In the flask was placed a 25% sodium hydroxide solution prepared from 126 g. (3.1 moles) of sodium hydroxide and 375 ml. of water. Ethylene was passed in at the top of the condenser at a rate of 460 ml. per minute and 160 g. (2 moles) of sulfur trioxide was distilled into the top of the condenser in about 90 minutes; approximately 1.9 moles of ethylene was used. Carbyl sulfate dripped into the solution as it formed, the temperature of the solution being kept at 25–30°. After all the carbyl sulfate had been added, the solution was heated at 65–70° for two hours, cooled, neutralized to pH 8 with 10% sulfuric acid, chilled, and the precipitated sodium sulfate filtered off. The precipitate was washed with two 100-ml. portions of ice-water, the combined filtrates weighing 942 g. This solution analyzed for 12.3% sodium ethylenesulfonate, equivalent to 116 g. or a yield of 89% based on sulfur trioxide.
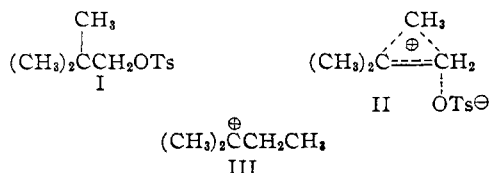
WILMINGTON, DELAWARE

The Acetolysis of cis- and trans-9-Decalylcarbinyl p-Toluenesulfonates

BY WILLIAM G. DAUBEN AND JOHN B. ROGAN[1]
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The acetolysis of cis- and trans-9-decalylcarbinyl p-toluenesulfonates has been studied. The rate of reaction of each isomer is the same, the rate being 5 times more rapid than that of neopentyl tosylate. The products of the acetolysis were olefins of the 5,4,0-undecene series showing that the 1,9-bond of the decalin system had migrated. The mechanistic consequences of this type of migration as compared to the 9,10-bond migration found in trans-9-decalylhydroperoxide are discussed.

The Wagner–Meerwein rearrangement of neopentyl-type systems (I) to t-amyl systems (III) under solvolytic conditions has been the subject of many investigations.[2] Of particular interest is the fact that the formolysis of neopentyl tosylate[3] is as rapid as that of ethyl tosylate despite the appreciable nucleophilic contribution at the rear by solvent in the latter case.[4] This rate of the neopentyl system has been attributed to the anchimeric assistance of the neighboring methyl group,[3] and, ac-

$$(CH_3)_2CCH_2OTs \qquad (CH_3)_2\overset{\oplus}{C}\!\!=\!\!=\!\!CH_2$$
$$I \qquad\qquad II \quad OTs^{\ominus}$$

$$(CH_3)_2\overset{\oplus}{C}CH_2CH_3$$
$$III$$

cordingly, the transition state would have a bridged-ion structure (II). Compounds of the type IV represent a neopentyl system wherein the migrating group is an integral part of a fused ring system.
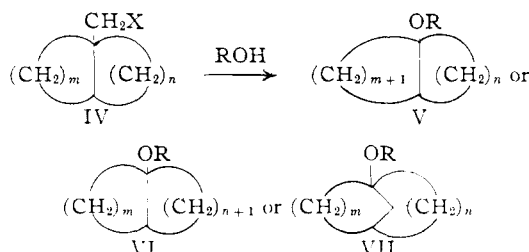

The products expected from IV on rearrangement would be of three types (V, VI, VII) depending upon which bond migrated. In view of the spacial requirements demanded in a bridge-ion transition state of type II, the size of the rings and the stereochemistry of the ring juncture as well as the usual migratory appitudes of alkyl groups would be expected to play a role in the rearrangement of compounds of type IV. In order to obtain some preliminary information with regard to the effect of these structural features on the rate and products of reaction, attention has been directed, first, to the decalin ring system (IV, $m = n = 4$) since only two products could be formed.

Synthesis.—The preparation and stereochemical assignment of trans-9-decalylcarbinyl tosylate has been described previously.[5–7] In attempts to obtain an entry into the cis series, various methods were evaluated and will be discussed below. While this work was being conducted, Idelson, Kronenthal and Becker[8] announced a synthesis of the cis-9-decalylcarbinol (XI) and more recently the experimental details of some similar experiments have been reported by Minckler, Hussey and Baker.[9] Their procedures with certain modifications were used to prepare the cis isomer.

Lithium aluminum hydride reduction of 2,2-ethylenedioxy - 10 - carbethoxy - Δ^8 - octalin (VIII) yielded a mixture of products from which a pure crystalline carbinol (IX) was separated. Hydrogenation of the pure ketal IX in ethanol over
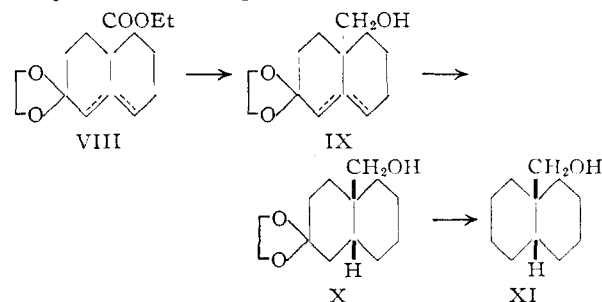
5% palladium-on-charcoal yielded 10-(cis-2,2-ethyl-

(1) United States Rubber Co. Predoctoral Fellow in Chemistry, 1954–1955.

(2) A. Streitwieser, Chem. Revs., 56, 571 (1956).

(3) S. Winstein and H. Marshall, THIS JOURNAL, 74, 1120 (1952).

(4) A. Streitwieser, ibid., 77, 1117 (1955).

(5) W. G. Dauben, J. B. Rogan and E. J. Blanz, Jr., ibid., 76, 6384 (1954).

(6) W. G. Dauben, R. C. Tweit and R. L. MacLean, ibid., 77, 48 (1955).

(7) A. S. Hussey, H. P. Liao and R. H. Baker, ibid., 75, 4727 (1953).

(8) M. Idelson, R. L. Kronenthal and E. I. Becker. Abstracts of the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29 to April 7, 1955, p. 49N.

(9) L. S. Minckler, A. S. Hussey and R. H. Baker, THIS JOURNAL, 78, 1009 (1956).

enedioxydecalyl)-carbinol (X) as a crystalline solid which upon hydrolysis of the ketal function followed by Wolff–Kishner reduction (Huang-Minlon modification) yielded cis-9-decalylcarbinol (XI). The p-toluenesulfonate ester of this material was prepared in the usual fashion.[6]

The possibility of obtaining the cis isomer by the direct hydrogenation of 2-keto-10-carbethoxy-$\Delta^{1(9)}$-octalin (XII) was investigated since the stereochemical results of hydrogenation of certain analogous steroidal unsaturated ketones has been shown to depend upon the acidity of the solvent employed.[10] It has been reported previously[6–7] that when XII is hydrogenated under neutral conditions mainly the trans isomer is formed. It has now been found that hydrogenation of XII in acetic acid over platinum, after distillation of the product, yields 8% of the hydrogenolysis product XIII, 27% of the lactone XIV and 65% of the hydroxy ester XV, all compounds being of the trans series.

XII → XIII

XIV   XV
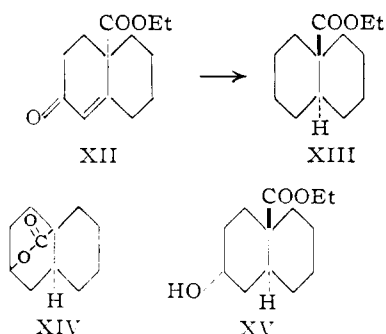
The stereochemical results of the hydrogenation of various substituted octalins, as has been pointed out by Minckler, Hussey and Baker,[9] appears to be controlled by the nature of the angular substituent. For example, when the angular grouping is carbethoxy a trans product is formed[6–7] whereas when the grouping is hydroxymethyl[8,9] or methyl[11] a cis product predominates. This feature alone, however, is not the only controlling factor since the influence of the angular substituent can be effected by small changes in other positions in the molecule. It has been found in the present study that $\Delta^{4(10)}$-9-octalylcarbinol (XVI) when hydrogenated under neutral conditions gave rise to a mixture of cis and

XVI   XVII   XVIII
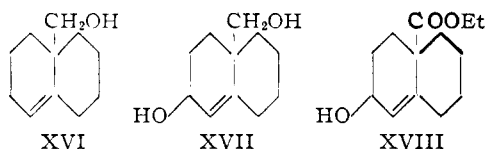
trans isomers, a result to be compared with the formation of practically pure cis isomer from hydroxylated analog XVII, a material differing only by the presence of an equatorial grouping. Also, the presence of an axial substituent trans to the angular grouping is of importance since it also has been found that when VIII is hydrogenated, a mixture of cis and trans isomers is formed whereas a pure

trans material is obtained from XVIII, a compound lacking only the axial oxygen function. Thus, when an axial substituent is on each side of the molecule, the approach of the catalyst is hindered on each side of the molecule and results in a less stereoselective reaction. This tendency of an axial group to hinder catalyst approach also has been found in the hydrogenation of 1-hydroxyl-4b-methyl-7-ethylenedioxy-4b,5,6,7,8,10-octahydro-phenanthrene[12] and cholest-5-en-3-α-ol.[13]

The Diels–Alder reaction for the preparation of the cis-9-substituted-decalin also was investigated since it has been reported that acetylenedicarboxylic acid reacts with 2 moles of butadiene to yield cis-$\Delta^{2,6}$-hexahydronaphthalene-9,10-dicarboxylic acid[14] and cyclopenten-1-carboxylic acid and butadiene give rise to cis-3a,4,7,7a-tetrahydro-indane-3a-carboxylic acid.[15] However, when propiolic acid was allowed to react with a large excess of butadiene (175° for 12 hours) only 1,4-cyclo-hexadiene-1-carboxylic acid was obtained. When the temperature was raised to 200°, only benzoic acid could be isolated.[16] Along these same lines, Szmuszkovicz and Bergmann[17] have found that cyclohexene-1-carboxaldehyde reacts with butadiene at 180° to form cis-1,2,3,4,5,8,9,10-octahydro-naphthalene-9-carboxaldehyde in very low yield.

For the purpose of comparison with other decalincarboxylic acid,[5] the cis-9-decalylcarbinol, prepared above, was oxidized to cis-9-decalincarboxylic acid and the amide of the acid prepared. Table I lists the melting points of the cis- and trans-9-decalincarboxylic acids and their amides as well as the corresponding carbinols and carbinyl tosylates.

TABLE I

PROPERTIES OF 9-SUBSTITUTED-DECALINS

Compound	Melting points, °C. cis	trans
9-Decalincarboxylic acid	122.0–122.3	134.6–135.4[7]
9-Decalincarboxamide	129.7–130.5	125.1–125.6[6]
9-Decalylcarbinol	59.4–60.2	84.2–84.7[7]
9-Decalylcarbinyl tosylate	78.5–79.6	141.0–141.6[7]

Solvolysis.—The solvolysis of both cis- and trans-9-decalylcarbinyl tosylates in anhydrous acetic acid exhibited first-order kinetics. The rate constants at 90° for both isomers were approximately the same: cis, $2.56 \pm 0.14 \times 10^{-6}$ sec.$^{-1}$; trans, $2.87 \pm 0.10 \times 10^{-6}$ sec.$^{-1}$. These values are to be compared with a rate of 5.4×10^{-7} sec.$^{-1}$ for the acetolysis of neopentyl tosylate at 90°.[3] Thus, the rates observed for the acetolysis of the isomeric 9-decalylcarbinyl tosylates are more rapid by a factor of approximately five.

(10) A. L. Wilds, J. A. Johnson, Jr., and R. E. Sutton, THIS JOURNAL, 72, 5524 (1950).

(11) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, ibid., 74, 4223 (1952).

(12) J. W. Cornforth, O. Kauder, J. E. Pike and R. Robinson, J. Chem. Soc., 3348 (1955).

(13) J. R. Lewis and C. W. Shoppee, ibid., 1365 (1955).

(14) K. Alder and K. H. Backendorf, Ber., 71, 2199 (1938).

(15) R. L. Kronenthal and E. I. Becker, THIS JOURNAL, 79, 1095 (1957).

(16) It has been reported recently by Emerman and Meinwald (J. Org. Chem., 21, 375 (1956)) and Jones, Mansfield and Whiting (J. Chem. Soc., 4073 (1956)) that these two compounds react readily at 55° to yield the dihydrobenzoic acid.

(17) J. Szmuszkovicz and E. D. Bergmann, Bull. Research Council Israel, 3, No. 1/2, 93 (1953).

The hydrocarbon products resulting from the acetolysis of each tosylate were isolated in 93% yield. The infrared spectra of the two solvolysis products were identical except for a few small differences in intensities. The *trans*-tosylate solvolysis product exhibited an ultraviolet spectrum in the region 205–225 mμ which was similar to that of pure Δ^9-octalin. When the olefin was ozonized, followed by treatment with hydrogen peroxide, 19% of an acidic fraction and 77% of a neutral fraction was obtained. The neutral fraction yielded an oxime and a semicarbazone, the melting points of which compared favorably to the corresponding derivatives of cycloundecane-1,6-dione.[18] Analysis for the types of unsaturation by means of nuclear magnetic resonance spectroscopy[19] revealed that the hydrocarbon contained 20 ± 1% of material with a trisubstituted double bond (or 10% of a disubstituted olefin). Therefore, the products resulting from the acetolysis of *trans*-9-decalylcarbinyl tosylate can be considered as consisting of 80% of Δ^{10}-bicyclo[5:4:0]undecene (XIX) and 20% of isomeric hydrocarbons (XX).
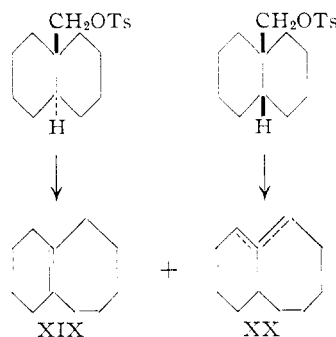

The hydrocarbon formed in the acetolysis of the *cis*-tosylate reacted with 99.8% of one mole of perbenzoic acid and 1.01 moles of hydrogen under catalytic conditions. Direct evidence concerning the carbon skeleton of the hydrogenated material was obtained by establishing its identity (superimposable infrared spectrum) with authentic bicyclo-[5:4:0]undecane which, in turn, was prepared from benzsuberone by a modification of the procedure of Plattner.[18] The nuclear magnetic resonance spectrum of the *cis*-tosylate solvolysis product indicated the presence of 26 ± 1% of material with a trisubstituted double bond. Thus, the acetolysis product of *cis*-9-decalylcarbinyl tosylate consists of 74% of the bicyclic olefin XIX and 26% of the isomer XX.

This finding of a preferred migration of the 1,9-bond in the acetolysis of the tosylates is of particular interest when the result is compared to the finding of a preferred migration of the 9,10-bond in the ionic decomposition of *trans*-9-decalylhydroperoxide esters.[20,21] An explanation of this difference is found readily by consideration of the

structure of the transition states of these two reactions.

As mentioned earlier, Winstein and Marshall[3] found that the rate of solvolysis of neopentyl tosylate was as rapid as that of ethyl tosylate and they invoked the concept of an anchimeric assistance to explain such a result. The structure of the transition state of such a reaction is shown again in II. Since this transition state closely resembles the
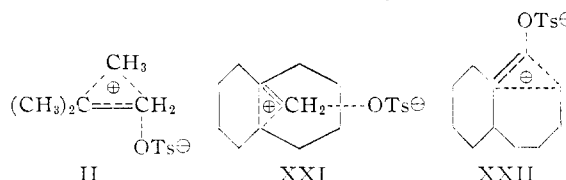
products of the reaction, *i.e.*, derivatives of a *t*-amyl system, it can be concluded that in going from the reactant to the transition state, much progress has been made along the reaction coördinate. Since in the present work on the solvolysis of the 9-decalylcarbinyl tosylates, it was found that the rate of reaction was five times that of neopentyl, it appears that also in this case a bridged-ion transition state is involved. In the decalyl case there are two possible bridged-ions, XXI and XXII. A transition state of structure XXI would be highly strained since it not only demands a partial double bond at a bridge head but also produces an extreme eclipsing of the hydrogens on C_1 and C_7 as shown in XXIII. Structure XXII, however, is relatively free from strain since it does not possess the above features and, in addition, it relieves the conformational strain (see XXIV) which is present in the starting material and which is due to nonbonded atom interactions between the C_9-substituent and the hydrogens on C_2, C_4, C_5 and C_7. Thus, structure XXII would be favored for the transition state in the solvolysis of the 9-decalyl series and the collapse of the transition state would then lead to ring-expanded products and not bridged structures.
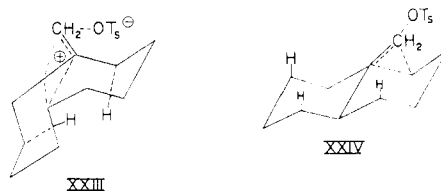
According to these postulates, the same products would be expected from both the *cis*- and *trans*-tosylates and such is the case. Also, it would be expected that in both cases, due to the relief of conformational strain, the rates of acetolysis would be slightly faster than that of neopentyl tosylate and it was found that their rates are about 5 times that of neopentyl.

In the ionic reaction[22] of the hydroperoxide of the *trans*-9-decalyl system, one of the important features of the reaction is the retention of the specific orientation of the benzoate anion.[21] Such an oriented ion pair indicates a close proximity of the

(18) Pl. A. Plattner, *Helv. Chim. Acta*, **27**, 801 (1944).

(19) These determinations were kindly performed by Dr. James N. Shoolery, Varian Associates, Palo Alto, Calif.

(20) R. Criegee, *Ann.*, **560**, 127 (1948).

(21) P. D. Bartlett and J. L. Kice, THIS JOURNAL, **75**, 5591 (1953); H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953); D. B. Denney, *ibid.*, **77**, 1706 (1955).

(22) The decomposition of 9-decalylhydroperoxide under conditions favoring a free radical mechanism occurs with the cleavage of the 1,9-bond (H. E. Holmquist, H. S. Rothrock, C. W. Theobold and B. E. Englund, THIS JOURNAL, **78**, 5339 (1956)).

anionic species to the reaction center and at such a close distance, conformational interactions of this species with the axial hydrogens on C_2, C_4, C_5 and C_7 must be considered. The favored orientation of the hydroperoxide benzoate would have the O–O bond directed away from the molecule, as shown in XXV, such that the C_9–C_{10} linkage of the

XXV
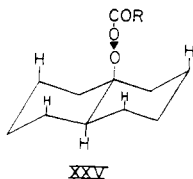
decalin nucleus would be directly behind the leaving group and as such would be well suited for migration. If a bridged ion is involved in the reaction, the conformational features would tend to lessen the energy difference between the transition states leading to 1,9- and 9,10-bond migration. Since the reaction product is of the bicyclic structure, it would indicate that the conformational interactions are, indeed, more controlling than other structural features discussed for the tosylate solvolysis case.

Experimental[23]

10-(2,2-Ethylenedioxy-Δ^3-octalyl)-carbinol (IX).—A solution of 283 g. (1.06 moles) of 2,2-ethylenedioxy-10-carbethoxy-Δ^3-octalin (VIII)[8,9] in 250 ml. of anhydrous ether was added dropwise, with stirring, to a slurry of 32.3 g. (0.85 mole) of lithium aluminum hydride in 1 l. of anhydrous ether. The reaction was heated under reflux with stirring for 22 hours, cooled and ethyl acetate added dropwise to decompose the excess hydride. Water then was added until the inorganic salts became gummy, the ether layer decanted, the solvent evaporated and the residue was distilled, b.p. 152–155° (1.2 mm.), to yield 199 g. (84%) of a colorless, viscous liquid which solidified on standing several days, m.p. 70–85°. Recrystallization from ether–hexane gave 129 g. of large dense crystals, m.p. 80–89° (sinter 63°). The solvent was removed from the filtrate and the infrared spectrum of the 70 g. of residue was almost identical with that of the crystalline material except for weak absorption due to ester and α,β-unsaturated ketonic functions.

The solid product was recrystallized to yield 102.9 g. (43%) of pure material, m.p. 90.6–92.0°.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.54; H, 8.88.

10-(cis-2,2-Ethylenedioxydecalyl)-carbinol (X).—A solution of 101.1 g. (0.452 mole, m.p. 90.6–92.0°) of IX in 400 ml. of ethanol was hydrogenated at atmospheric pressure in the presence of 2.5 g. of 5% palladium-on-charcoal catalyst. The catalyst was removed by filtration through Supercel and the ethanol distilled on the steam-bath under reduced pressure. The residue was crystallized from ether–hexane to yield a total of 86.1 g. (84.4%) of pure cis isomer, m.p. 65.3–67.0° (reported[24] for $trans$, m.p. 73–74°).

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.85; H, 9.76.

The 2,4-dinitrophenylhydrazone of the parent ketone was prepared by allowing 245 mg. of the solid saturated ketal X in 3 ml. of methanol to react with 300 mg. of 2,4-dinitrophenylhydrazine in 25 ml. of dilute sulfuric acid. Solid formed immediately and the product was recrystallized from aqueous ethanol to yield 320 mg. (82%) of orange crystals, m.p. 125–127°, which upon recrystallization from benzene–hexane yielded material melting at 127.1–128.6° (reported[9] m.p. 122–123.5°). The $trans$ isomer melts at 105–107°.[24]

(23) All analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California. All melting points are corrected and all boiling points are uncorrected.

(24) A. S. Dreiding and A. J. Tomasewski, This Journal, **77**, 411 (1955).

Anal. Calcd. for $C_{17}H_{22}N_4O_5$: C, 56.34; H, 6.12; N, 15.46. Found: C, 56.47; H, 6.07; N, 15.56.

cis-9-Decalylcarbinol (XI).—A solution of 59.8 g. (0.309 mole) of cis-ketal X in 100 ml. of ethanol was poured into 1 l. of 1 N sulfuric acid and the resulting two-phase mixture stirred at room temperature. After 45 minutes the reaction mixture was homogeneous, the solution then was saturated with sodium chloride, extracted three times with ether, the ether extracts washed with saturated sodium chloride solution, saturated sodium bicarbonate solution, again with saturated sodium chloride solution and the solvent removed.

The crude oily ketone carbinol, 300 ml. of diethylene glycol, 38 ml. of 85% hydrazine hydrate (0.646 mole) and 59.2 g. (0.900 mole) of 85% potassium hydroxide pellets were heated under reflux for 30 minutes, the condenser removed until the inner reaction temperature reached 210°, the condenser replaced and the heating continued for an additional 2 hours (bath temperature 220–230°). At the end of this period the evolution of nitrogen had ceased. The reaction mixture was cooled, poured into ice-water and the solid which formed was filtered and dried, yield 47.2 g. (91%), m.p. 48–54°.

A small sample of the material was sublimed to give a white solid, m.p. 59.4–60.2° (sinter 58.2°). The $trans$ isomer melts at 82.1–82.9°.[6,7]

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.28; H, 11.64.

When the 70 g. of the liquid portion of the unsaturated ketal X, prepared above, was carried through the sequence of hydrogenation, hydrolysis and reduction, the saturated carbinol melted at 54–58°. A tosylate prepared from this crude carbinol had a m.p. 100–120° after recrystallization from hexane (cis, m.p. 79°; $trans$, m.p. 141°).

cis-9-Decalylcarbinyl p-Toluenesulfonate.—cis-9-Decalylcarbinol (40.0 g., 0.238 mole) was dissolved in 300 ml. of anhydrous pyridine and 50.0 g. (0.263 mole) of p-toluenesulfonyl chloride was added. The solution was allowed to stand for 24 hours at 0° and then poured into 1000 ml. of water containing 55 ml. of concentrated ammonia. After standing, the oily tosylate crystallized and was removed by filtration. The product was recrystallized twice from hexane, m.p. 78.5–79.6°, yield 55.8 g. (69.6%).

Anal. Calcd. for $C_{19}H_{26}O_3S$: C, 67.04; H, 8.13; S, 9.94. Found: C, 67.16; H, 8.13; S, 9.79.

cis-9-Decalincarboxylic Acid.—To 808 mg. (4.8 mmoles) of cis-9-decalylcarbinol dissolved in 5 ml. of acetic acid was added, with swirling and cooling, to a solution of 2.08 g. (7 moles) of sodium dichromate dihydrate in 10 ml. of acetic acid, 2 ml. of concentrated sulfuric acid and 5 ml. of water. The reaction mixture was allowed to stand at room temperature overnight and then heated on the steam-bath for 5 minutes. After pouring into water, hexane was added and the organic layer separated and extracted with sodium bicarbonate solution. Acidification of the bicarbonate extracts yielded a solid acid which was recrystallized from aqueous ethanol, m.p. 122.0–122.3°, yield 629 mg. (71.5%).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.58; H, 10.06.

cis-9-Decalylcarboxamide.—A solution of 2.0 ml. (27.4 mmoles) of thionyl chloride, 10 ml. of anhydrous benzene and 550 mg. (3.02 mmoles) of cis-9-decalincarboxylic acid was heated under reflux for 30 minutes. The excess thionyl chloride and benzene were removed under reduced pressure on the steam-bath. To the residue was added 25 ml. of anhydrous ether, 20 ml. of dry liquid ammonia and 1.00 g. of lithium amide and the resulting mixture stirred for 30 minutes. Most of the ammonia was allowed to evaporate and then 3.5 g. of ammonium chloride was added. After pouring into water, the organic layer was separated and the solvent evaporated to yield 0.30 g. of crude amide. Recrystallization of the material from benzene–hexane gave 225 mg. (46.7%) of amide as well-formed needles, m.p. 129.7–130.5°. Acidification of the basic aqueous layer gave 158 mg. (28.8%) of recovered acid, m.p. 121–122°.

Anal. Calcd. for $C_{11}H_{19}ON$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.63; H, 10.44; N, 7.88.

Hydrogenation of 2-Keto-10-carbethoxy-$\Delta^{1(9)}$-octalin (XII) in Acetic Acid.—A solution of 20.0 g. (0.09 mole) of XII in 50 ml. of glacial acetic acid was hydrogenated over 0.2 g. of platinum oxide. When about two-thirds of the theoretical amount of hydrogen had been absorbed, the rate

decreased and so an additional 0.20 g. of catalyst was added. After consumption of 2 mole equivalents of hydrogen, the catalyst was filtered and the solvent removed under reduced pressure. The residue was distilled through a screen-packed column at 5.0 mm.: fraction 1, b.p. 99–102°, 1.4 g., n^{25}D 1.4709; fraction 2, b.p. 146–149°, 17.0 g., n^{25}D 1.4879.

Fraction 1 displayed no band in the infrared spectrum in the hydroxyl region but did show a strong symmetrical band at 5.80 μ. Fraction 2 displayed bands in the infrared spectrum characteristic of hydroxyl and ester and/or lactone groupings. Fraction 1 was saponified in sodium hydroxide-diethylene glycol to yield trans-9-decalincarboxylic acid, m.p. 134.9–135.6°. Fraction 2 when treated with acetic acid containing hydrogen bromide, yielded trans-trans-2-bromo-10-decalincarboxylic acid, m.p. 161.0–162.5°, which could only be derived from a lactone, amounting to 25% of the fraction. Oxidation of fraction 2 yielded only trans 10-carbethoxy-2-decalone in the neutral fraction. These data give the following composition of the hydrogenation mixture on a mole % yield basis: trans-9-decalincarboxylic acid, 8%; trans-cis-2-hydroxy-10-decalincarboxylic acid lactone, 27%; trans-cis-2-hydroxy-10-decalincarboxylic acid, 65%.

$\Delta^{4(10)}$-9-Octalylcarbinol (XVI).—Ethanedithiol (20 ml., 22.3 g., 0.237 mole) was added in small portions over a period of 5 minutes to a mixture of 20.5 g. (0.093 mole) of 2-keto-10-carbethoxy-$\Delta^{1(9)}$-octalin and 25 g. of crushed, freshly fused, anhydrous zinc chloride. After standing several minutes, the reaction mixture became warm and was cooled in an ice-bath. The reddish-brown mixture was allowed to stand at room temperature for three days. Ether then was added, the solid removed by filtration and the ether evaporated. The residue was diluted with 400 ml. of absolute ethanol, the solid which formed was filtered, and 100 ml. of washed commercial Raney nickel was added to the ethanol solution. The mixture was refluxed for 6 hours with stirring, the ethanol decanted and the residue washed twice with hot ethanol. The combined ethanol solutions were filtered, the ethanol removed on the steam-bath, water added to the residue and the organic material extracted with ether. The ethereal solution was washed with dilute ammonia, saturated sodium chloride solution and dried. After removal of the solvent, the residue was distilled through a screen-packed column at 10 mm. After a forerun (4.4 g.) boiling from 57–59°, the 9-carbethoxy-$\Delta^{4(10)}$-octalin distilled at 118–121°, yield 2.4 g. The distillation residue was mainly unreacted dithio ketal.

Lithium aluminum hydride (0.68 g., 0.018 mole) was added in one portion to a solution of 2.10 g. (0.01 mole) of the unsaturated ester in 60 ml. of anhydrous di-n-butyl ether. The mixture was heated under reflux with stirring for one hour and then allowed to stand at room temperature overnight. The excess hydride was decomposed by the dropwise addition of water with stirring and the inorganic salts dissolved in dilute hydrochloric acid. The ethereal layer was washed with sodium bicarbonate solution, dried and the solvent removed under reduced pressure. The residue solidified on cooling, 1.28 g., m.p. 67.5–68.6°. The material was not readily recrystallized but could be sublimed to yield the material as needles, m.p. 68.1–69.9°.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.36; H, 10.84.

Hydrogenation of $\Delta^{4(10)}$-9-Octalylcarbinol (XVI) in Ethanol.—The carbinol (375 mg., 2.26 mmoles) was hydrogenated in 30 ml. of ethanol in the presence of 0.10 g. of platinum oxide. After 2.5 hours slightly more than one mole equivalent of hydrogen had been adsorbed. The catalyst was filtered and the filtrate concentrated under reduced pressure. The residue solidified upon standing to yield 351 mg. (92.3%), m.p. 48.5–49.6°. A 50-mg. sample was sublimed, m.p. 49.2–50.6° (sinter 46.5°). The melting point for the pure cis isomer is 59.4–60.2° and for the trans, 84.2–84.6°.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.49; H, 12.12.

The tosylate was prepared from 111 mg. (0.66 mmole) of the crude carbinol by allowing it to stand in a solution of 4 ml. of anhydrous pyridine and 0.20 g. (1.05 mmoles) of p-toluenesulfonyl chloride for 12 hours. To the homogeneous solution there was added 5 ml. of water and 5 ml. of concentrated ammonia. The oil that separated solidified on scratching and was filtered. Recrystallization from 95%

ethanol gave 77 mg. (36%) of material, m.p. 110–127°. Recrystallization again from 95% ethanol yielded 37 mg., m.p. 131–137° and a second crop of 13 mg., m.p. 121–130°. The first crop on recrystallization gave 32 mg., m.p. 137.0–139.2°, mixed m.p. with authentic trans tosylate (m.p. 141.4–142.1°) gave m.p. 139.8–141.3°.

Hydrogenation of $\Delta^{4(10)}$-9-Octalylcarbinol (XVI) in Acetic Acid.—The carbinol (0.60 g., 3.7 mmoles) was hydrogenated in 15 ml. of acetic acid in the presence of 0.20 g. of platinum oxide, one mole equivalent of hydrogen being adsorbed in 30 minutes. The catalyst was filtered and the filtrate diluted with 75 ml. of water. The product was extracted with hexane and the hexane solution washed with sodium bicarbonate solution and water. The residual oil, remaining after removal of the solvent, solidified on cooling to give 590 mg. (97%) of material. A 75-mg. portion of this crude material was sublimed to yield 67 mg. of product, m.p. 55.7–56.8° (sinter 54°).

The tosylate was prepared from 452 mg. (2.59 mmoles) of the carbinol, 0.57 g. (3 mmoles) of p-toluenesulfonyl chloride in 3 ml. of pyridine as described above, yield 850 mg. (102%), m.p. 72–112°. Upon recrystallization from hexane, a first crop of 415 mg. (49.8%), m.p. 75–110°, was obtained which clearly displayed two distinct crystalline forms. A second crop of 297 mg. (28.1%), m.p. 76.0–79.2°, and a third crop of 58 mg. (7.0%), m.p. 65–71°, were obtained.

Acetolysis of trans-9-Decalylcarbinyl Tosylate.—A solution of 61.6 g. (0.19 mole) of tosylate, 22.0 g. (0.268 mole) of sodium acetate and 900 ml. of anhydrous acetic acid was heated under reflux for 22 hours. The slightly colored reaction mixture was poured into an equal volume of water and extracted twice with hexane. The extracts were washed with sodium bicarbonate solution and then the solvent was removed on the steam-bath. The residue was distilled through a screen-packed column at 62 mm. pressure; fraction 1, b.p. 127.0–128.5°, 4.64 g., n^{25}D 1.4956; fraction 2, b.p. 128.5–129.5°, 8.42 g., n^{25}D 1.4960; fraction 3, b.p. 129.5°, 7.61 g., n^{25}D 1.4964; fraction 4, b.p. 129.5°, 4.92 g., n^{25}D 1.4968; fraction 5, b.p. forced, 1.26 g., n^{25}D 1.4985. The ultraviolet spectrum of the combined material was taken in n-heptane solution: ϵ_{225} 900, ϵ_{220} 1970, ϵ_{215} 3840, ϵ_{210} 5250, ϵ_{205} 6400. The ultraviolet spectrum of pure Δ^9-octalin under similar conditions was: ϵ_{225} 750, ϵ_{220} 1300, ϵ_{215} 2240, ϵ_{210} 3620, ϵ_{205} 5060.

Anal. Calcd. for $C_{11}H_{18}$ (150.25): C, 87.93; H, 12.07. Found: C, 87.84; H, 12.01.

Acetolysis of cis-9-Decalylcarbinyl Tosylate.—A solution of 40.0 g. (0.124 mole) of tosylate, 14.3 g. (0.174 mole) of sodium acetate and 500 ml. of anhydrous acetic acid was heated under reflux for 24 hours and processed as described for the trans isomer. The residue was distilled through a screen-packed column at 62 mm. pressure: fraction 1, b.p. 126–129°, 16.10 g. (86.6%), n^{25}D 1.4972; fraction 2, b.p. forced, 1.11 g. (6.0%), n^{25}D 1.4987. The infrared spectrum was identical with the solvolysis product from the trans tosylate except for a few minor differences in intensities. The hydrocarbon upon titration with perbenzoic acid in purified chloroform showed the presence of exactly one double bond.

Anal. Calcd. for $C_{11}H_{18}$ (150.25): C, 87.93; H, 12.07. Found: C, 88.60; H, 11.52.

Ozonization of Acetolysis Product.—Ozone (140 mmoles) was passed into a solution of 1.00 g. (6.67 mmoles) of trans-solvolysis product in 50 ml. of ethyl acetate cooled in a Dry Ice-bath. The resulting blue solution was allowed to come to room temperature and then 3.0 ml. of 30% hydrogen peroxide was added. After standing overnight, the reaction mixture was heated under reflux for 30 minutes, cooled and water added. The organic layer was extracted twice with sodium bicarbonate solution. Acidification of the alkaline extracts followed by extraction with ether yielded 245 mg. of oily acid material (18.5% assuming keto acid).

The ethyl acetate was evaporated from the neutral fraction to yield 930 mg. (77% assuming diketone) of a viscous oil whose infrared spectrum indicated the presence of carbonyl groups (5.86 μ).

A 113-mg. portion of the neutral material, 4 ml. of methanol, 160 mg. of hydroxylamine hydrochloride, 350 mg. of sodium acetate and 3 ml. of water were heated under reflux for 20 minutes. The solid which formed was filtered, yield 59 mg. (45%), m.p. 228.0–229.5° dec. (rapid heating,

inserted at 210°, darkening immediately). Plattner[18] reports a m.p. 232–234° for the dioxime of cycloundecane-1,6-dione.

A solution of 198 mg. of the neutral material, 0.40 g. of semicarbazide hydrochloride and 0.60 g. of sodium acetate was refluxed for 20 minutes. The white solid was filtered but it was too insoluble in all common solvents to permit recrystallization; yield 114 mg. (35%), m.p. 220.0–220.5° dec. (darkening 190°). Plattner[18] reports a m.p. 218° for the disemicarbazone of cycloundecane-1,6-dione.

Anal. Calcd. for $C_{13}H_{24}O_2N_6$ (296.37): C, 52.68; H, 8.16; N, 28.36. Found: C, 52.94; H, 8.16; N, 28.36.

Hydrogenation of Acetolysis Product.—A mixture of 2.08 g. of the *cis* solvolysis product, 40 ml. of glacial acetic acid and 0.12 g. of platinum oxide was hydrogenated at 45 pounds pressure. After 1 hour, the reaction ceased and the uptake amounted to exactly 1 mole equivalent of hydrogen. The catalyst was filtered, the filtrate diluted with water, extracted with pentane and the extract washed with water and sodium bicarbonate solution. The pentane was removed under reduced pressure and the product distilled in short-path molecular type still at a block temperature of 90–95° (15–20 mm.); yield 1.71 g. (81.3%), $n^{25}D$ 1.4819. The infrared spectrum of the material was identical with that of an authentic sample of bicyclo[5.4.0]undecane.

Benzsuberane.[18]—A mixture of 5.00 g. (31.2 mmoles) of benzsuberone,[18,25] 3.7 ml. (63 mmoles) of 85% hydrazine hydrate and 25 ml. of diethylene glycol was heated under gentle reflux for 30 minutes. The reaction mixture was cooled, 4.16 g. of 85% sodium hydroxide was added and the mixture then heated at a bath temperature of 210° and the volatile components allowed to distil. The mixture then was heated under reflux until the evolution of nitrogen ceased (40 minutes). The cooled reaction mixture and distillate were combined, poured into water and extracted with pentane. The extracts were washed with water, concentrated on the steam-bath and the residue distilled through a screen packed column, b.p. 108–109° (22 mm.), yield 3.87 g. (84.8%), $n^{25}D$ 1.5386 (lit.[18] b.p. 99.8–100.0° (13 mm.), $n^{20}D$ 1.5520).

Anal. Calcd. for $C_{11}H_{14}$ (146.22): C, 90.35; H, 9.65. Found: C, 90.34; H, 9.77.

Bicyclo[5.4.0]undecane.—A mixture of 2.00 g. of benzsuberane, 30 ml. of glacial acetic acid and 0.30 g. of plati-

(25) J. W. Cook, R. Philip and A. R. Sommerville, *J. Chem. Soc.*, 164 (1948).

num oxide was hydrogenated at pressure of 45 pounds. The reaction ceased when 3 mole equivalents of hydrogen had been adsorbed. The mixture was processed and distilled as described for the hydrogenation of *cis* acetolysis product; yield 1.77 g. (85%), $n^{25}D$ 1.4818 (lit.[18] $n^{20}D$ 1.4845).

Anal. Calcd. for $C_{11}H_{20}$ (152.27): C, 86.76; H, 13.24. Found: C, 87.03; H, 13.09.

Kinetic Measurements.—A solution (250 ml.) of the tosylate (approx. 0.05 M) and sodium acetate (approx. 0.1 M) in anhydrous acetic acid was placed in a constant temperature bath and allowed to come to thermal equilibrium for 30 minutes before any aliquots were withdrawn. Each kinetic point was determined by withdrawing an aliquot with a 5-ml. calibrated automatic pipet, diluting with approximately 40 ml. of anhydrous acetic acid and titrating potentiometrically using a model G Beckman pH meter. The electrodes

TABLE II

ACETOLYSIS OF *trans*-9-DECALYLCARBINYL TOSYLATE AT 90.03 ± 0.03°

Time, sec.	Titer, ml.	$10^1\ k$, sec.$^{-1}$
0	8.73	..
16,200	8.55	2.83
31,800	8.30	2.60
77,400	7.78	2.87
99,000	7.56	2.92
120,600	7.37	2.68
163,800	7.01	2.92
185,400	6.84	2.92
207,000	6.67	3.07
268,800	6.28	2.92
348,900	5.84	2.95
	4.29	..

Average 2.87 ± 0.10

employed were silver chloride platinum wire and a glass electrode. The solutions were titrated with 0.0545 M p-toluenesulfonic acid monohydrate in anhydrous acetic acid with the stoichiometric amount of acetic anhydride added to react with the water of crystallization present in the toluenesulfonic acid. The data for one run are given in Table II.

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Flue-cured Tobacco. II. Neophytadiene

By R. L. ROWLAND

An unsaturated hydrocarbon, neophytadiene, has been isolated from aged flue-cured tobacco leaf and has been shown to be 3-methylene-7,11,15-trimethyl-1-hexadecene. Neophytadiene also has been obtained in small amounts from the dehydration of phytol. The dehydration of phytol has produced different olefins depending upon the acidity of the dehydration media.

In a continuation of our study of the ether-soluble materials extracted from aged flue-cured tobacco,[1] we have investigated the hydrocarbon fraction. The hydrocarbons were isolated by chromatography using silicic acid and alumina. The saturated hydrocarbons were separated from the unsaturated hydrocarbons by crystallization from acetone. The saturated hydrocarbons, which made up 0.06–0.1% of the dry weight of the tobacco leaf, appeared to be identical with those studied

by Chibnall, *et al.*,[2] who found a mixture of straight-chain hydrocarbons containing an odd number of carbon atoms ranging from $C_{25}H_{52}$ to $C_{33}H_{68}$. The unsaturated hydrocarbon, which also constituted 0.06–0.1% of the dry weight of the tobacco leaf, has been named neophytadiene. Our studies have shown that neophytadiene is 3-methylene-7,11,-15-trimethyl-1-hexadecene (I).

The infrared absorption of neophytadiene, Fig. 1, showed absorption at 6.27 μ, indicating conju-

(1) R. L. Rowland, P. H. Latimer and J. A. Giles, THIS JOURNAL, 78, 4680 (1956).

(2) A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams and P. N. Sahai, *Biochem. J.*, 28, 2189 (1934).