point most of the magnesium had reacted. Sulfuric acid (100 ml., 1 *M*) was added cautiously with stirring, the ether layer was separated and dried, and the solution was distilled until the b.p. reached 100°. At this point dehydration appeared to be starting. The residue in the distilling flask (24 g.) was chromatographed on 300 g. of alumina. The column was eluted with the following solvents in succession: petroleum ether, petroleum ether–ether (6:1), pure ether, ether–methanol (6:1, then 1:1), and pure methanol. Ten fractions were collected, most of the product coming off with petroleum ether (10.0 g.), and ether–methanol (6.0 g. and 4.5 g.). The last two fractions were apparently identical, showing similar infrared spectra with strong hydroxyl bands; they represented a combined yield of 32%. The first fraction of 10.0 g. showed no hydroxyl band. The analytical sample was prepared from fraction 10 (4.5 g.) by chromatographing twice more in the system above.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 66.56; H, 10.39.

Ethyl *dl*-α-(3-Methylcyclopentyl)-isobutyrate (VIIa).—The hydroxyester above (6.0 g.) was dehydrated by heating to 125° for 15 hours with 10.0 g. of anhydrous magnesium sulfate; the mixture was thoroughly extracted with ether, which yielded, after evaporation, 5.05 g. of unsaturated ester showing no hydroxyl absorption in the infrared. This unsaturated ester (5.0 g.) was hydrogenated in ethanol with palladium-on-charcoal catalyst, with the absorption of the theoretical amount of hydrogen. The analytical sample was prepared by distillation (b.p. 84° (5 mm.)) of a sample from an earlier run which had not been chromatographed. Purification by chromatography is preferable, however.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 73.19; H, 10.78.

***dl*-(3-Methylcyclopentyl)-isobutyric Acid (VII).**—The ester VIIa (3.0 g.) was refluxed for 72 hours with 2.0 g. of potassium hydroxide in 70 ml. of dioxane and 15 ml. of water. The mixture was worked up in the conventional way, and yielded 1.70 g. of unchanged ester and 600 mg. of the acid VII.

The amide of the synthetic acid was prepared with thionyl chloride and ammonia, and melted at 124–125°; its infrared spectrum was identical with that of the samples of amide prepared from samples VII obtained by catalytic reduction of both α- and γ-*dl*-fencholenic acids; further, a mixed m.p. with amide derived from the reduced α-acid showed no depression.

***dl*-2,2-Dimethyl-2-(3-methylcyclopentyl)-ethanol (XI).**—Ethyl α-(3-methylcyclopentyl)-isobutyrate (1.70 g., prepared by the Reformatsky reaction) dissolved in 25 ml. of anhydrous ether, was added dropwise to 0.65 g. of lithium aluminum hydride in 25 ml. of ether. The mixture was refluxed with stirring for 4 hours. Ethyl acetate (2 ml.) was added carefully, followed by 3.5 ml. of saturated sodium sulfate solution. The mixture was stirred for 15 minutes to coagulate the salts, which were then removed by filtration. The ethereal filtrate was dried and the solvent was removed, leaving 1.0 g. of 2,2-dimethyl-2-(3-methylcyclopentyl)-ethanol (XI).

This was characterized by preparation of the **3,5-dinitrobenzoate XIa**; the alcohol XI (1.0 g.) and freshly prepared 3,5-dinitrobenzoyl chloride (1.25 g.) in 5 ml. of anhydrous pyridine was heated on the steam-bath for 1.5 hours. The mixture was then poured into 10 ml. of saturated bicarbonate solution, and the resulting cloudy suspension was extracted with ether. The ether solution was washed with water and concentrated. The resulting oil was dissolved in ethanol, made turbid with water, and cooled. The crystals which formed melted, after recrystallization from ethanol–water, at 58.5–59.5°.

Anal. Calcd. for $C_{17}H_{22}N_2O_6$: C, 58.27; H, 6.33. Found: C, 58.13; H, 6.64.

A sample of this same derivative was prepared by lithium aluminum hydride reduction of ethyl dihydro-γ-fencholenate, followed by acylation with dinitrobenzoyl chloride. The two crystalline samples showed no depression on mixed m.p.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

Syntheses in the Terpene Series. V.[1] A Synthesis of DL-1,1,6α,10β-Tetramethyl-*trans*-decal-2β-ol-5-one, the Racemate of a Degradation Product of α-Amyrin

BY FRANZ SONDHEIMER AND DOV ELAD

RECEIVED NOVEMBER 15, 1957

The previously described 1,1,10β-trimethyl-Δ^8-octal-5β-ol-2-one benzoate (IIa) has been converted by a seven-step sequence to 1,1,10β-trimethyl-*trans*-decal-2β-ol-5-one benzoate (VIIb). The latter substance has been found to differ from the compound of King, *et al.*, to which structure VIIb had been ascribed, but the corresponding keto-acetate VIIc was identical with the substance prepared independently by Halsall, *et al.* Methylation of the keto-benzoate VIIb gave 1,1,6α,10β-tetramethyl-*trans*-decal-2β-ol-5-one (Xa), which was shown to be the racemate of an optically active degradation product of α-amyrin and of ursolic acid. Condensation of the tetramethyl keto-benzoate Xb with sodium acetylide yielded the acetylenic carbinol XI, which appears to be a useful intermediate for syntheses in the triterpene field.

In Part III of this series[2] the conversion of the readily available 10-methyl-$\Delta^{1(9)}$-octalin-2,5-dione (Ia) *via* 1,1,10β-trimethyl-Δ^8-octal-5β-ol-2-one benzoate (IIa) to 1,1,10-trimethyl-*trans*-decal-5-one (VIId) was reported. The last-mentioned substance, which was prepared independently by Cocker and Halsall[3] by a similar route, appears to be a useful intermediate for the synthesis of some of the diterpene alcohols and acids. However for the synthesis of members belonging to the onocerin[4] and pentacyclic triterpene group of substances, it was necessary to keep intact the C-2 oxygen function of IIa instead of removing it as had been done previously.[2,3] In this paper we describe the conversion of the ketol benzoate IIa to 1,1,10β-trimethyl-*trans*-decal-2β-ol-5-one (VIIa) and thence to 1,1,6α,10β-tetramethyl-*trans*-decal-2β-ol-5-one (Xa).[5] The latter was shown to be the racemate of the optically active substance Xa which had been obtained previously by the degradation of α-amyrin[6a] and of ursolic acid.[6b]

The majority of the diterpenes, the tetracyclic triterpenes and the pentacyclic triterpenes have all

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[1] For Part IV, see F. Sondheimer and D. Elad, *Proc. Chem. Soc.*, 320 (1957).

[2] F. Sondheimer and D. Elad, THIS JOURNAL, **79**, 5542 (1957).

[3] J. D. Cocker and T. G. Halsall, *J. Chem. Soc.*, 3441 (1957).

[4] D. H. R. Barton and K. H. Overton, *ibid.*, 2639 (1955); K. Schaffner, R. Viterbo, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 174 (1956); J. D. Cocker and T. G. Halsall, *J. Chem. Soc.*, 4262 (1956).

[5] For a preliminary communication, see footnote 1.

[6] (a) R. Rüegg, J. Dreiding, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **33**, 889 (1950); (b) D. Arigoni, H. Bosshard, J. Dreiding and O. Jeger, *ibid.*, **37**, 2173 (1954).

been shown to have the same A-B ring junction.[7] That this is the *trans* junction follows from numerous independent pieces of evidence based on considerations involving X-ray studies,[8] the stereochemistry expected from methods used in total syntheses[9] molecular rotation arguments,[10a] dissociation constant measurements of a tricarboxylic acid obtained from abietic acid,[10b] etc. However the present synthesis, taken together with the work of Halsall, *et al.*, referred to in the sequel, provides the first direct interrelationship between rings A and B of the above-mentioned classes of terpenoids with authentic 9-methyl-*trans*-decalin derivatives.

10-Methyl-$\Delta^{1(9)}$-octalin-2,5-dione (Ia) was reduced with lithium aluminum hydride and then oxidized with manganese dioxide, as described previously,[2] to give 10β-methyl-$\Delta^{1(9)}$-octal-5β-ol-2-one (Ib) in 82% yield. Benzoylation quantitatively gave the keto-benzoate Ic which was methylated with methyl iodide and potassium *t*-butoxide in *t*-butyl alcohol.[2] The latter reaction was carried out without cooling the reaction mixture and in this way 1,1,10β-trimethyl-Δ^{8}-octal-5β-ol-2-one benzoate (IIa) was obtained in 70% yield.

One method for bringing about the necessary reversal of the keto and ester functions in the keto-ester IIa necessitated as a first step the reduction of the C-2 keto grouping to the alcohol without affecting the benzoate. This objective however could not be realized; the action of sodium borohydride in tetrahydrofuran or ethanol solution caused no reaction when carried out at room temperature overnight, whereas this reagent in ethanol at 78° yielded 1,1,10β-trimethyl-Δ^{8}-octalin-2β,5β-diol (III), m.p. 186°, in which the benzoate grouping had been lost. The glycol III was obtained more efficiently from the keto-benzoate IIa through reduction with lithium aluminum hydride.

After some experimentation it was found that an effective method for reversing the keto and ester groupings of IIa and hydrogenating the double bond involved the following succession of steps.[11] Saponification of the keto-ester IIa led to the previously described 1,1,10β-trimethyl-Δ^{8}-octal-5β-ol-2-one (IIb),[3] m.p. 93°, which readily was hydrogenated in ethanol solution over palladium-charcoal to 1,1,10β-trimethyl-*trans*-decal-5β-ol-2-one (IVa).[12] The *trans* configuration was assigned to this and the subsequent substances since hydrogenation of IIb would be expected to occur from the α-side of the molecule, from steric considerations. A rigid proof for the correctness of this assignment is given below.

The hydroxyl group of IVa was protected through conversion to the tetrahydropyranyl ether and the carbonyl group of the resulting keto-ether IVb was then reduced with lithium aluminum hydride to the hydroxy-ether Va. Benzoylation gave the corresponding benzoate Vb, acid treatment of which regenerated the 5-hydroxy group and produced highly crystalline 1,1,10β-trimethyl-*trans*-decalin-2β,5β-diol 2-monobenzoate (VI), m.p. 155°. By careful attention to reaction conditions it was possible to realize a 75–80% over-all yield in the sequence IIa → VI, despite the six steps involved and the two new asymmetric centers introduced. The C-2 ester grouping in the diol monobenzoate VI and subsequent compounds has been assumed to be in the equatorial β-configuration since triterpene ketones containing the 1,1,10β-trimethyl-2-keto system present in the keto-ether IVb on lithium aluminum hydride reduction predominantly give the equatorial alcohols.[13] The 2β-configuration is confirmed by the conversion of VI to a degradation product of α-amyrin, which contains the 2β-hydroxyl group.[14]

Oxidation of the diol monobenzoate VI with chromium trioxide in acetic acid yielded 77% of 1,1,10β-trimethyl-*trans*-decal-2β-ol-5-one benzoate (VIIb), m.p. 93° and 131° (different polymorphic forms). This substance was further characterized through saponification to the keto-alcohol VIIa, m.p. 75°, which on acetylation gave the keto-acetate VIIc, m.p. 97°.

Before proceeding with the synthesis it was our intention to prove the *trans* ring junction of the keto-alcohol VIIa by interrelating it with 10-methyl-*trans*-decal-2-one (VIIIb). However at this stage we learned from Dr. T. G. Halsall that he and his co-workers had independently effected a synthesis of the keto-acetate VIIc.[15] Further, this group had conclusively demonstrated the *trans*-stereochemistry by converting VIIc to 1,1,10-trimethyl-*trans*-decal-2-one (VIIIa), the same as was obtained from 10-methyl-*trans*-decal-2-one (VIIIb).[15b,16] A direct comparison with a sample

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[7] For leading references, see D. H. R. Barton, *Quart. Revs.*, **3**, 63 (1949); O. Jeger, *Forschr. Chem. org. Naturstoffe*, **7**, 74 (1950); D. H. R. Barton in "Chemistry of Carbon Compounds," Editor E. H. Rodd, Elsevier Publishing Co., Amsterdam, 1953, Vol. IIB, pp. 748, 762; E. Kyburz, B. Riniker, H. R. Schenk, H. Heusser and O. Jeger, *Helv. Chim. Acta*, **36**, 1891 (1953).

[8] R. G. Curtis, J. Fridrichsons and A. M. Mathieson, *Nature*, **170**, 321 (1952); J. Fridrichsons and A. M. Mathieson, *J. Chem. Soc.*, 2159 (1953).

[9] R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives and R. B. Kelly, THIS JOURNAL, **76**, 2852 (1954); *J. Chem. Soc.*, 1131 (1957); G. Stork and J. W. Schulenberg, THIS JOURNAL, **78**, 250 (1956).

[10] (a) W. Klyne, *J. Chem. Soc.*, 2916 (1952); 3072 (1953); C. S. Barnes, D. H. R. Barton, J. S. Fawcett and B. R. Thomas, *ibid.*, 576 (1953); (b) D. H. R. Bacton and G. A. Schmeidler, *ibid.*, 1197 (1948); S 232 (1949).

[11] The presently described method for reversing the keto and ester groupings of a keto-ester by use of the tetrahydropyranyl protecting group has previously been applied in the steroid series (A. C. Ott, M. F. Murray and R. L. Pederson, THIS JOURNAL, **74**, 1239 (1952); F. Sondheimer, M. Velasco and G. Rosenkranz, *ibid.*, **77**, 5673 (1955)).

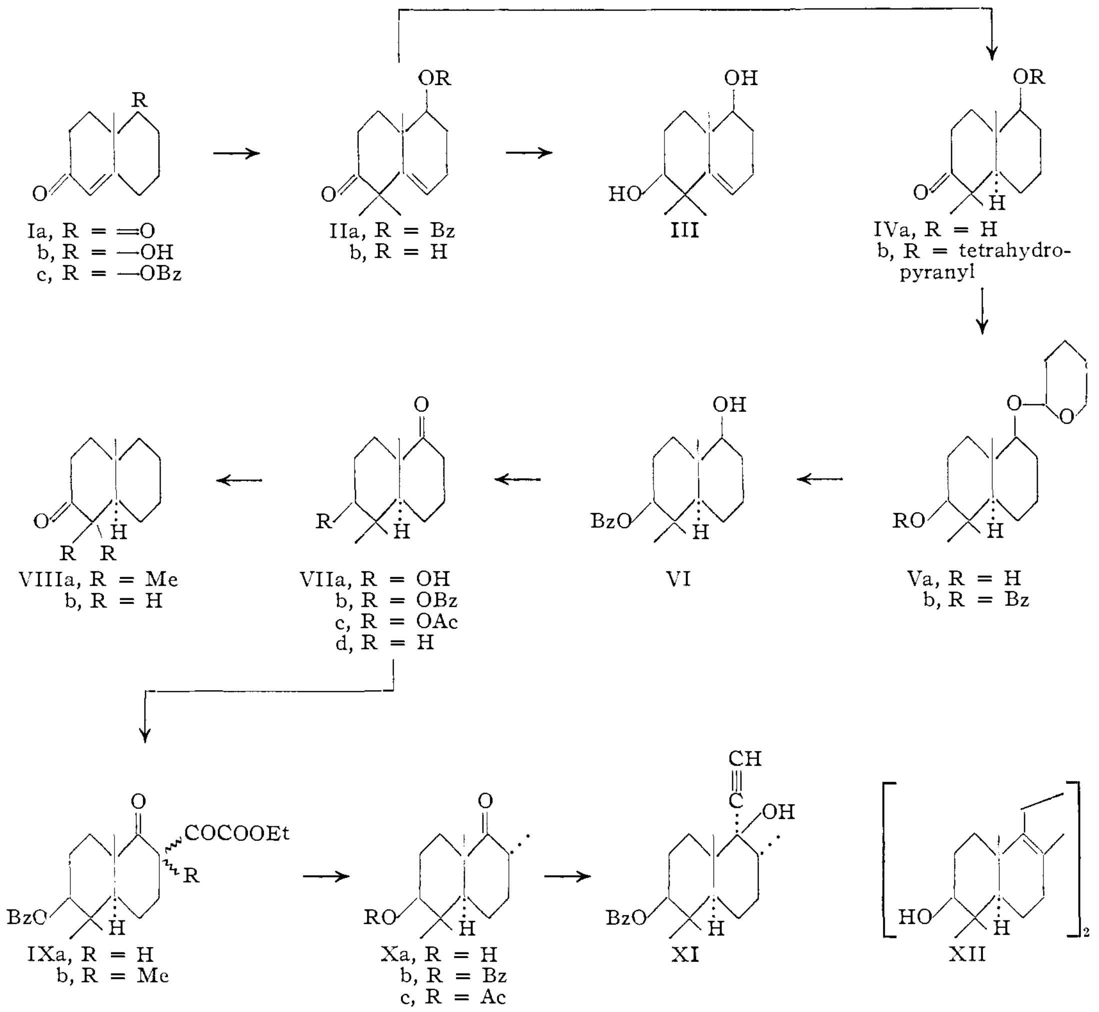
[12] In addition a small amount (*ca.* 5%) of the unsaturated diol III was formed in this reaction. It is interesting to note that the double bond in this 1,1,10-trimethyl-Δ^{8}-octal-2β-ol derivative is considerably more hindered than in the corresponding 1,1,10-trimethyl-Δ^{8}-octal-2-one derivative IIb and is not reduced under the hydrogenation conditions used.

[13] *Inter al.* T. R. Ames, T. G. Halsall and E. R. H. Jones, *J. Chem. Soc.*, 450 (1951).

[14] G. Giacomello, *Gazz. chim. ital.*, **68**, 363 (1938); L. Ruzicka and W. Wirz, *Helv. Chim. Acta*, **24**, 248 (1941); L. Ruzicka and H. Gubser, *ibid.*, **28**, 1054 (1945); D. H. R. Barton, *Experientia*, **6**, 316 (1950).

[15] (a) T. G. Halsall, Abstracts of Division of Organic Chemistry, XVIth International Congress of Pure and Applied Chemistry, Paris, July, 1957, p. 242; (b) B. Gaspert, T. G. Halsall and D. Willis, *J. Chem. Soc.*, in press.

[16] The 10-methyldecal-2-one was prepared by the reduction of 10-methyl-$\Delta^{1(9)}$-octal-2-one with lithium in ammonia. The ring fusion obtained by this reduction cannot be predicted from the generalization of D. H. R. Barton and C. H. Robinson (*J. Chem. Soc.*, 3045 (1954)), since there is very little difference in energy content between the *cis* and *trans* isomers of derivatives of 9-methyldecalin (*cf.* footnote 17).



kindly provided by Dr. Halsall showed the keto-acetates VIIc prepared by the two routes to be identical. On the other hand, we found our keto-benzoate VIIb to differ from the compound (m.p. 92°) to which the structure and stereochemistry VIIb had been assigned by King, Ritchie and Timmons,[18] through comparison with a sample kindly provided by Dr. Timmons. A difference in the steric configuration of the hydroxyl group or of the ring junction may well be responsible for this difference.

The keto-benzoate VIIb was methylated at C-6 through condensation with ethyl oxalate by means of sodium hydride in benzene to the ethoxyoxalate IXa, which with methyl iodide in boiling acetone containing potassium carbonate was converted to the methylated ethoxyoxalate IXb, m.p. 200°. Treatment with sodium ethoxide in ethanol effected removal of the α-keto ester grouping and saponification of the benzoate and gave the required *dl*-1,1,6α,10β-tetramethyl-*trans*-decal-2β-ol-5-one (Xa), m.p. 115°, in *ca.* 55% yield based on VIIb. Benzoylation produced the keto-benzoate Xb, m.p. 108°, whereas acetylation led to the keto-acetate Xc, m.p. 100°. The C-6 methyl group in the keto-alcohol Xa must be in the thermodynamically stable configuration, considering the conditions under which it was formed, and Xa is therefore assigned the equatorial 6α-methyl structure.

When asked for a comparison sample of the optically active keto-alcohol Xa derived from α-amyrin, Professor O. Jeger informed us that Drs. Kalvoda and Loeffel in his laboratory had also just effected a synthesis of racemic Xa,[19] a small amount of which was kindly sent to us. We could show by direct comparison that the synthetic racemic materials made by the two different routes were identical with each other and the Swiss workers in turn have shown that their synthetic sample of Xa is the racemate of the optically active material derived

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Moreover the m.p. of the 2,4-dinitrophenylhydrazone of VIIIb does not distinguish between the *cis* and *trans* isomers, since the 2,4-dinitrophenylhydrazones of the two isomers melt only 3° apart (R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952)). That the main product from the reduction is indeed the *trans* isomer follows from the work of M. Yanagita, K. Yamakawa, A. Tahara and H. Ogura (*J. Org. Chem.*, **20**, 1767 (1955)). F. Sondheimer and D. Rosenthal (footnote 17) have investigated the reduction further and have found that at least 90% of the *trans* isomer is formed, by removing the carbonyl group from the total saturated ketone mixture and comparing the resulting 9-methyldecalin mixture with authentic samples of *trans*- and *cis*-9-methyldecalin.

(17) F. Sondheimer and D. Rosenthal, Part VI of this series, THIS JOURNAL, in press.

(18) F. E. King, C. F. Ritchie and C. J. Timmons, *Chemistry & Industry*, 1230 (1956).

(19) J. Kalvoda and H. Loeffel, *Helv. Chim. Acta*, in press.

from α-amyrin[6] since the infrared spectra are completely identical.

The tetramethyl keto-alcohol Xa appears to be a useful intermediate for the total synthesis of substances of the onocerin and of the pentacyclic triterpene type. Our first target was β-onocerin (XII) which should be obtainable from Xa by methods similar to those used by us for the conversion of the trimethyl ketone VIId to dinoronocerane.[20] This type of synthesis requires the condensation of Xa with sodium acetylide. Although the possibility existed that the extra methyl group at C-6 might hinder the carbonyl function, it was found in fact that the keto-benzoate Xb reacted smoothly with sodium acetylide in liquid ammonia and readily gave the acetylenic hydroxy-benzoate XI, m.p. 231°, in over 90% yield. This work is being continued.

Acknowledgments.—We are indebted to Professor O. Jeger, Dr. T. G. Halsall and Dr. C. J. Timmons for interesting discussions, for information prior to publication and for supplying comparison samples.

Experimental[21]

1,1,10β-Trimethyl-Δ⁸-octalin-2β,5β-diol (III).—1,1,10β-Trimethyl-Δ^8-octal-5β-ol-2-one benzoate (IIa) (370 mg., m.p. 82–84°),[2] dissolved in 15 cc. of dry ether, was added to a solution of 450 mg. of lithium aluminum hydride in 15 cc. of ether. The mixture was boiled under reflux for 2 hr., cooled and ethyl acetate was added carefully. Dilute hydrochloric acid was then added and the product was extracted into ether. The residue obtained after evaporation of the ether on trituration with petroleum ether gave 210 mg. (84%) of the unsaturated diol III, m.p. 176–183°. The analytical sample, obtained by crystallization from petroleum ether–benzene, showed m.p. 184–186°, $\nu_{\max}$ 3600 and 3420 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.52; H, 10.53.

The same diol was obtained in *ca.* 70% yield when 140 mg. of the unsaturated keto-benzoate IIa was boiled for 2 hr. with 200 mg. of sodium borohydride in 5 cc. of ethanol. No appreciable reaction occurred when this experiment was carried out at room temperature.

1,1,10β-Trimethyl-Δ⁸-octal-5β-ol-2-one (IIb).—The keto-benzoate IIa (15 g.)[2] was boiled under reflux for 2 hr. with 20 g. of potassium hydroxide in 300 cc. of ethanol. Most of the solvent was removed under reduced pressure, water was added to the residue and the product was isolated with ether in the usual way. The total product (10.0 g., 100%), m.p. 84–89°, consisting of the ketol IIb, was of satisfactory purity for use in the next step. A purified sample, prepared by crystallization from petroleum ether–benzene, showed m.p. 91–93°, $\nu_{\max}$ 3450 and 1701 cm.$^{-1}$; reported[3] m.p. 92–94°.

1,1,10β-Trimethyl-*trans*-decal-5β-ol-2-one (IVa).—The unsaturated ketol IIb (9.4 g.) dissolved in 120 cc. of alcohol, was shaken in hydrogen over 2.5 g. of a 10% palladium–charcoal catalyst at 24° and 764 mm. After 8 hr. slightly over 1 molar equivalent of hydrogen had been absorbed and uptake stopped. The catalyst was removed and the solvent was evaporated under reduced pressure. Petroleum ether was added to the residue, the mixture was cooled and the small amount of crystalline material (m.p. 174–179°) which remained insoluble was collected. The filtrate on evaporation gave the crude saturated ketol IVa (8.8 g., 93%) as a colorless oil. A purified sample, obtained by distillation at 135–140° (bath temp.) (0.3 mm.), showed $\nu_{\max}$ 3470 and 1700 cm.$^{-1}$. It was characterized as its 2,4-dinitrophenylhydrazone which crystallized from methanol as light orange crystals, m.p. 184–186°.

Anal. Calcd. for $C_{19}H_{26}N_4O_5$: C, 58.45; H, 6.71; N, 14.35. Found: C, 58.78; H, 7.13; N, 14.63.

The material which had been insoluble in petroleum ether was crystallized from petroleum ether–benzene and yielded 0.5 g. (5%) of the unsaturated diol III, m.p. 183–185°, identified with the sample obtained above through mixture m.p. determination and infrared comparison. In other experiments the yield of this diol varied from 3 to 10%.

1,1,10β-Trimethyl-*trans*-decal-5β-ol-2-one Tetrahydropyranyl Ether (IVb).—Phosphorus oxychloride (1 cc., freshly distilled) was added to a solution of 8 g. of the saturated ketol IVa in 120 cc. of chloroform and 35 cc. of dihydropyran (freshly distilled over potassium hydroxide). The solution, the temperature of which spontaneously rose to 45°, was allowed to stand at room temperature for 1.5 hr. It was then poured into sodium bicarbonate solution and the product was extracted into ether. The organic extract on being washed with water, dried and evaporated left 15.1 g. of the crude tetrahydropyranyl ether IVb which was used in the next step. The fact that the yield appears to be higher than theoretical is due to contamination with a non-polar material derived from dihydropyran. Thus, chromatography of 300 mg. of the crude product on 15 g. of alumina first gave 80 mg. of an oil (no carbonyl bands in the infrared), eluted with petroleum ether–benzene (4:1) and then 210 mg. of the purified ether IVb, eluted with petroleum ether–benzene (1:1). Distillation at 150–160° (bath temp.) (0.2 mm.) gave an analytically pure specimen of IVb as an oil, $\nu_{\max}$ 1700 cm.$^{-1}$, no hydroxyl band.

Anal. Calcd. for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 73.19; H, 10.37.

1,1,10β-Trimethyl-*trans*-decalin-2β,5β-diol 5-Monotetrahydropyranyl Ether (Va).—A solution of 14.5 g. of the crude ketol tetrahydropyranyl ether IVb in 200 cc. of dry ether was added dropwise to a stirred solution of 12 g. of lithium aluminum hydride in 400 cc. of ether at such a rate as to maintain a slow reflux (*ca.* 30 minutes). The stirred mixture was then boiled under reflux for 2 hr., cooled and the excess reagent was destroyed by the careful addition of ethyl acetate. Saturated sodium sulfate solution was then added dropwise until the precipitate began to adhere to the sides of the flask, and then solid sodium sulfate. The precipitate was collected, washed well with ether and the combined filtrates were evaporated by dryness. The residue (14.1 g.) was chromatographed on 700 g. of alumina. Benzene–ether (1:1) then eluted 9.5 g. (88% based on IVa) of the diol mono-ether Va as an oil which was used in the next step. Distillation of a small sample at 180–185° (bath temp.) (0.3 mm.) gave a pure specimen, $\nu_{\max}$ 3625 and 3465 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{32}O_3$: C, 72.92; H, 10.88. Found: C, 72.71; H, 10.86.

1,1,10β-Trimethyl-*trans*-decalin-2β,5β-diol 2-Benzoate 5-Tetrahydropyranyl Ether (Vb).—The diol monotetrahydropyranyl ether Va (9 g.) and benzoyl chloride (25 cc.) in dry pyridine (80 cc.) were allowed to stand overnight at room temperature. The mixture was then poured into dilute hydrochloric acid, the product was extracted with ether and the organic layer after being washed with sodium hydroxide solution and water, was dried and evaporated. The residual crude diol benzoate ether Vb (27.1 g.; this large residue is due to contamination with substances derived from the benzoyl chloride which are removed in the next step)[22] was used in the next step.

A pure sample was obtained from a separate experiment by pouring the total benzoylation mixture into water, extracting with ether and removing the pyridine from the ether extract by brief washing with cold dilute hydrochloric acid. The oil remaining after removal of the ether, dissolved in petroleum ether–benzene (3:1), was filtered through a short column of alumina. The resulting diol benzoate ether Vb on being allowed to stand in pentane solution for a few days at 0° crystallized to give a product with m.p. 88–92°, $\nu_{\max}$ 1708 cm.$^{-1}$, no hydroxyl band. The

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[20] D. Elad and F. Sondheimer, *Proc. Chem. Soc.*, 206 (1957).

[21] Melting points are uncorrected. All chromatograms were done with "Alcoa" activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). We are indebted to Dr. S. Pinchas for the infrared spectra which were determined in chloroform solution on a Perkin-Elmer model 12 C single-beam spectrophotometer with sodium chloride prism. Analyses were carried out in our microanalytical laboratory under the direction of Mr. Erich Meier.

[22] Only little cleavage of the ether grouping had occurred, as judged by the infrared spectrum.

m.p. range probably is due to the presence of two stereoisomers involving the C-2 atom of the tetrahydropyran grouping.

Anal. Calcd. for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 75.38; H, 8.84.

1,1,10β-Trimethyl-*trans*-decalin-2β,5β-diol 2-Monobenzoate (VI).—The crude diol benzoate ether Vb (27.1 g.) from the previous experiment in 100 cc. of methanol containing 2 cc. of concentrated hydrochloric acid was allowed to stand at room temperature for 1.5 hr. The solution was diluted with water and the product was isolated with ether. The residue obtained after evaporation of the solvent was chromatographed on 500 g. of alumina, when elution with benzene–ether (1:1) gave 9.1 g. (95% based on Va; 77% in the six-step sequence from IIa) of the diol monobenzoate VI, m.p. 146–149°. An analytical sample, obtained by crystallization from pentane, showed m.p. 153.5–155°, $\nu_{\max}$ 3490 and 1707 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.88; H, 9.07.

1,1,10β-Trimethyl-*trans*-decal-2β-ol-5-one Benzoate (VIIb).—Chromium trioxide (9 g.) dissolved in water (20 cc.) and acetic acid (100 cc.) was added gradually to a stirred solution of the diol monobenozoate VI (8.2 g., m.p. 146–149°) in acetic acid (100 cc.), the internal temperature being kept below 30° by ice cooling. The mixture was allowed to stand overnight and the product was then isolated with ether in the usual way. This procedure gave 6.3 g. (77%) of the ketol benzoate VIIb, m.p. 86–90°. Crystallization from pentane furnished the analytical sample, m.p. 92–93.5°, $\nu_{\max}$ 1701 cm.$^{-1}$ (superimposed benzoate and saturated ketone). On admixture with a sample of the ketol benzoate (m.p. 89–91°) of King, *et al.*,[18] the m.p. was depressed by about 20°.

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.38; H, 8.23.

After this substance had been prepared several times, a new polymorphic form was obtained, which on crystallization from pentane showed m.p. 129–131°. The infrared spectrum was identical with that of the lower melting form and the latter was converted to the higher melting one on being seeded.

1,1,10β-Trimethyl-*trans*-decal-2β-ol-5-one (VIIa) and Acetate (VIIc).—The ketol benzoate VIIb (300 mg.) was boiled under reflux in nitrogen for 2 hr. with 500 mg. of potassium hydroxide in 7 cc. of ethanol. Isolation with ether yielded 198 mg. of the ketol VIIa as a heavy oil, which after chromatography on alumina and then being allowed to stand in pentane slowly solidified. Crystallization from pentane gave a pure sample, m.p. 73–75°, $\nu_{\max}$ 3480 and 1701 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.48; H, 10.54.

The acetate VIIc (acetic anhydride, pyridine, overnight at room temperature) after crystallization from petroleum ether showed m.p. 96–97°, $\nu_{\max}$ 1720 and 1700 cm.$^{-1}$. There was no depression on admixture with a sample (m.p. 96–97°) obtained from Dr. Halsall and the infrared spectra were identical.

Anal. Calcd. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.74.

1,1,10β-Trimethyl-6-ethoxyoxalyl-*trans*-decal-2β-ol-5-one Benzoate (IXa) and 1,1,6,10β-Tetramethyl-6-ethoxyoxalyl-*trans*-decal-2β-ol-5-one Benzoate (IXb).—A solution of 550 mg. of the ketol benzoate VIIb in 10 cc. of dry benzene containing 0.7 cc. of freshly distilled ethyl oxalate was stirred in nitrogen with 200 mg. of sodium hydride for 24 hr. Excess hydride was destroyed by the careful addition of methanol. Ether and cold 3% sodium hydroxide solution was then added and the aqueous alkaline layer was acidified with cold 5% hydrochloric acid and immediately extracted with ether. This ether extract, after being washed with water, dried and evaporated gave 665 mg. (92%) of the crude ethoxyoxalyl derivative IXa as an oil which gave a red-brown color with alcoholic ferric chloride.

The total crude IXa dissolved in 6 cc. of dry acetone was boiled under reflux with 2 cc. of methyl iodide over 500 mg. of dry powdered potassium carbonate for 20 hr. under nitrogen. Ether and cold 3% sodium hydroxide solution were added and the ether extract, after being washed with sodium hydroxide solution, sodium thiosulfate solution and water, was dried and evaporated. The resulting solid crude tetramethyl-ethoxyoxalate IXb (605 mg., 88%) which gave no color with alcoholic ferric chloride, was used in the next step. An analytical sample, obtained by crystallization from acetone–hexane, showed m.p. 198–200°; $\nu_{\max}$ 1725, 1719 and 1705 cm.$^{-1}$.

Anal. Calcd. for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53. Found: C, 70.10; H, 7.26.

1,1,6α,10β-Tetramethyl-*trans*-decal-2β-ol-5-one (Xa), the Benzoate Xb and the Acetate Xc.—The crude tetramethyl ethoxyoxalate IXb (570 mg.) was boiled under reflux for 15 hr. under nitrogen with a solution prepared by dissolving 180 mg. of sodium in 15 cc. of ethanol. Isolation with ether in the usual way, with subsequent chromatography on 15 g. of alumina and elution with ether, gave 196 mg. (66%; 53% based on VIIb) of the tetramethyl-ketol Xa, m.p. 110–113°. A pure sample, prepared by crystallization from pentane, showed m.p. 114.5–115°, $\nu_{\max}$ 3500 and 1700 cm.$^{-1}$. The m.p. was undepressed on admixture with the synthetic racemic compound of Kalvoda and Loeffel[19] (m.p. 114.5–115°) and the infrared spectra were completely identical.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.16; H, 10.87.

The benzoate Xb (benzoyl chloride, pyridine, overnight at room temperature) after crystallization from pentane showed m.p. 107–108°. *Anal.* Calcd. for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.53; H, 8.44.

The acetate Xc (acetic anhydride, pyridine, overnight at room temperature) after crystallization from pentane and sublimation at 95° (0.3 mm.) showed m.p. 99.5–100.5°, $\nu_{\max}$ 1727 and 1702 cm.$^{-1}$. *Anal.* Calcd. for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.31; H, 9.76.

1,1,6α,10β-Tetramethyl-5α-ethynyl-*trans*-decalin-2β,5β-diol 2-Monobenzoate (XI).—The tetramethyl keto-benzoate Xb (86 mg.) dissolved in 10 cc. of dry ether was added to a solution of sodium acetylide in liquid ammonia (previously prepared from 500 mg. of sodium in *ca.* 30 cc. of liquid ammonia by conversion to sodamide by the addition of a little ferric nitrate, and then by the passage of purified acetylene for 15 minutes). The mixture was stirred and cooled in a Dry Ice–acetone-bath for 4 hr. Ammonium chloride (3 g.) next was added, the ammonia was allowed to evaporate and water and ether were added to the residue. The ether layer was washed successively with dilute hydrochloric acid, sodium bicarbonate solution and water and was then dried and evaporated. The brown residue was chromatographed on 5 g. of alumina, when ether–benzene (1:1) eluted 85 mg. (92%) of the acetylenic hydroxy-benzoate XI, m.p. 225–227°. The analytical sample, obtained by crystallization from petroleum ether, showed m.p. 229–231°; $\nu_{\max}$ 3610 (hydroxyl), 3305 (acetylenic hydrogen) and 1707 cm.$^{-1}$ (benzoate).

Anal. Calcd. for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 78.16; H, 8.58.

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