ppm (d, 6 H, J = 6 Hz, $(CH_3)_2C$); ir (CCl_4) 1560, 1320 (NO_2), and 1110 cm^{-1} (C–O–C).

Anal. Calcd for $C_6H_{12}N_2O_5$: C, 37.49; H, 6.30. Found: C, 37.62; H, 6.36.

Isopropyl 2,2,2-Trinitroethyl Ether.—Isopropyl triflate (0.040 mol) and 2,2,2-trinitroethanol (9.05 g, 0.050 mol) were allowed to react using the above procedure, except that washing with sodium hydroxide solution was omitted and the crude product was passed through a short column of silica gel to give isopropyl 2,2,2-trinitroethyl ether in 38% yield. The analytical sample was distilled in a molecular still at 0.1 mm, bath temperature 50°: nmr (CCl_4) δ 4.60 (s, 2 H, CH_2), 3.80 (septet, 1 H, J = 7 Hz, CH), and 1.25 ppm (d, 6 H, J = 6 Hz, CH_3); ir (CCl_4) 1565, 1315 (NO_2), and 1120 cm^{-1} (C–O–C).

Anal. Calcd for $C_5H_9N_3O_7$: C, 26.91; H, 4.06. Found: C, 27.30; H, 4.29.

Reaction of Isopropyl Triflate with Pentanol.—A mixture of 0.44 g (0.0050 mol) of pentanol, 0.95 g (0.0050 mol) of isopropyl triflate, 1.0 g of sodium sulfate, and 10 ml of methylene chloride was stirred for 1 hr. The mixture was washed with 30 ml of water, dried, and stripped of solvent. Vacuum transfer of the residue gave 0.57 g of a mixture containing 60% isopropyl pentyl ether (52% conversion) and 40% 1-pentanol, separated by glpc and compared with authentic samples. A reference sample of isopropyl pentyl ether was prepared by the reported method:[20] bp 131–132°; nmr (CCl_4) δ 3.40 (septet, 1 H, J = 6 Hz, CHO), 3.27 (t, 2 H, J = 6 Hz, CH_2O), 1.37 (m, 6 H, CH_2), 1.08 (d, 6 H, J = 6 Hz, $(CH_3)_2C$), and 0.90 ppm (m, 3 H, CH_3).

Registry No.—Trifluoromethanesulfonic anhydride, 358-23-6; 1,2-bis(2-fluoro-2,2-dinitroethoxy)ethane, 41029-52-1; 2-fluoro-2,2-dinitroethyl pentyl ether, 41029-53-2; allyl 2-fluoro-2,2-dinitroethyl ether, 25171-99-7; 2-fluoro-2,2-dinitroethyl propargyl ether, 40696-43-3; 1,4-bis(2-fluoro-2,2-dinitroethoxy)butane, 41029-56-5; 3-(2-fluoro-2,2-dinitroethoxy)-2-propenyl triflate, 41029-57-6; pentyl 2,2,2-trifluoroethyl ether, 41029-58-7; allyl 2,2,2-trinitroethyl ether, 41029-59-8; allyl 2,2-dinitropropyl ether, 41029-60-1; 2,2-dinitro-1,3-di(allyloxy)propane, 41029-61-2; 2,2-dinitropropyl 2-pentyl ether, 41029-62-3; 2,2-dinitropropyl 1-pentyl ether, 41029-63-4; 2,2-dinitropropyl 3-pentyl ether, 41029-64-5; 2-fluoro-2,2-dinitroethyl isopropyl ether, 41029-65-6; 2,2-dinitropropyl isopropyl ether, 41029-66-7; isopropyl 2,2,2-trinitroethyl ether, 41029-67-8; 2,2,2-trifluoroethanol, 75-89-8; 2,2,2-trinitroethanol, 918-54-7; 2,2-dinitropropanol, 918-52-5; 2,2-dinitro-1,3-propanediol, 2736-80-3; isopropyl pentyl ether, 5756-37-6; trifluoromethanesulfonic acid, 1493-13-6; tetrahydrofuran, 109-99-9.

(20) C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, **87**, 5747 (1965).

Stereochemistry in the Solvolytic Ring Contraction of 2,2,4aα-Trimethyl-1-decalyl Methanesulfonate. A Model Reaction Pertaining to Triterpene Biogenesis[1a]

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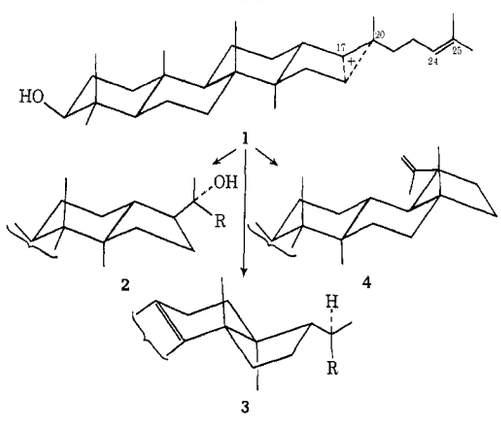
2,2,4aα-Trimethyl-1,2,3,4,4aα,5,6,7,8,8aβ-decahydronaphthalen-1β-ol (**5**-OH) and its 2β-trideuteriomethyl analog (**5**-d_3-OH) were synthesized by reduction-methylation of 4aβ-methyl-2-*n*-butylthiomethylene-3,4,4aβ,-5,6,7,8,8a(α and β)-octahydronaphthalen-1(2*H*)-ones (**8b**) and, after separation of the trans isomer from the mixture of trimethyldecalones (**9** and **10**), lithium–ammonia reduction. Solvolysis of the corresponding methanesulfonates (**5**-OMs and **5**-d_3-OMs) effects efficient ring contraction to 3aα,4,5,6,7,7aβ-hexahydro-3aα-methyl-1β-indanyldimethylcarbinol derivatives (**6**-OR and **6**-d_3-OR). Since the trideuteriomethyl group in the labeled product (**6**-d_3-OR) was equally distributed between the two diastereotopic positions, a bridged species (**21**), akin to a bridged ion (**1**) postulated in triterpene biogenesis, cannot be the sole intermediate in the rearrangement. Intervention of the classical tertiary carbocation (**22**) is presumed to cause the label distribution. Attempts to intercept the intermediate by azide trapping and the use of leaving groups bearing a second nucleophilic site (*o*-carboxysulfonate and *o*-thiocarboxysulfonate) were unsuccessful.

The hypothetical bridged ion **1** (Scheme I)[1c] represents a key branching point in the traditional schemes for the biogenesis of many tetracyclic and pentacyclic triterpenes.[2–4] Three different reaction modes are proposed for this intermediate: (a) direct capture by a water molecule to give dammarenediol I (**2**); (b) 17 → 20 hydride shift followed by a backbone rearrangement to tirucallol (**3**); (c) cyclization into the side chain double

SCHEME I



(1) (a) Taken in part from the Ph.D. Thesis of S. K. C., University of Illinois, 1972. (b) A. P. Sloan Foundation Fellow, 1971–1973. (c) The carbonium ion intermediates in such biogenetic schemes are represented by the bridged type formulation (*e.g.*, **1**) chiefly as a convenient method to correlate and predict the stereochemistry of the individual transformations. The importance of internal stabilization due to delocalization *via* bridging in the course of the biosynthetic transformation remains a matter of speculation.

(2) (a) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955); (b) G. Stork and A. W. Burgstahler, *J. Amer. Chem. Soc.*, **77**, 5069 (1955); (c) L. Rúzicka, *Proc. Chem. Soc.*, 341 (1959).

(3) For reviews and discussion see (a) G. Ourisson, P. Crabbé, and O. R. Rodig, "Tetracyclic Triterpenes," Holden-Day, San Francisco, Calif., 1964; (b) T. A. Geissman and D. H. G. Crout, "Organic Chemistry of Secondary Plant Metabolism," W. H. Freeman, San Francisco, Calif., 1969; (c) J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes, and Acetogenins," W. A. Benjamin, New York, N. Y., 1964; (d) K. B. Sharpless, Ph.D. Thesis, Stanford University, 1968.

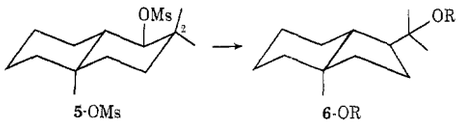
(4) (a) A biogenetic scheme involving temporary nucleophilic interception of the carbonium ion at certain stages (X group) has recently been suggested. Although different in some stereochemical details, this scheme postulates similar stereoelectronically controlled mechanisms: J. W. Cornforth, *Angew. Chem., Int. Ed. Engl.*, **7**, 903 (1968). (b) A similar bridged ion in the E ring of β-amyrin has been proposed.[2a,c] Recent biosynthetic experiments have verified that the identity of the geminal E ring methyl groups is maintained in the predicted manner in the formation of the E ring of β-amyrin: T. Suga, T. Shishibori, and S. Komoto, *Chem. Lett.*, 313 (1972).

That the distinction between these two methyl groups is also preserved in the biosynthesis of lupeol and the related triterpenes, betulin and betulinic acid, has been verified by D. Arigoni and coworkers at the ETH, Zurich: L. Botta, Dissertation No. 4098 (1968); L. Guglielmetti, Dissertation No. 3299 (1962).

bond and either proton loss to lupeol (**4**) or further rearrangement to other pentacyclic triterpenes.

Explicit in this scheme, as in most biogenetic pathways to terpenes, is the assumption that the bridged intermediate will react with a nucleophile (water, migrating hydrogen, or carbon–carbon double bond) from the side opposite the bridging carbon.[1c] It seemed of interest to determine whether or not a carbonium ion such as **1** could be captured stereoselectively in solution in the absence of the biosynthetic enzymes. Stereoselective capture is frequently observed in solvolysis reactions and is one significant criterion for designating the intermediate carbonium ion as nonclassical.[5]

The solvolytic ring contraction of the trans,anti decalyl methanesulfonate **5**-OMs to the trans,anti hydrindan **6** was selected as a model reaction. The **5** → **6** rearrangement, while differing from the well-

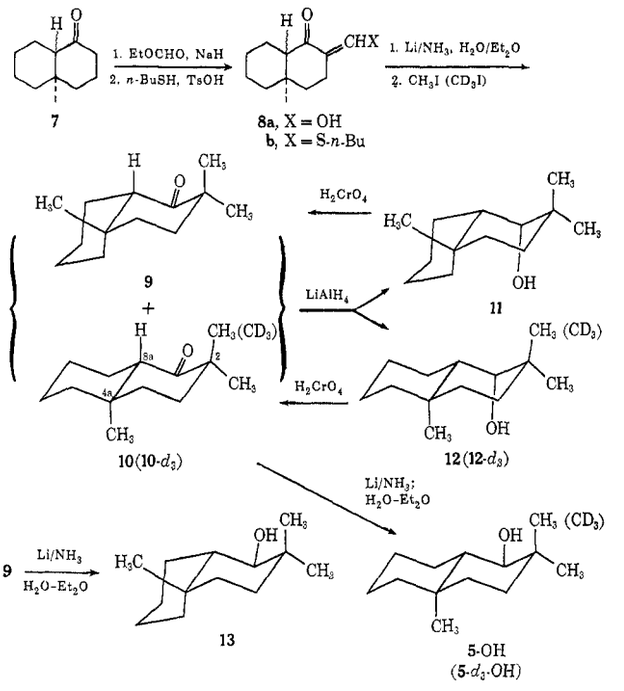


precedented ring A contraction of 4,4-dimethylsterols and triterpenes[6] in producing the natural trans,anti stereochemistry, finds analogy in silver ion assisted transformation of 19α-chloro-β-amyrin into lupeol.[7]

The ring contraction of **5**-OMs must pass through a bridged configuration similar to **1** which, if sufficiently long lived, would undergo substitution at C-2 of the decalin nucleus with net inversion. The stereochemistry of the overall reaction would be revealed by labeling one of the two methyl groups of **5** and determining whether the label appears in one of the two diastereotopic methyl groups in **6**. While the bridged ion might be expected to be less stable than the classical tertiary cation, there is nevertheless precedent for stereoselective capture of potentially symmetrical tertiary carbonium ions.[8]

The requisite decalol **5**-OH was secured by means of the reactions summarized in Scheme II, taking advantage of a new method for regioselective geminal alkylation.[9] Reduction–methylation of the α-*n*-butylthiomethylene derivative (**8b**)[10] of decalone **7** (cis,trans mixture)[11] afforded a mixture (~1:1) of the cis and trans trimethyldecalones (**9** and **10**) in 67% yield. The ketone mixture, after sodium methoxide–methanol equilibration (**9**:**10**, 1:3), was reduced with lithium aluminum hydride to the chromatographically separable axial alcohols **11** (16%) and **12** (68%). Oxidation with aqueous chromic acid afforded the pure cis and trans ketones. The equatorial alcohols **13** and **5**-OH were

SCHEME II



obtained in essentially quantitative yield by reduction with lithium in liquid ammonia.

The deuterium-labeled ketone **10**-d_3 was similarly prepared using deuteriomethyl iodide in the alkylation step. In this case, the excess lithium was first quenched by careful titration with methyl iodide and the *n*-butylmercaptide was consumed by alkylation with isopropyl iodide in order to utilize the labeled reagent more efficiently. With 1.5 equiv of deuteriomethyl iodide the deuterated ketones **9**-d_3 and **10**-d_3 were obtained in comparable yield to the unlabeled compounds.

The trans stereochemistry (**10**) assigned to the major trimethyldecalone is based upon the position of equilibrium (see above) and nmr spectral data. The nmr spectrum of the major isomer exhibits a broadened doublet of doublets (δ 2.30, J = 3, 10 Hz) for the lone α proton (**8a**), while the spectrum of the minor isomer shows a broad singlet (δ 2.30, $W_{1/2}$ = 7 Hz). The α proton of **10**, having a neighboring axial proton, is expected to be more extensively coupled.

The relatively high field position (δ 0.73) for angular methyl in the major ketone is similar to that of *trans*-**7** (δ 0.80)[11] and significantly different from that of the conformationally mobile *cis*-**7** (δ 1.05).[11] The increased proportion of trans isomer in the **9** ⇄ **10** equilibrium (1:3) compared to the *cis*-**7** ⇄ *trans*-**7** equilibrium (1:2)[11] is attributed to destabilization of the alternate conformation of **9** by a 1:3 diaxial dialkyl interaction.

That the deuteriomethyl group was introduced principally (85%) in the 2-axial position of **10**-d_3 was ascertained from the intensities of the geminal methyl peaks in the nmr spectrum. The individual signals for the three methyl groups in **10** (δ 1.17, 0.98, 0.73) may be assigned to the 2-axial, 2-equatorial, and angular methyl groups, respectively, on the basis of benzene solvent shifts ($\Delta\delta$ +0.20, −0.11, +0.11). These shifts are in accord with data for various 2-methyl ($\Delta\delta_{axial}$ +0.2 to 0.3, $\Delta\delta_{equatorial}$ −0.05 to −0.10) and

(5) For leading references see G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 301 (1966); G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(6) (a) J. F. King and P. de Mayo in "Molecular Rearrangements," Part 2, P. de Mayo, Ed., Interscience, New York, N. Y., 1964, pp 826, 827. (b) C. W. Shoppee and G. A. R. Johnston, *J. Chem. Soc.*, 3261 (1961). (c) Monocyclic analogs: J. C. Richer and P. Belanger, *Can. J. Chem.*, **47**, 3281 (1969); R. M. Delaney, S. Middleton, and W. F. Norfolk, *Aust. J. Chem.*, **23**, 1015 (1970).

(7) T. G. Halsall, E. R. H. Jones, and G. D. Meakins, *J. Chem. Soc.*, 2862 (1952).

(8) (a) H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965); (b) J. A. Berson, R. T. Luibrand, N. G. Kunda, and D. G. Morris, *J. Amer. Chem. Soc.*, **93**, 3075 (1971).

(9) R. M. Coates and R. L. Sowerby, *ibid.*, **93**, 1027 (1971).

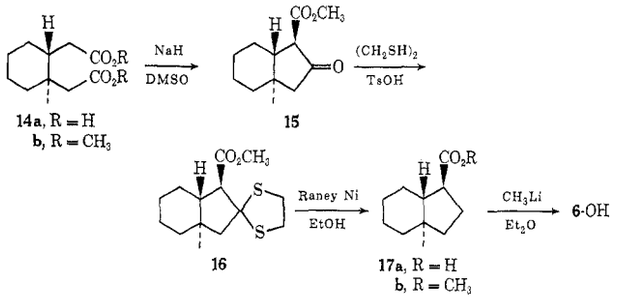
(10) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

(11) J. A. Marshall and A. R. Hochstetler, *J. Amer. Chem. Soc.*, **91**, 648 (1969).

3-methyl ($\Delta\delta_{axial}$ +0.2) cyclohexanones.[12,13] The substantial preference for axial methylation in this case is in line with the trend[14] that substitution on an enolate enhances the extent of axial alkylation.[12,14,15] The long-range steric effect of the angular methyl group may also contribute to this stereoselectivity. The stereochemistry of the hydroxyl group in the four decalols follows from the extent of coupling of the protons on carbon-bearing oxygen (**11** and **12**, s; **13** and **5**-OH, d, J = 10 Hz).

The trans fused hydrindanyl carbinol **6**-OH was independently synthesized from *trans*-1-methylcyclohexane-1,2-diacetic acid (**14a**)[16] (Scheme III). Dieckmann cyclization of the diester **14b** with sodium hydride in dimethyl sulfoxide[17] furnished a crystalline keto ester (68%) which must have structure and stereochemistry **15** judging from the nmr coupling of the proton on carbon bearing the ester group (d, J = 12.7 Hz). The ketone group was then removed by Raney nickel desulfurization of the thioketal **16**, and the resulting ester **17b** (68%) was converted to **6**-OH by reaction with methyllithium.[18]

SCHEME III



(12) (a) R. S. Mathews, S. J. Girgenti, and E. A. Folkers, *Chem. Commun.*, 708 (1970); (b) B. J. L. Huff, F. N. Tuller, and D. Caine, *J. Org. Chem.*, **34**, 3070 (1969).

(13) (a) S. Bory, M. Fétizon, P. Laszlo, and D. H. Williams, *Bull. Soc. Chim. Fr.*, 2541 (1965); (b) M. Fétizon, J. Goré, P. Laszlo, and B. Waegell, *J. Org. Chem.*, **31**, 4047 (1966); (c) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 348 (1967); (d) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 159–170.

(14) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, New York, N. Y., 1972, pp 586–595.

(15) Since the cis,trans mixture of decalones **9**-d_3 and **10**-d_3 was equilibrated with base prior to the nmr analysis, it is not possible to determine the stereoselectivity of methylation of the individual cis and trans enolate intermediates. However, in view of the high proportion of **10**-d_3 with an axial CD_3, the minimum stereoselectivity for methylation from the face opposite to the angular methyl group in one of the two isomeric enolates is 2:1 (*i.e.*, if methylation of its isomer were stereospecific in the same sense).

(16) (a) R. L. Kronenthal and E. I. Becker, *J. Amer. Chem. Soc.*, **79**, 1095 (1957); (b) G. Stork and S. D. Darling, *ibid.*, **86**, 1761 (1964).

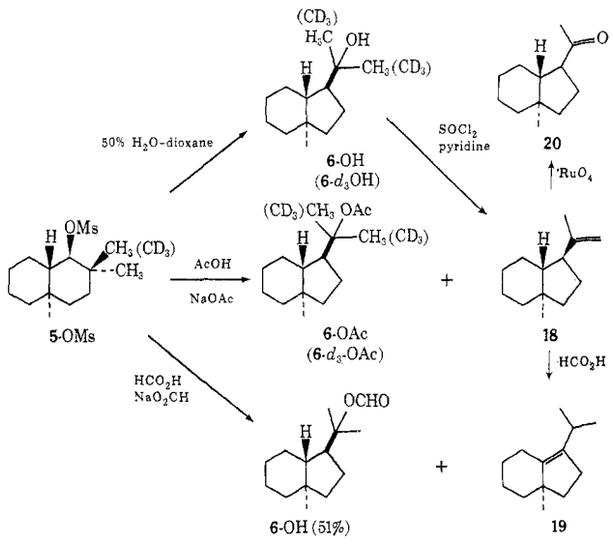
(17) I. J. Bolton, R. G. Harrison, and B. Lythgoe, *J. Chem. Soc. C*, 2950 (1971).

(18) The following less efficient and nonstereospecific routes were also investigated. (a) Ketalization of methyl 4aα-methyl-2-oxo-1α,2,3,4aα,-5,6,7,8,8aβ-decahydronaphthoate[19a] followed by lithium aluminum hydride reduction, oxidation with Collins reagent,[19b] and ketal hydrolysis with 1% hydrochloric acid in aqueous methanol gave 1-hydroxymethylene-4aα-methyl-3,4,5aα,5,6,7,8,8aβ-octahydronaphthalen-2(1*H*)-one (62% overall). Irradiation of the diazo ketone resulting from reaction with tosyl azide and triethylamine in methylene chloride (45%)[19c] in aqueous tetrahydrofuran containing sodium bicarbonate[19d] afforded an 80:20 mixture of **17b** and its 1α epimer (43%). (b) The diazo transfer reaction[19c] carried out as above with **8a** (trans:cis 57:43) provided mainly the cis fused diazo ketone (60%), photolysis of which furnished the epimeric cis isomers of **17b** (82%; 4:1 cis,syn:cis,anti). For details see Ph.D. Thesis of S. K. Chung, University of Illinois, Urbana, Ill., 1972.

(19) (a) G. Stork, P. Rosen, N. Golman, R. V. Coombs, and J. Tsuiji, *J. Amer. Chem. Soc.*, **87**, 275 (1965); (b) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970); (c) M. Regitz and J. Ruter, *Chem. Ber.*, **101**, 1263 (1968); (d) M. Regitz and J. Ruter, *ibid.*, **102**, 3877 (1969).

Solvolysis of **5**-OMs under various conditions effected efficient ring contraction to hydrindanyl derivatives (Scheme IV). The tertiary alcohol produced (80%) by

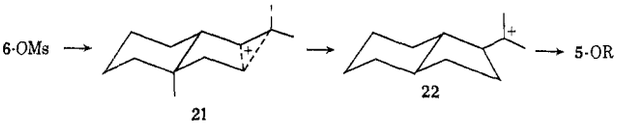
SCHEME IV



hydrolysis in 50% aqueous dioxane was identical with synthetic **6**-OH. The acetate (**6**-OAc) and formate (**6**-OCHO) obtained from acetolysis and formolysis were identified by conversion to **6**-OH. The rearranged olefin **19**, the major product from formolysis of **6**-OMs, is evidently formed by secondary isomerization of the isopropenyl hydrindan **18**.

Hydrolysis of the labeled sulfonate **5**-d_3-OMs gave rise to **6**-d_3-OH in which the two methyl groups had become equivalent. The nmr spectrum of **6**-d_3-OH in the presence of europium trisdipivaloylmethane revealed two separate, equally intense resonances (δ 2.94 and 3.04) for the diastereotopic side chain methyl groups. Similarly the acetate (**6**-d_3-OAc) obtained from acetolysis of **5**-d_3-OMs had the deuterium label equally distributed between the geminal methyl groups.

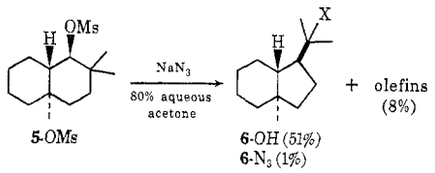
The complete scrambling of the methyl groups in the solvolyses of **5**-d_3-OMs establishes that the bridged ion **21** cannot be the sole carbonium ion intermediate in the ring contraction rearrangement. Evidently the bridged species **21**, which must exist along the reaction pathway either as a transition state or a transient intermediate, proceeds to the more stable, classical tertiary ion **22**



prior to solvent capture. The distinction between the two diastereotopic methyl groups may then be lost either by rapid rotation about the exocyclic single bond, or a nonspecific reaction of **22** with a solvent molecule from its two nonequivalent faces.

In view of the documented examples of stereoselective capture of potentially symmetrical tertiary carbonium ions,[8] we investigated other means for faster interception of the carbonium ion intermediate. One approach involved rearrangement in the presence of the highly nucleophilic azide ion. Since the efficiency of azide trapping with *tert*-butyl chloride is relatively high

(k_{N_3}/k_{H_2O} = 74),[20] we hoped that with high concentrations of azide the carbonium ion would be captured as the hydrindanyl azide **6**-N_3. In practice, however, hydrolysis of **5**-OMs in 50% aqueous acetone containing 2 *M* sodium azide gave only 5% of **6**-N_3. The value of

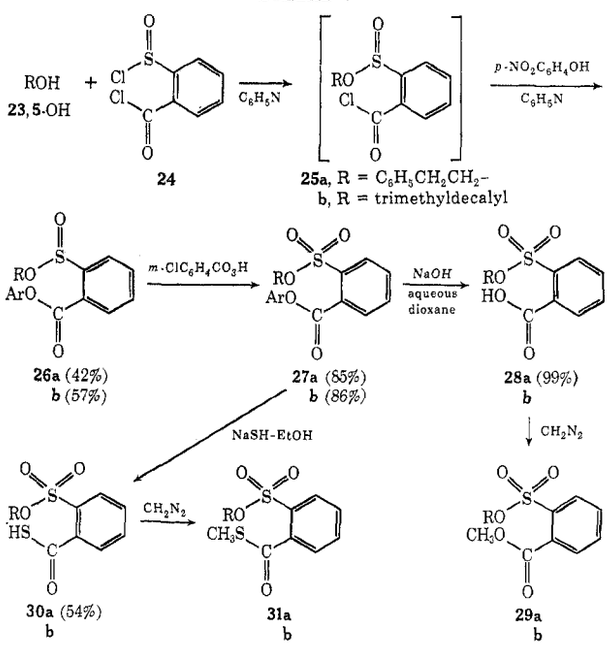


k_{N_3}/k_{H_2O} (determined with 0.1 *M* sodium azide) is 2.5, considerably less than the value for *tert*-butyl chloride cited above. The large decrease is probably attributable to the change in leaving group and indicates once again that azide trapping may involve ion pair intermediates.[20,21]

Another method which has been employed for more rapid interception of carbonium ions involves the use of a leaving group bearing a second, more nucleophilic site.[22] We considered that the *o*-carboxybenzenesulfonate or *o*-thiocarboxybenzenesulfonate might be successful in the present case in view of the proximity of the relatively nucleophilic carboxylate or thiocarboxylate group to the carbonium ion site. Since the hydroxyl group in **5**-OH is too sterically hindered to permit direct conversion to the tosylate with tosyl chloride,[23] an indirect, three-step route *via* a mixed sulinate carboxylate diester was developed in order to introduce these bidentate leaving groups (Scheme V).

The reaction between 1 equiv of either 2-phenylethanol (**23**) or the trimethyldecalol **5**-OH and *o*-chlorosulfinylbenzoyl chloride (**24**)[26] in the presence of *pyridine* occurs selectively at the sulfinyl function. The resulting *o*-(alkoxysulfinyl)benzoyl chlorides (**25**) are converted directly to the *p*-nitrophenyl esters (**26**) by treatment with *p*-nitrophenol. The sulfinates are then oxidized[27] to the *o*-carboxysulfonates (**27**), which upon alkaline hydrolysis in aqueous dioxane or sulfhydrolysis with sodium hydrosulfide in ethanol[28,29] liberate the *o*-carboxybenzenesulfonates (**28**) and *o*-thiocarboxybenzenesulfonates (**30**), respectively.[30] The latter were reesterified with diazomethane for characterization.

SCHEME V



The ready loss of the *p*-nitrophenyl group in the hydrolyses of **27** and the incorporation of the sulfhydryl group in the sulfhydrolyses provides proof that the alkoxy group (RO) from the original alcohols is in fact bound to sulfur. Hydrolysis or sulfhydrolysis of the isomer of **27** (R and Ar exchanged) at the ester function would give a carboxylic acid retaining the *p*-nitrophenyl moiety. In the alternative event of aryl oxygen cleavage at the sulfonate group of the isomer, a common, presumably water soluble, sulfonic acid would have been formed from both hydrolysis and sulfhydrolysis.

The greater reactivity of the chlorosulfinyl group over the acyl chloride function of **24** is noteworthy. The facile formation of the *o*-carboxysulfonate of the hindered trimethyldecalol **5**-OH indicates that the method is relatively insensitive to steric hindrance.

Acetolysis of the carboxysulfonate **28b** in the presence of sodium acetate afforded **6**-OAc (13%) and olefin **18** (51%) as the major products (Scheme VI). Similarly hydrolysis of the thiocarboxysulfonate **30b** led to the ring-contracted alcohol **6**-OH (51%) and olefin **18** (17%). It is clear from these results that the major reaction pathway is a normal solvolysis of both **28b** and **30b**. Although relatively small amounts of the internal return isomers **31** could have been formed in these reactions, the amount would have been insufficient for a deuterium-labeling experiment to be feasible. Evidently ion pair dissociation is faster than internal return. The possibility that the major products are formed by subsequent ionization of an intermediate hydrindanyl benzoate (**31**) is rendered unlikely by control experiments. *tert*-Butyl benzoate was recovered from the acetolysis medium while *tert*-butyl thiolbenzoate was stable for a prolonged period in 50% aqueous dioxane at 105°. Since the σ values for the sulfonate anion are quite small (σ_m = 0.05, σ_p = 0.09),[31] the presence of the sulfonate group in **31** should not unduly alter the reactivity, unless there is a special proximity effect due to its ortho position.

(20) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4821 (1971).

(21) C. D. Ritchie, *ibid.*, **93**, 7324 (1971); D. Kovačević, Z. Majeraski, S. Borčić, and D. E. Sunko, *Tetrahedron*, **28**, 2469 (1972).

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(30) Attempts to prepare the *o*-(alkoxysulfinyl)benzoic acids by hydrolysis of the acid chloride group of *o*-(alkoxysulfinyl)benzoyl chlorides (**3**) afforded *o*-(hydroxysulfinyl)benzoic acid as the only acidic product. Evidently hydrolysis of the sulfinate is very rapid owing to intramolecular assistance by the neighboring free carboxyl group.

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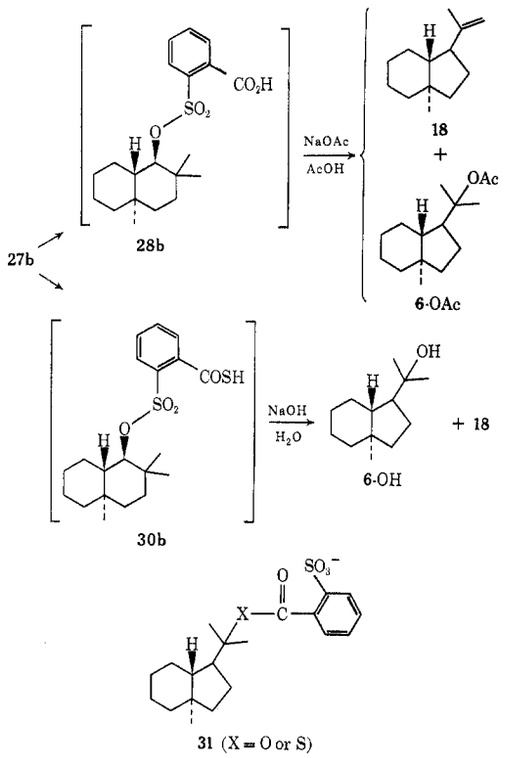
SCHEME VI



In closing it is appropriate, albeit highly speculative, to consider briefly means by which the biosynthetic enzyme(s) could maintain the stereospecifity expressed in Scheme I. One obvious possibility is for the active site to fix the side chain in a particular conformation and thus restrict rotation about the 17,20 bond until either reaction with a water molecule or cyclization into the terminal double bond occurs. A specific, clockwise, 90° rotation of the side chain would set the stage for 17 → 20 hydride shift and backbone rearrangement to **3**. Temporary attachment to a nucleophilic site (X) within the active site as suggested by Cornforth[4a] offers a second possible mechanism for stereochemical control. This explanation would require either formal front-side nucleophilic attack by the X group on **1** (*i.e.*, from the bridged face) followed by a "normal" inversion or "normal" back-side attack on **1** followed by a formal front-side replacement of the X group.

A recent investigation (subsequent to the original submission of this manuscript)[32] has established that the related ring contraction rearrangement of 4β-dueteriomethyl-4α-methylandrostane-3β,17β-diol 17-acetate (phosphorus pentachloride in hexane) and the corresponding tosylate (sodium acetate, acetic acid) to 3-isopropylidene-*A*-norandrostan-17β-ol acetate proceeds stereospecifically, maintaining the integrity of the geminal methyl groups in the overall reactions. As noted above, this well-known rearrangement[6] differs significantly from the bicyclic model examined here; the dimethylandrostane precursors possess a 1,3-diaxial steric interaction in ring A not present in **5**-OMs and the intermediate (or incipient) carbonium ion(s) from the androstane precursors has a trans,syn stereochemistry of positions 10, 5, and 3 of the *A*-norandrostane ring system. Nevertheless, it is surprising that these reactions are stereospecific. Perhaps the proton elimination occurs earlier along the reaction coordinate (*e.g.*, ion pair) while the substitution reaction giving **6**-OAc occurs later (*e.g.*, dissociated ions).

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Experimental Section[33]

4αβ-Methyl-2-*n*-butylthiomethylene-3,4,4aβ,5,6,7,8a(α and β)-octahydronaphthalen-1(2*H*)-ones (8b).—A solution of 41.5 g (250 mmol) of the isomeric decalones **7** in 800 ml of benzene was slowly added with stirring to hexane-washed sodium hydride (24 g of 60% oil dispersion, 600 mmol).[10] After 30 min, ethyl formate (55 g, 750 mmol) and 20 drops of methanol were slowly introduced. After 14 hr at room temperature (nitrogen atmosphere), water (300 ml) and ether (300 ml) were added. The organic layer was separated and washed four times with 5% sodium hydroxide. The combined aqueous phase was acidified and thoroughly extracted with ether. The ether extracts were washed, dried, and evaporated to give 45.7 g (94%) of the hydroxymethylene derivative **8a** as a yellow, viscous oil: ir 1130 1580, 1635, 1710, 2500–3500 cm^{-1}; nmr δ 0.88 (cis) and 0.98 (trans) (2 s, total 3 H, C-4 CH_3), 8.04 (cis), and 8.64 (trans) (2 s, total 1 H, =CHOH). The ratio of cis/trans was 43:57 (by nmr).

A solution of 45 g (231 mmol) of **8a**, 21.6 g (240 mmol) of *n*-butanethiol, and 3 g of *p*-toluenesulfonic acid in 500 ml of benzene was refluxed with removal of water (Dean–Stark separator) for 3 hr.[10] After cooling, the benzene solution was successively washed with 800 ml of 5% sodium hydroxide, water, and brine, dried, and evaporated to give 58.5 g (95%) of the *n*-butylthiomethylene derivative **8b** as a dark yellow oil: ir 1545, 1660 cm^{-1}; nmr δ 0.85 and 1.0 (2 s, 3 H total), 7.25–7.40 (m, 1 H).

2,2,4a(α and β)-Trimethyl-2,3,4,4aβ,5,6,7,8-octahydronaphthalen-1(8aβ*H*)-ones (9 and 10).—A solution of 17 g (64 mmol) of **8b** and 2.34 g (130 mmol) of water in 300 ml of ether was added to a refluxing solution of 2.7 g (384 mmol) of lithium in 1.2 l. of liquid ammonia over 40 min with efficient stirring.[9] After an additional 1 hr, 57 g (400 mmol) of methyl iodide in 300 ml of ether was added and the stirring was continued for 30 min before the addition of 25 g of ammonium chloride. Evaporation of ammonia followed by a standard extractive work-up[33] with ether gave 13 g of tan-colored oil. The crude product was equilibrated in a solution of 3 g of sodium methoxide in 200 ml of methanol over 11 hr at room temperature. An extractive work-up[33] followed by column chromatography on silica gel afforded 8.35 g (67%) of an epimeric mixture of decalones **9** and **10** (eluted with 3% ether in hexane). The ratio of trans/cis at equilibrium was 3:1 in favor of trans by nmr and glpc (column D, 160°) analyses. For further characterization see below.

2α,4a(α and β)-Dimethyl-2β-trideuteriomethyl-2,3,4,4aβ,5,6,7,8-octahydronaphthalen-1(8aβ*H*)-ones (9-d_3 and 10-d_3).—A solution of 6.6 g (24.8 mmol) of **8b** and 894 mg (49.6 mmol) of water in 100 ml of ether was added to a refluxing solution of 1.04 g (148 mmol) of lithium in 500 ml of ammonia as above. After an ad-

(33) Melting points were taken in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Spectra were recorded on the following instruments: Perkin-Elmer Model 137 or 521 ir spectrophotometers; Varian Associates Model A-60A, A-56/60, HA-100, or HR 220 nmr spectrophotometers; Atlas CH_4, MAT CH-5, or MAT-SM-1B mass spectrometers. All nmr spectra were determined in deuterated chloroform unless otherwise specified and chemical shifts are reported as δ values using tetramethylsilane as internal standard. Refractive indices were measured on an Abbe refractometer. Combustion analyses were performed in the University of Illinois Microanalytical Laboratory. The gas chromatographic (glpc) analyses were performed with a Hi-Fe Model 600-D or a Varian Aerograph Model A90-P3 instrument using the following columns: A, 5 ft × 0.125 in., 5% SE-30 on 60/80 mesh DMCS Chromosorb W; B, 5 ft × 0.125 in., 5% Carbowax 20M on 60/80 mesh SMCS Chromosorb W; C, 5 ft × 0.125 in., 5% Apiezon L on 60/80 mesh SMCS Chromosorb W; D, 5 ft × 0.125 in., 5% FFAP on 60/80 mesh DMCS Chromosorb W; E, 5 ft × 0.375 in., 15% FFAP on 60/80 mesh DMCS Chromosorb W; F, 6 ft × 0.375 in., 20% SE-30 on 60/80 mesh DMCS Chromosorb W; G, 6 ft × 0.375 in., 15% Apiezon L on 60/80 mesh DMCS Chromosorb W. The standard extractive work-up procedure consisted of pouring into a large amount of water, extracting with the organic solvent indicated, washing the combined extracts successively with water and brine, drying the extract on anhydrous sodium sulfate, and evaporating the solvent.

ditional 15 min, the blue color of the solution was titrated by very careful addition of methyl iodide, and then 4.22 g (24.8 mmol) of isopropyl iodide in 50 ml of ether was added in one portion. After 1 hr, 5.4 g (37.2 mmol) of trideuteriomethyl iodide in 50 ml of ether was added. The solution was stirred for 20 min and the same isolation and purification procedure as described above was followed, yielding 3.5 g (72%) of the labeled ketone mixture 9-d_3 and 10-d_3.

2,2,4aβ-Trimethyl-1,2,3,4,4aβ,5,6,7,8,8a(α and β)-decahydronaphthalen-1α-ol (11 and 12).—The epimeric mixture of 9 and 10 (10.6 g, 54.6 mmol) was reduced with 4.15 g (108.5 mmol) of lithium aluminum hydride in 400 ml of ether over 2.5 hr at room temperature and 1 hr at reflux temperature. The excess hydride was destroyed by cautious addition of 5% hydrochloric acid and the alcohol mixture (10.6 g) isolated by ether extraction was chromatographed on 300 g of silica gel. The trans-axial alcohol (12, 7.29 g, 68%) was first eluted with 3% ether in hexane and was immediately followed by the cis-axial alcohol (11, 1.7 g, 16%): nmr δ 0.94 (s, 3 H, C-4a CH_3), 0.98 [s, 6 H, $C(CH_3)_2$], 3.64 (br s, 1 H, CHOH).

The less polar alcohol (12) had the following spectral properties: nmr δ 0.96 [s, 6 H, $C(CH_3)_2$], 1.03 (s, 3 H, C-4a CH_3), 3.17 (s, 1 H, CHOH); ir 3500 cm^{-1}; mass spectrum *m/e* (rel intensity 196 (M^+, 11), 178 (20), 163 (18), 125 (81), 109 (100).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.56; H, 12.21.

2,2,4aα-Trimethyl-2,3,4,4aα,5,6,7,8-octahydronaphthalen-1-(8aβH)-one (10).—To a solution of 7.29 g (37 mmol) of decalol 12 in 15 ml of acetone was added 14.3 ml of Jones reagent.[34] After 30 min at room temperature, a standard extractive work-up[33] with ether gave 7.21 g (100%) of the liquid ketone **10**. An analytical sample was obtained by preparative glpc (column E, 170°): $n^{24.5}D$ 1.4782; ir 1705 cm^{-1}; nmr (CCl_4) δ 0.73 (s, 3 H, C-4a CH_3), 0.98 (s, 3 H, equatorial C_2 CH_3), 1.17 (s, 3 H, axial C_2 CH_3); nmr (C_6H_6) δ 0.62 (s, 3 H, C-4a CH_3), 0.97 (s, 3 H, axial C_2 CH_3), 1.09 (s, 3 H, equatorial C_2 CH_3).

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.22; H, 11.13.

2,2,4aβ-Trimethyl-2,3,4,4aβ,5,6,7,8-octahydronaphthalen-1-(8aβH)-one (9) was similarly obtained from 11 and displayed the following properties after preparative glpc (column E, 170°): $n^{24.5}D$ 1.4810; ir 1700 cm^{-1}; nmr (CCl_4) δ 1.0 (s, 3 H, equatorial C_2 CH_3), 1.13 (s, 6 H, C-4a CH_3 and axial C_2 CH_3); nmr (C_6H_6) δ 0.94 (s, 6 H, C-4a CH_3 and axial C_2 CH_3), 1.09 (s, 3 H, equatorial C_2 CH_3).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.22; H, 11.05.

2,2,4aβ-Trimethyl-1,2,3,4,4aβ,5,6,7,8,8aβ-decahydronaphthalen-1β-ol (13).—Reduction of 9 with lithium in ammonia as described below for 10 afforded the cis-fused decalol 13: mp 62–64°; ir 3500 cm^{-1}; nmr δ 0.85 (s, 3 H), 1.0 (s, 6 H), 3.47 (d, J = 10 Hz, 1 H, CHOH).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.33; H, 12.12.

2,2,4aα-Trimethyl-1,2,3,4,4aα,5,6,7,8,8aβ-decahydronaphthalen-1β-ol (5-OH).—A solution of 7.1 g (36.8 mmol) of 10 and 1.4 g (77.5 mmol) of water in 300 ml of ether was added to a refluxing solution of 1.03 g (147 mmol) of lithium in 1 l. of ammonia over 20 min with rapid stirring. After an additional 30 min, 8 g (149 mmol) of ammonium chloride was cautiously added. Evaporation of the ammonia followed by the standard extractive work-up with ether[33] gave 7.1 g (98%) of the alcohol 5-OH: mp 66–68°; ir 3500 cm^{-1}; nmr δ 0.83 (s, 3 H, C-4aα CH_3), 0.88 (s, 3 H, axial C_2 CH_3), 1.00 (s, 3 H, equatorial C_2 CH_3), 3.10 (d, J = 10 Hz, 1 H, CHOH).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.25; H, 12.19.

2,2,4aα-Trimethyl-1,2,3,4,4aα,5,6,7,8,8aβ-decahydronaphthalen-1β-ol Methanesulfonate (5-OMs).—A solution of 1.76 g (15.3 mmol) of methanesulfonyl chloride in 50 ml of benzene was slowly added to a solution of 3 g (15.3 mmol) of 5-OH and 1.62 g (16 mmol) of triethylamine in 50 ml of benzene at 0°.[35] After 2 hr at room temperature the precipitate was filtered and washed with benzene; the combined benzene filtrate was washed with 5% hydrochloric acid, water, and brine and then dried and evaporated to give 3.9 g (93%) of methanesulfonate 5-OMs as a viscous oil: nmr δ 0.88 (s, 3 H, C-4aα CH_3), 0.98 (s, 3 H, axial C_2 CH_3), 1.08 (s, 3 H, equatorial C_2 CH_3), 3.02 (s, 3 H, OSO_2CH_3), 4.42 (d, J = 11 Hz, 1 H, $CHOSO_2CH_3$).

2α,4aα-Dimethyl-2β-trideuteriomethyl-1,2,3,4,4aα,5,6,7,8,8aβ-decahydronaphthalen-1β-ol methanesulfonate (5-d_3-OMs) was prepared from the labeled mixture of ketones 9 and 10 in the same way as described for the nonlabeled compounds. The nmr spectra of the labeled compounds are the same as those of the nonlabeled ones except for the intensities of the C-2β CH_3 peaks: 10-d_3 (equatorial C_2 CH_3:axial C_2 CH_3 ~2.5H:0.5H); 5-d_3-OH (equatorial C_2 CH_3:axial C_2 CH_3 ~2.5H:0.5H); 5-d_3-OMs (equatorial C_2 CH_3:axial C_2 CH_3 ~2.5H:0.5H).

4aβ-Methyl-3,4,4aβ,5,6,7,8,8aα-octahydronaphthalen-2(1H)-one was prepared from 4a-methyl-4,4a,5,6,7,8-hexahydronaphthalene-2(3H)-one[36a] according to a literature procedure[36b] in 95% yield: bp 76–78° (0.2 mm) [lit.[36b] bp 73–80° (0.1 mm)]; ir 1715 cm^{-1}; nmr (CCl_4) δ 1.05 (s, 3 H).

Dimethyl-*trans*-1-methylcyclohexane 1,2-Diacetate (14b).[37a,b]—Concentrated nitric acid (230 ml) was heated to boiling (~110°), and 23.2 g (0.142 mol) of 4aβ-methyl-3,4,4aβ,5,6,7,8,-8aα-octahydronaphthalen-2(1H)-one was very slowly added. During the addition period, the oil bath was removed, and the temperature was kept over 90°[37c] by controlling the rate of addition. Ten minutes was allowed at reflux temperature after addition was over. Water (100 ml) was added, and the solution was refluxed for 30 min. A crystalline product was obtained upon cooling the mixture in an ice bath. Recrystallization from 50% aqueous acetic acid gave 11 g (37%) of *trans*-1-methylcyclohexane-1,2-diacetic (14a) acid, mp 190–195° (lit.[37a] mp 192–194°).

The dimethyl ester 14b was prepared by treatment with diazomethane in ether: ir 1725 cm^{-1}; nmr (CCl_4) δ 0.92 (s, 3 H), 3.60 (s, 3 H), 3.61 (s, 3 H).

Methyl 3aα-Methyl-2-oxo-3aα,4,5,6,7,7aβ-hexahydroindan-1β-carboxylate (15).—A slurry of 38 g (0.157 mol) of diester 14b and 18.8 g (0.47 mol) of 60% sodium hydride (hexane washed) in 2 l. of DMSO was heated at 85° for 4 hr.[17] After cooling, the mixture was acidified with concentrated hydrochloric acid and thoroughly extracted with ether. The combined extracts were treated with diazomethane, dried, and evaporated, and the resulting solid was recrystallized from hexane to yield 22.5 g (68%) of β-keto ester 15: mp 70–74°; ir 1720, 1750 cm^{-1}; nmr δ 0.95 (s, 3 H, CH_3), 2.18 (s, 2 H), 2.98 (d, J = 12.7 Hz, 1 H, C-1α H), 3.74 (s, 3 H, CO_2CH_3).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.52; H, 8.56.

Methyl 3aα-Methyl-3aα,4,5,6,7,7aβ-hexahydroindan-1β-carboxylate (17b).—A solution of 30 g (0.143 mol) of keto ester 15, 19 g (0.202 mol) of ethanedithiol, and 14 g of *p*-toluenesulfonic acid in 220 ml of acetic was stirred for 26 hr at room temperature. A standard extractive work-up with ether[33] gave 38.7 g (94%) of oily thioketal 16 which slowly solidified: mp 75–77° (recrystallized from hexane); ir 1725 cm^{-1}; nmr δ 0.99 (s, 3 H, CH_3), 2.24 (d, J = 13 Hz, C-1α H), 2.8–3.5 (m, 4 H, $-SCH_2CH_2S-$), 3.70 (s, 3 H, CO_2CH_3).

A mixture of 38.6 g (0.135 mol) of 16 and 160 g of freshly prepared W-2 Raney nickel[38] in 750 ml of ethanol was stirred for 2 hr at room temperature and for 5 hr at reflux temperature. The slurry was filtered and washed with ethanol. The combined filtrate and washing was concentrated, and the residue was redissolved in ether. The ether solution was washed with water and brine, dried, and evaporated to give a crude oily product. Chromatography on silica gel effected separation of ester 17b (18 g, 68%, elution with 10% ether–hexane) from a more polar material (9 g) corresponding in R_f value to starting ketal.

Further purification was carried out on ester similarly obtained from a small scale, preliminary desulfurization. Since glpc analysis indicated the presence of two minor impurities (~10% each), the analytical specimen of ester 17b was purified by preparative glpc (column E, 160°): ir 1720 cm^{-1}; nmr δ 0.77 (s, 3 H, CH_3), 3.66 (s, 3 H, CO_2CH_3). The appearance of small

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(37) (a) R. L. Kronenthal and E. I. Becker, *J. Amer. Chem. Soc.*, **79**, 1095 (1957); (b) G. Stork and S. D. Darling, *ibid.*, **86**, 1761 (1964); (c) B. A. Ellis, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 18.

(38) R. Mozingo, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 181.

extraneous signals [δ 0.85 (s), 3.66 (s), 5.68 (2 d, J = 1.5 Hz, 6), 5.97 (2 d, J = 2.5 Hz; 6)] in the nmr spectrum of this collected sample, however, reveals the presence of a minor (~15–20%) contaminant.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.29; H, 10.06.

3aα,4,5,6,7aβ-Hexahydro-3aα-methyl-1β-indanyldimethylcarbinol (6-OH).—Methyllithium (3 mmol) in ether was added to ester **17b** (~60 mg, 0.32 mmol) in 4 ml of ether and the solution was heated under reflux for 5 hr. Addition of saturated ammonium chloride solution followed by an extractive work-up with ether gave ~68 mg (97%) of oily alcohol **6-OH** which compared satisfactorily with a sample obtained from hydrolysis of **5-OMs** [nmr, tlc, and glpc (column D, 150°) comparisons]. For characterization data, see below.

Solvolyses of Methanesulfonates 5-OMs and 5-d_3-OMs. A. Hydrolyses.—A solution of 600 mg (2.2 mmol) of **5-OMs** in 300 ml of aqueous dioxane (1:1 by volume) containing 1.0 g (10 mmol) of calcium carbonate was heated under reflux for 24 hr. After cooling, the solution was saturated with sodium chloride. The mixture, obtained after a standard extractive work-up with ether,[33] was chromatographed on 35 g of silica gel. The hydrocarbon mixture (10% yield) was eluted with hexane and found to consist of predominantly olefin **18**: ir 3100, 1640, 890 cm^{-1}; nmr δ 0.79 (s, 3 H, CH_3), 1.6 (t, J = 1 Hz, 3 H, $=CCH_3$), 4.60 (q, J = 1 Hz, 2 H, $=CH_2$).

The alcohol **6-OH** (80%) was eluted with 5% ether in hexane: ir 3620 cm^{-1}; nmr δ 0.80 (s, 3 H, C-3a CH_3), 1.19 [s, 6 H, C-$(CH_3)_2$]; nmr (with 0.2 molar equiv of europium trisdipivalomethane) δ 1.12 (s, 3 H, C-3a CH_3), 2.94 and 3.04 [2 s, 3 H, $C(CH_3)_2$].

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.30; H, 12.17.

The *p*-nitrobenzoate of **6-OH** had mp 95–97°; nmr δ 0.87 (s, 3 H, C-3a CH_3), 1.6 (s, 6 H), 8.1–8.5 (quartet, 4 H, ArH).

Hydrolysis of the labeled substrate (**5-d_3-OMs**) was performed in exactly the same manner as described for **5-OMs**. The nmr spectrum of the resulting tertiary alcohol **6-d_3-OH** in the presence of 0.2 molar equiv of europium trisdipivalomethane showed the diastereotopic methyl peaks at δ 2.95 and 3.04 with essentially equal intensities (94:100).

B. Acetolyses.—A solution of 500 mg (1.82 mmol) of **5-OMs** in 50 ml of acetic acid containing 820 mg (10 mmol) of sodium acetate was kept at ~75° for 5 hr 20 min. A standard extractive work-up[33] followed by chromatography on 12 g of silica gel gave a hydrocarbon mixture (72 mg, 22%, eluted with hexane) consisting of olefins **18** and **19** (83:17 by glpc) and acetate **6-OAc** (160 mg, 37%, eluted with 2% ether in hexane): ir 1725 cm^{-1}; nmr δ 0.79 (s, 3 H, C-4a CH_3), 1.40 and 1.42 [each s, 3 H, C-$(CH_3)_2$], 2.08 (s, 3 H, OAc). The acetate was treated with $LiAlH_4$, and the resulting alcohol was identical with **6-OH** by glpc (column D) and nmr analyses.

A solution of 548 mg (2 mmol) of the labeled methanesulfonate **5-d_3-OMs** in 50 ml of acetic acid containing 820 mg (10 mmol) of sodium acetate was kept at ~75° for 5 hr (acetolysis was not complete). Work-up identical with that discussed above gave a hydrocarbon mixture (120 mg, 34%) and the acetate (115 mg, 24%). The ester was cleaved with $LiAlH_4$ and the nmr spectrum of the alcohol was determined in the presence of the europium shift reagent as described above. Again the intensities of the shifted methyl signals were essentially equal (91:100).

C. Formolysis.—A solution of 548 mg (2 mmol) of **5-OMs** in 50 ml of formic acid (0.04 M concentration) containing 680 mg (10 mmol) of sodium formate was stirred for 80 min at room temperature. A standard extractive work-up with ether,[33] followed by treatment with 5% methanolic potassium hydroxide (1 hr at reflux), and a silica gel chromatography gave mainly hydrocarbon (46%) and alcohol **6-OH** (17%). The structure of the hydrocarbon was assigned as **19** based on nmr: δ 0.93 and 0.98 [each d, J = 7 Hz, 3 H, $CH(CH_3)_2$], 0.98 (s, 3 H, C-4a CH_3). The same olefin **19** was obtained from **18** by treatment with formic acid containing sodium formate at room temperature for 90 min in *ca.* 70% yield.

3aα,4,5,6,7,7aβ-Hexahydro-3aα-methyl-1β-indanyl Methyl Ketone (20).—To a solution of 2 g (10.2 mmol) of **6-OH** in 13.5 ml of pyridine was added 2.48 g (20.4 mmol) of thionyl chloride at 0°. The solution was stirred for 13 min at 0° and poured into 135 ml of ice–water. The standard extractive work-up with petroleum ether[33] (bp 30–60°) followed by chromatography on silica gel gave 1.25 g (68%) of colorless oil (eluted with hexane). The major product (88%) was separated from two minor products (12%) by preparative glpc (column G, 135°) and identified as **18** by nmr comparison.

The olefin mixture (500 mg, 2.8 mmol) in 25 ml of acetone and 2 ml of carbon tetrachloride was added slowly to a yellow solution of ruthenium dioxide dihydrate (475 mg, 2.80 mmol) and sodium periodate (3 g, 14 mmol) in 60 ml of water.[39] Two additional 3-g portions of periodate were added to the reaction at 12 and 17 hr, then at 18 hr isopropyl alcohol (~30 ml) was added. After 1 hr with stirring the precipitate was filtered and washed with acetone and ether. The filtrate was concentrated and diluted with ether, and the product (350 mg) was isolated by a standard extractive work-up. Chromatography on silica gel afforded the methyl ketone **20** (250 mg, 50%): nmr δ 0.80 (s, 3 H, C-3a CH_3), 2.14 (s, 3 H, $COCH_3$).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.87; H, 11.15.

Hydrolysis of 5-OMs in the Presence of Sodium Azide. A.—A solution of 274 mg (1 mmol) of **5-OMs** and 650 mg (10 mmol) of freshly recrystallized sodium azide[20] in 100 ml of 80% aqueous acetone (water–acetone 20–80, v/v before mixing) was heated under reflux for 46 hr. The acetone solvent was partially evaporated and a standard extractive work-up with ether was followed.[33] The oily product was chromatographed in 12 g of silica gel, affording 17 mg of a mixture of olefins (8%) and alkyl azide **6-N_3** (1%) (eluted with hexane). From glpc analysis (column B, 100°) the relative ratio of alkyl azide:olefins:tertiary alcohol was estimated as 1.9:13.4:84.7, and the ratio of $k_{N_3^-}/k_{H_2O} \cong 2.5$.[20]

B.—A solution of 274 mg (1 mmol) of **5-OMs** and 6.5 g (100 mmol) of freshly recrystallized sodium azide in 50 ml of 50% aqueous acetone was heated under reflux for 6.7 hr and worked up as described in A. The ir (2100 cm^{-1}) absorbance of the alkyl azide was about 5.6 times stronger than that above. A pure sample of azide **6-N_3** was obtained by preparative glpc (column E, 162°): ir 2100 cm^{-1}; nmr δ 0.78 (s, 3 H, C-3 CH_3), 1.20 and 1.27 [each s, 3 H, $C(CH_3)_2$]; mass spectrum m/e (rel intensity) 179 ($M^+ - N_3$, 4), 178 ($M^+ - HN_3$, 4), 137 [$M^+ - N_3C(CH_3)_2$, 26], 95 (62), 81 (100).

***o*-Chlorosulfinylbenzoyl chloride (24)** was prepared according to the literature procedures[26] in 96% yield, mp 58–62° (lit. mp 62–64°). The dichloride decomposes upon storage.

2-Phenylethyl [*o*-Carbo(*p*-nitrophenoxy)]benzenesulfonate (27a).—A solution of 3.67 g (30 mmol) of freshly distilled 2-phenylethanol (**23**), 2.37 g (30 mmol) of pyridine, and 6.7 g (30 mmol) of the sulfinyl chloride **24** in 60 ml of ether was stirred for 35 min at 0°; then 2.37 g (30 mmol) of pyridine and a solution of 4.17 g (30 mmol) of *p*-nitrophenol in 40 ml of ether were added successively. The mixture was stirred for 2 hr at 0°, then diluted with chloroform. The solution was washed with 5% potassium carbonate, saturated sodium bicarbonate, and water, then dried (Na_2SO_4) and evaporated. The resulting oil crystallized from acetone to give 5.1 g (42%) of the sulfinate **26a**: mp 120–123°; ir 1700, 1620, 1590, 1530, 1495, 1355 cm^{-1}; nmr δ 2.87 (t, J = 7 Hz, 2 H, $PhCH_2$), 3.7–4.4 (m, 2 H, CH_2OSO_2Ar), 7.23 and 8.21 (each d, J = 9.5 Hz, 2 H, *p*-nitrophenyl), 7.4–8.0 (m, 4 H, ArH).

Anal. Calcd for $C_{21}H_{17}NSO_6$: C, 61.31; H, 4.14; N, 3.41; S, 7.79. Found: C, 60.91; H, 4.33; N, 3.25; S, 7.91.

A solution of sulfinate **26a** (4.11 g, 10 mmol) and 85% *m*-chloroperoxybenzoic acid (2.22 g, 11 mmol) in 85 ml of methylene chloride was allowed to stand for 5 hr at room temperature.[27] After extraction with 5% potassium carbonate and water, the solution was dried (Na_2SO_4) and evaporated. The initially oily sulfonate **27a** (85%) crystallized upon storage overnight in a refrigerator: mp 74–78° (from acetone); ir 1710, 1620, 1595, 1530, 1495, 1365, 1345 cm^{-1}; nmr (CCl_4) δ 2.90 (t, J = 7 Hz, 2 H, $PhCH_2$), 4.26 (t, J = 7 Hz, 2 H, CH_2OSO_2Ar), 7.01 (br s, 5 H, phenyl), 7.30 and 8.12 (each d, J = 10 Hz, 2 H, *p*-nitrophenyl), 7.4–8.0 (m, 4 H, ArH).

2,24aα-Trimethyl-1,2,3,4,4aα,5,6,7,8,8aβ-decahydronaphthalen-1β-yl [*o*-Carbo(*p*-nitrophenoxy)]benzensulfonate (27b).—To a solution of 1.96 g (10 mmol) of decalol **5-OH** and 791 mg (10 mmol) of pyridine in 50 ml of ether at 10° was added 2.7 g (12 mmol) of freshly prepared sulfinyl chloride **2** in one portion. The mixture was stirred for 1 hr at room temperature, and then

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791 mg (10 mmol) of pyridine and 1.3 g (10 mmol) of *p*-nitrophenol were added in succession. The reaction mixture was stirred vigorously for an additional 2 hr at room temperature. The precipitate was filtered and washed with ether. The combined ether solution was washed with 0.1 *N* sodium carbonate and saturated sodium bicarbonate until no yellow color was observed in the washing, and then with water and brine. The ether solution was dried and evaporated and the residue was chromatographed on 100 g of silica gel, yielding 2.75 g (57%) of the amorphous sulfinate **26b** (eluted with 20% ether in hexane): ir 1740, 1580, 1608, 1520, 1340, 1132 cm^{-1}; nmr (CCl_4) δ 0.83 (s, 3 H), 0.88 (s, 3 H), 1.0 (s, 3 H), 3.90 [d, J = 10 Hz, 1 H, CHOS(O)-Ar], 7.42 and 8.31 (each d, 2 H, *p*-nitrophenyl), 7.3–8.4 (m, 4 H, ArH).

A solution of 1.16 g (5.7 mmol) of 85% *m*-chloroperbenzoic acid in 30 ml of methylene chloride was added to a solution of 2.75 g (5.7 mmol) of sulfinate **4b** in 20 ml of methylene chloride at 0°.[27] The resulting solution was stirred for 12 hr at room temperature and then chilled to 0° to induce precipitation. After filtration, the filtrate was evaporated and redissolved in hexane and ether. The organic phase was successively washed with 0.1 *N* sodium carbonate, saturated sodium bicarbonate, and water, dried, and evaporated at room temperature to give 2.45 g (86%) of the crystalline sulfonate **27b**: mp 101–103°; ir 1750 (C=O), 1607, 1580 (aromatic), 1518, 1340 (NO_2), 1355, 1170 cm^{-1} (SO_3); nmr δ 0.78 (s, 3 H), 0.84 (s, 3 H), 0.87 (s, 3 H), 4.61 (d, J = 10.5 Hz, 1 H, $CHOSO_2Ar$), 7.35–8.64 (m, 8 H, ArH).

Anal. Calcd for $C_{26}H_{31}O_7SN$: C, 62.28; H, 6.19; S, 6.39. Found: C, 61.93; H, 6.29; S, 6.48.

***o*-(2-Phenylethoxy)sulfonylbenzoic Acid (28a).**—A solution of 429 mg (1 mmol) of *p*-nitrophenyl ester **5a** in 40 ml of dioxane and 40 ml (4 mmol) of 0.1 *N* sodium hydroxide was stirred for 10 min at room temperature. The progress of saponification was followed by tlc and the starting material was observed to disappear after 10 min. The solution was poured into a large amount of water and any neutral material was removed by ether extraction. The aqueous phase was acidified and extracted with ether, and the ether extract was dried (Na_2SO_4) and evaporated. The resulting oily material (*ca.* 400 mg, 99%) proved to be a 1:1 mixture of *p*-nitrophenol and carboxylic acid **28a**: ir 1730, 3400–2800, 1590–1610, 1360 cm^{-1}; nmr δ 2.96 (t, J = 7 Hz, 2 H, $PhCH_2$) 4.34 (t, J = 7 Hz, 2 H, CH_2OSO_2Ar), 7.09 (br s, 5 H, Ph), 7.35–7.80 (m, 4 H, ArH).

Esterification with diazomethane afforded the methyl ester **29a** contaminated by a small amount of *p*-nitroanisole: ir 1735, 1360 cm^{-1}; nmr δ 2.96 (t, J = 7 Hz, 2 H, $PhCH_2$), 3.85 (s, 3 H, CO_2CH_3), 4.32 (t, J = 7 Hz, CH_2OSO_2Ar), 7.09 (br s, 5 H, Ph), 7.35–7.80 (m, 4 H, ArH).

Anal. Calcd for $C_{16}H_{16}SO_5$: C, 60.00; H, 5.00. Found: C, 60.45; H, 5.17.

***o*-(2-Phenylethoxy)sulfonylthiobenzoic Acid (30a).**—To a solution of 1.71 g (4 mmol) of *p*-nitrophenyl ester **5a** in 40 ml of ethanol and 60 ml of dioxane was added 20 ml (20 mmol) of 1 *N* sodium hydrogen sulfide in ethanol prepared by saturating 1 *N* sodium ethoxide in ethanol with hydrogen sulfide.[28,29] The mixture was stirred for 30 min at room temperature. Tlc analysis showed no starting material left after 30 min. Neutral material (~600 mg) was removed by chloroform extraction, the aqueous solution was acidified and extracted with chloroform, and the chloroform extract was washed with water twice, dried, and evaporated. The residual oil (0.99 g) was a 1:1 mixture of *p*-nitrophenol and the thio acid **30a** (54%): ir 1700, 1670, 1595, 1340 cm^{-1}; nmr δ 3.0 (t, J = 7 Hz, 2 H, $PhCH_2$), 4.34 (t, J = 7 Hz, 2 H, CH_2OSO_2Ar), 7.12 (br s, 5 H, Ph), 7.4–8.0 (m, 4 H, ArH).

Exposure of the acid to diazomethane effected conversion to the *S*-methyl ester **31a**, which was further purified by preparative tlc: ir 1670, 1360, 1180 cm^{-1}; nmr δ 2.50 (s, 3 H, $COSCH_3$), 3.16 (t, J = 7 Hz, 2 H), 4.34 (t, J = 7 Hz, 2 H), 7.20 (br s, 5 H), 7.5–8.2 (m, 4 H).

Anal. Calcd for $C_{16}H_{16}S_2O_4$: C, 57.14; H, 4.76. Found: C, 57.38; H, 4.98.

Saponification of 2,2,4aα-Trimethyl-1,2,3,4,4aα,5,6,7,8,8aβ-decahydronaphthalen-1β-yl [*o*-Carbo(*p*-nitrophenoxy)]benzenesulfonate (27b).—A solution of 501 mg (1 mmol) of *p*-nitrophenyl ester **27b** in 120 ml of dioxane and 20 ml of 0.1 *N* sodium hydroxide was stirred for 2.5 hr at room temperature. During this period the tlc spot for **27b** disappeared and a very polar spot appeared, and the pH of the solution became almost neutral. The reaction mixture was poured into ice–water, acidified with concentrated hydrochloric acid, saturated with sodium chloride, and extracted with ether. The extracts were combined, washed with cold brine, and dried.

About one third of the dried extract was treated with diazomethane in ether and then washed with 0.1 *N* ammonium hydroxide, saturated sodium bicarbonate, and water, successively dried, and evaporated to give 140 mg of an oily material which was a 43:57 mixture of *p*-nitroanisole [67%; nmr δ 3.90 (s, 3 H), 6.96 and 8.17 (AB doublet, J_{AB} = 9.3 Hz)] and methyl ester **29b** (88%) according to the following nmr data: δ 0.78 (s, 3 H), 0.90 (s, 3 H), 0.98 (s, 3 H), 3.98 (s, 3 H, CO_2CH_3), 4.56 (d, J = 10.5 Hz, 1 H, $CHOSO_2Ar$), 7.3–8.3 (m, 4 H). A sample of methyl ester **29b** obtained free of *p*-nitroanisole in another run had spectral data identical with the preceding data obtained from the spectrum of the mixture. Another one third of the extract was evaporated at 10° to give an oil, which decomposed rapidly at room temperature.

Acetolysis of *o*-Carboxybenzenesulfonate 28b.—The *p*-nitrophenyl ester **27b** (501 mg, 1.00 mmol) was saponified and worked up as described above. The volume of the ether extract was reduced to 5 ml at 10°, and then diluted with 50 ml of high-boiling petroleum ether. After the concentration–dilution was repeated twice (to remove residual dioxane), the volume was finally reduced to *ca.* 1 ml. The solution was diluted with 100 ml of glacial acetic acid containing 820 mg (10 mmol) of sodium acetate, heated at 60° for 30 min, poured into ice–water, and extracted with ether. The combined ether extracts were washed successively with 0.2 *N* sodium carbonate, saturated sodium bicarbonate, and brine, dried, and evaporated to give *ca.* 210 mg (~97%) of oil, which was found by glpc analyses to consist of olefin **18** and **19**, alcohol **6-OH**, and acetate **6-OAc** in the ratio 40:12:34:14. Alcohol **6-OH** apparently arises from partial hydrolysis of **24** under the conditions of saponification and/or the isolation procedure prior and/or subsequent to acetolysis. Aliquots taken at various times from another acetolysis at 25° and processed as described above indicated that the amount of **6-OAc** was increasing with time while the amount of **6-OH**, which was present from the beginning, was decreasing, albeit with some irregularity.

Sulfhydrolysis of *p*-Nitrophenyl Ester 27b.—Sodium hydrogen sulfide (5 ml of 1 *N*) in ethanol, prepared by saturating 1 *N* sodium ethoxide in ethanol with hydrogen sulfide,[28,29] was added to a solution of 510 mg (1 mmol) of *p*-nitrophenyl ester **27b** in 120 ml of dioxane. After 40 min at room temperature (**23** consumed according to tlc analysis) the mixture was poured into ice–water, the pH was adjusted to about 9 by addition of potassium carbonate, and a small amount of neutral material (66 mg, mostly **6-OH**) was removed by ether extraction. The aqueous solution was acidified and extracted with ether. The extracts were washed with cold water, dried, and concentrated to *ca.* 4 ml. A part (1 ml) of the concentrated extract was treated with diazomethane, washed with saturated sodium bicarbonate and water, dried, and evaporated, giving an 85:15 mixture of the *S*-methyl ester **31b** and *p*-nitroanisole, containing a trace of the tertiary alcohol **6-OH**. The nmr data for **31b** are as follows: δ 0.75 (s, 3 H), 0.88 (s, 3 H), 0.98 (s, 3 H), 2.50 (s, 3 H, $COSCH_3$), 4.33 (d, J = 11 Hz, 1 H, $CHOSO_2Ar$), 7.5–7.6 and 7.8–8.2 (*m*, total 4 H, ArH).

Hydrolysis of *o*-Thiocarboxybenzenesulfonate 30b.—The *p*-nitrophenyl ester **27b** (250 mg, 0.5 mmol) was subjected to sulfhydrolysis as described above. The concentrated ether solution of the thio acid was diluted with 10 ml of 0.1 *N* sodium hydroxide and 20 ml of water and then heated for 70 min at 70°. A standard extractive work-up followed by chromatography on silica gel afforded olefin **18** (15 mg, 17%) and the ring-contracted alcohol **6-OH** (50 mg, 51%).

Control Experiments. A.—A solution of *tert*-butyl benzoate (K & K Laboratories, 182 mg, 1.02 mmol) in 75 ml of acetic acid containing 821 mg (10 mmol) of sodium acetate was heated at 60° for 30 min. The solution was diluted with water and extracted three times with pentane. The combined pentane extracts were washed once each with water and saturated sodium bicarbonate, then dried ($MgSO_4$) and evaporated. The remaining oil (128 mg, 98%) had ir and nmr spectra identical with those of the starting *tert*-butyl ester.

B.—Benzoyl chloride (11.7 ml, 14.1 g, 0.10 mol) was added slowly (5–10 min) with stirring to a cooled (0°) solution of *tert*-butyl mercaptan (9.0 g, 0.10 mol) in 24 ml of pyridine.[40] The

(40) R. L. Buckson and S. G. Smith, *J. Org. Chem.*, **32**, 634 (1967).

suspension was allowed to warm to room temperature over a 5–10-min period, diluted with ether, and extracted once each with water, 10% sulfuric acid, saturated sodium bicarbonate, and saturated brine. The dried ($MgSO_4$) ethereal solution was evaporated, a 1.4-g crop of yellow crystals (from petroleum ether, bp 60–68°) was separated by filtration, and the concentrated filtrate was distilled under reduced pressure. *tert*-Butyl thiolbenzoate (8.7 g, 45%) was obtained as a water-white liquid: bp ~135–145°(15–25 mm) [lit.[41] bp 127° (11 mm)]; ir (all s) 687, 772, 908, 1060, 1205, 1655 cm^{-1} (C=O); nmr δ 1.55 (s, 9 H), 7.2–7.4 (m, 3 H), 7.7–7.9 (m, 2 H).

A solution of the thiolbenzoate (99 mg, 0.51 mmol) in ~30 ml 50% aqueous dioxane (v/v before mixing) was heated at 105° for 12 days in a sealed ampoule. The ester (83 mg, 84%), recovered by extraction with pentane, had unchanged ir and nmr spectra.

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(41) H. Reinholt, F. Mott, and E. Motzkers, *J. Prakt. Chem.*, **134**, 274 (1932).

Registry No.—**5**-OH, 40599-63-1; **5**-OMs, 40599-64-2; **5**-d_3-OMs, 40625-59-0; **6** (R = H), 40599-65-3; **6** (R = H) *p*-nitrobenzoate, 40599-66-4; **6**-d_3 (R = H) (R*), 40599-67-5; **6**-d_3 (R = H) (S*), 40625-60-3; **6** (R = Ac), 40599-68-6; **6** (X = N_3), 40625-61-4; *cis*-**7**, 32166-40-8; *trans*-**7**, 21370-71-8; *cis*-**8a** (X = OH), 40599-69-7; *trans*-**8a** (X = OH), 40599-70-0; *cis*-**8b** (X = S-*n*-Bu), 40599-71-1; *trans*-**8b** (X = S-*n*-Bu), 40599-72-2; **9**, 40599-73-3; **9**-d_3, 40625-62-5; **10**, 40599-74-4; **10**-d_3, 40625-63-6; **11**, 40599-75-5; **12**, 40724-84-3; **13**, 40599-77-7; **14a**, 40599-78-8; **14b**, 40599-79-9; **15**, 40599-80-2; **16**, 40599-81-3; **17b**, 40599-82-4; **18**, 40599-83-5; **19**, 40599-84-6; **20**, 40599-85-7; **23**, 60-12-8; **24**, 40625-64-7; **26a**, 40599-86-8; **26b**, 40599-87-9; **27a**, 40599-88-0; **27b**, 40599-89-1; **28a**, 40599-90-4; **28b**, 40599-91-5; **29a**, 40599-92-6; **29b**, 40599-93-7; **30a**, 40599-94-8; **30b**, 40599-95-9; **31a**, 40599-96-0; **31b**, 40599-97-1; *n*-butanethiol, 109-79-5; methanesulfonyl chloride, 124-63-0; 4α,β-methyl-3,4,4aβ,5,6,7,8,8aα-octahydronaphthalen-2(1*H*)-one, 938-07-8; sodium azide, 12136-89-9; *p*-nitrophenol, 100-02-7.

Triterpenes of *Datura innoxia* Mill. Structure of Daturadiol and Daturaolone

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Two new pentacyclic triterpenes, daturadiol and daturaolone, have been isolated from *Datura innoxia* Mill. seeds (Solanaceae). The structures—3β,6β-dihydroxyolean-12-ene and 3-oxo-6β-hydroxyolean-12-ene—were established by chemical degradation and supported by the spectral properties.

Two new pentacyclic triterpenes have been isolated from *Datura innoxia* Mill. (Solanaceae), a known source of tropane alkaloids.[1] A mixture of these two compounds crystallized from the oil extracted from the seeds.[2] The determination of their structure is presented below.

The pmr spectrum of the more polar *Datura* triterpene—daturadiol **1a**—shows the presence of two secondary hydroxyl groups and a trisubstituted double bond (Table I). The spectrum shows also the presence of eight tertiary methyl groups. The latter observation, combined with the shape and position of the olefinic proton signal [triplet δ 5.22 (J = 3 Hz)], suggested that the compound was most probably a diol of the β-amyrin type. Acetylation at room temperature gave the monoacetate **1d**; its pmr spectrum (Table I) showed that only the triplet-like signal, ascribed to the 3α-H, was shifted downfield with a slight change in shape. The molecular rotation change caused by the acetylation ($\Delta[M]_D$ = −57°) is consistent with similar values for 3β-hydroxytriterpenes (*e.g.*, β-amyrin −33°, α-amyrin, −29°, lupeol −69°, taraxasterol −67°, and ψ-taraxasterol −53°).

The low reactivity of the second secondary hydroxyl group, and the shape of the signal corresponding to the HCOH [broad singlet at δ 4.54 ($W_{1/2}$ = 10 Hz)] indicated that it was axially oriented. Prolonged reaction time at boiling temperature with pyridine–acetic anhydride or acetic anhydride–boron trifluoride etherate at room temperature led to daturadiol diacetate **1c**.

This diacetate, when oxidized with a stoichiometric amount of selenium dioxide, gave a derivative typical for a β-amyrin, that is the 11,13(18)-diene[3] **2**, with characteristic uv absorption. Prolonged oxidation with an excess of selenium dioxide led to a second characteristic product[4] **3**, showing typical uv and ir absorption.

To assure the presence of the β-amyrin skeleton the axial hydroxyl group was removed by the following series of reactions. The monoacetate **1d** was oxidized with Jones reagent to the keto acetate **1e**. The latter underwent Wolff–Kishner reduction only under drastic conditions (anhydrous hydrazine, sodium in ethylene glycol), yielding β-amyrin in 25% yield.

Evidence for the location of the second hydroxyl group is provided by the pmr spectrum of keto acetate **1e** (Table I). The broad singlet of the equatorial proton was replaced by a slightly broadened doublet at δ 2.51 (J = 12.5 Hz) and a singlet at δ 2.23. Thus the fragment $\gtrless CCHCOCH_2C \lessgtr$ should be present in the keto acetate. In β-amyrin there is only one such possible location for a carbonyl group, *i.e.*, position 6.

The second new triterpene, daturaolone **1b**, was less polar than daturadiol. Its ir spectrum showed the presence of hydroxyl and carbonyl groups. As in the case of daturadiol, an olefinic proton signal and a broad singlet of 6α-H are present (Table I), as well as a one-proton multiplet (doublet of triplets) at 2.76 ppm. In addition, eight tertiary methyl group signals are

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