the data and refinement was continued. The hydrogen positions were located by difference Fourier techniques and were added to the structure-factor calculation. Refinement with anisotropic temperature factors reduced the *R* index to 16.1%. A final difference Fourier at this point revealed no missing or misplaced atoms, thus indicating that the model was indeed correct.

Results of X-Ray Analyses.—The three structures obtained in the analyses were stereographically plotted (Figure 1) using the ORTEP computer program of Johnson.[23] An estimate of errors in positional parameters, bond lengths, and bond angles are summarized in Table III. Owing to limitations in space, other pertinent crystallographic data and parameters cannot be listed here. *F* tables, atomic coordinates, anisotropic temperature factors, and bond angles and distances have been filed with NAPS.[24]

(23) C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratories, Oak Ridge, Tenn.

Registry No.—**6**, 22932-90-7; **6** methyl ether, 22932-91-8; **10**, 16957-32-7; **10** semicarbazone, 16957-33-8; **12**, 16957-34-9; **12** semicarbazone, 16957-35-0; **14**, 22932-96-3; **15**, 22932-97-4; **18**, 22932-98-5; **19**, 22932-99-6; **20**, 22933-00-2; **21**, 16957-31-6; **22**, 22933-02-4; **22** semicarbazone, 22933-03-5; **24**, 22933-04-6; **24** semicarbazone, 22979-21-1; **30**, 22933-05-7; **31**, 22933-06-8; **32**, 22979-22-2; **33**, 22933-07-9; **34**, 22933-08-0; **35**, 22933-09-1; **36**, 22933-10-4; **37**, 22933-11-5; **38**, 22933-12-6; 4β,7aβ-dimethyl-1-acetoxy-4α-phenyl-*cis*-hexahydro-2-indanone, 22933-13-7; 2α-acetyl-2β,6β-dimethyl-6α-phenylcyclohexanone, 22933-14-8; 4β,7aβ-dimethyl-4α-phenyl-4,5,6,7-tetrahydroindan-1,2-dione, 22933-15-9; *syn*-9-(1,5-dimethyl-2,3-benzobicyclo[3.3.1]nonanyl)-2-ethyl alcohol, 22933-16-0; *syn*-9-(1,5-dimethyl-2,3-benzobicyclo[3.3.1]nonanyl)-acetaldehyde, 22933-17-1.

(24) Material supplementary to this article has been deposited as Document No. NAPS 00647 with the ASIS National Auxiliary Publication Service, % CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to ASIS-NAPS.

Photochemical Reactions of γ-Keto Sulfides[1,2]

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Irradiation of thiacyclohexan-4-one (**1**) in *t*-butyl alcohol gave thiacyclobutan-2-one (27%) and *t*-butyl 4-thiahexanoate (18%). The photochemical reactions of cyclic γ-keto sulfides **2**–**8** and cyclic δ-keto sulfide **9** in *t*-butyl alcohol were investigated. The irradiation of **1** and **5** was studied under a variety of conditions. Irradiation of 5-thiaoctan-2-one and thiachroman-4-one in *t*-butyl alcohol did not give appreciable quantities of monomeric products.

Photochemical studies of β-keto sulfides[4] have received attention in recent years because of the nature of the excited-state interaction of the two chromophores[5] and the possibility that they might undergo unusual photochemical reaction as a result of this interaction. Acyclic γ-keto sulfides show no evidence of charge-transfer interaction, but cyclic γ-keto sulfides[5] and some cyclic δ-keto sulfides[6] show an excited-state interaction which is probably similar to that observed in β-keto sulfides. The photochemical reactions of a number of γ-keto sulfides and a δ-keto sulfide have been investigated in order to determine the nature of the products under the conditions studied.

The ultraviolet spectra of the cyclic keto sulfides (**1**–**9**) irradiated are listed in Table I with the products formed on irradiation in *t*-butyl alcohol. (See Experimental Section for reaction conditions.) Irradiation of thiacyclohexan-4-one (**1**) in *t*-butyl alcohol until disappearance of 93% of the starting material gave 27% thiacyclobutan-2-one (**10**) and 18% *t*-butyl 4-thiahexanoate (**11**). In order to check the wavelength dependence of this reaction and because the intensity of the charge-transfer band is the same order of magnitude as the n $\rightarrow$ π^* band (shoulder) in the 280–290-nm region, **1** was irradiated with a Vycor filter to effect more excitation *via* the charge-transfer band. Irradiation under these conditions gave 22% **11**, 4% unreacted **1**, and no **10**, although the concentration of **10** was observed to build up to as high as several per cent in the first few hours. Thus irradiation with the Vycor filter appears to effect the same reaction and secondary photochemical polymerization of the thiolactone. Cyclic thiolactones were shown to form polymer upon irradiation at 254 nm. Irradiation of **1** in Freon-113 (1,1,2-trichlorotrifluoroethane) with a Pyrex filter resulted in 74% reaction of **1** after 48 hr and formation of **10** (23%) and some polymeric material. Formation of **11** was observed if *t*-butyl alcohol was added to the photolysis mixture after irradiation of **1** in Freon-113 for a short period of time. This suggests the ketene intermediate, $C_2H_5SCH_2C{=}C{=}O$, in the formation of **11**.

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