1.5508. The infrared absorption spectrum showed that no alcoholic hydroxyl or secondary amine group was present, but it did disclose some carbonyl impurity (1699 cm.$^{-1}$). A picrate, formed in ethanol and recrystallized from the same solvent, separated as yellow prisms, m.p. 165°, with the correct analysis for either the picrate of benzo[c]-1-azabicyclo[5.5.0]dodecane (VIId) or the picrate of benzo-[j]-1-azabicyclo[6.4.0]dodecane (VId).

Anal. Calcd. for $C_{21}H_{24}N_4O_7$: C, 56.75; H, 5.44; N, 12.61. Found: C, 57.04; H, 5.68; N, 12.61.

When triturated with absolute ether, the higher-boiling product crystallized as colorless prisms, m.p. 92–93°, yield 2.031 g. (48%). The infrared spectrum showed OH and/or NH absorption (a sharp band at 3615 cm.$^{-1}$ and a broad band in the 3400 cm.$^{-1}$ region). Analysis was consistent with the proposed formula, benzo[c]-7-hydroxyazacyclododecane (IXd), and not with the tricyclic aminoalcohol formula, benzo[j]-7-hydroxy-1-azabicyclo[6.4.0]dodecane (VIIId).

Anal. Calcd. for $C_{15}H_{23}NO$ (IXd): C, 77.20; H, 9.94; N, 6.00. Calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 76.92; H, 10.03; N, 6.09.

Methylations of the Aminoalcohols

Benzo[c]-1-methyl-7-hydroxyazacyclohendecane (Xc).—The formaldehyde–formic acid procedure[2] was used. Distillation of the product from 0.668 g. of benzo[c]-7-hydroxyazacyclohendecane (IXc) yielded 0.490 g. (69%) of a substance which solidified after standing for several days at room temperature. This material was recrystallized from petroleum ether in the form of colorless prisms, m.p. 82.5–84°. The infrared absorption spectrum (chloroform solution) showed strong OH absorption (3610 cm.$^{-1}$) and showed new absorption peaks indicative of the introduction of a methyl group (1345 and 2770 cm.$^{-1}$).

Anal. Calcd. for $C_{15}H_{23}NO$: C, 77.20; H, 9.94; N, 6.00. Found: C, 77.08; H, 9.71; N, 5.81.

Benzo[c]-1-methyl-7-hydroxyazacyclododecane (Xd).—A 1.137-g. (4.9 millimoles) sample of benzo[c]-7-hydroxyazacyclododecane (IXd) was methylated with methyl iodide in the presence of potassium bicarbonate.[3] The product distilled as a viscous yellow-green liquid, b.p. 151–155° (1 mm.), $n^{20}D$ 1.5484, yield 0.659 g. (55%). The infrared spectrum (chloroform solution) still showed OH absorption (a sharp band at 3610 cm.$^{-1}$ and a wide band about 3420 cm.$^{-1}$), and new methyl absorption (1350 and 2770 cm.$^{-1}$). A trace of carbonyl impurity was also indicated (1700 cm.$^{-1}$).

Anal. Calcd. for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.41; H, 10.31; N, 5.68.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Chlorination of *trans*-Decalin

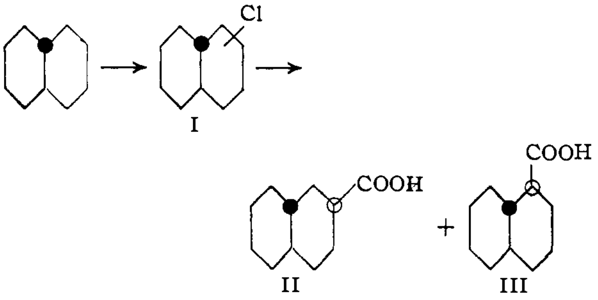
BY WILLIAM G. DAUBEN AND ROBERT C. TWEIT[1]

RECEIVED DECEMBER 8, 1953

trans-Decalin was chlorinated and the product was shown to consist of approximately equal amounts of the 1- and 2-isomers.

In the course of a study related to the determination of the steric relationship existing between the various decalols and decalylamines,[2] the chlorination of decalin was investigated as a possible route for starting materials. This reaction has been widely utilized for the past 50 years[3–9] for the preparation of *trans*-decalin derivatives and in all cases only products derived from a 2-chlorodecalin have been reported. Recently, Zlatkis and Smith[9] published an improved method of chlorination of this decalin and claimed the material formed could be separated, by distillation, into two isomeric *trans*-2-chlorodecalins, identified by conversion to known *trans*-2-decalols, m.p. 53.5° and 74°.[10,11]

The chlorination of *trans*-decalin has been repeated utilizing the procedure of Tsatsas[8] and a 58% yield of chlorodecalins (I) was obtained (based upon recovered decalin). The product was converted to the Grignard reagent which upon carbonation gave a mixture of acids in 41% yield. By recrystallization, the known *trans*-decahydro-2-naphthoic acid (II),[12] m.p. 105–106° (lit.[8] 109°), was readily obtained. Fractional crystallization of the acids in the mother liquor gave no pure acid.



In an attempt to separate this remaining isomeric mixture, partition chromatography was investigated. Using the method of Ramsey and Patterson[13] it was found that the material could be separated into two fractions. The faster moving fraction was found to consist of the *trans*-2-acid (II) while the slower moving fraction yielded the previously unreported *trans*-1-acid (III), m.p. 102.0–102.8°. The structures of these acids were established by degradation to known decalylam-

---

[1] U. S. Rubber Company Fellow, 1952–1953.

[2] W. G. Dauben and E. Hoerger, THIS JOURNAL, **73**, 1504 (1951).

[3] H. Leroux, *Compt. rend.*, **139**, 672 (1904).

[4] W. Borsche and E. Lange, *Ann.*, **434**, 219 (1923).

[5] N. D. Zelinsky, *Ber.*, **57**, 2062 (1924).

[6] E. Gysin, *Helv. Chim. Acta*, **9**, 59 (1926).

[7] P. Ferrers and M. Fehlmann, *ibid.*, **11**, 763 (1928).

[8] G. Tsatsas, *Ann. chim.*, **19**, 217 (1944).

[9] A. Zlatkis and E. A. Smith, *Can. J. Chem.*, **29**, 162 (1951).

[10] W. Hückel, R. Mentzel, E. Brinkmann and E. Kamenz, *Ann.*, **451**, 109 (1926).

[11] W. Hückel, R. Danneel, A. Gross and H. Naab, *ibid.*, **502**, 99 (1933).

[12] In formulas II and III, the open circles denote that the configuration of the carboxyl group with respect to the nearest ring juncture hydrogen atom is not known at present. In all formulas, the hydrogen at carbon 9 of the decalin nucleus has arbitrarily been written as above the plane of the paper.

[13] L. L. Ramsey and W. J. Paterson, *J. Assoc. Offic. Agr. Chemists*, **31**, 139 (1938).

ines.[10,11,14,15] The acid II yielded a *trans*-2-decalylamine (Hückel[10,15] *trans*-2-II, acetamide, m.p. 163°) and the acid III, a *trans*-1-decalylamine (Hückel[11,14,15] *trans*-1-II, acetamide, m.p. 182°).

In view of the fact that the previous workers[3-9] had not reported finding 1-decalyl derivatives when the Grignard reagents were converted to decalols by oxidation, this phase of the problem was reinvestigated. It was found that the crude yield of mixed decalols obtained in the above fashion was the same as that reported by Tsatsas.[8] From this liquid decalol mixture a small amount of a *trans*-2-decalol, m.p. 75° (Hückel[10,15] *trans*-2-II, m.p. 75°) crystallized. The remaining oil was converted to a mixture of hydrogen phthalate esters which in turn were roughly separated by solubility in petroleum ether. Such a procedure did not proceed in the manner described by Tsatsas[8] since both fractions were oily solids. When the fraction insoluble in petroleum ether was saponified, pure *trans*-2-decalol, identical with the above, was obtained only after extensive fractional crystallization. The residue from the crystallizations was converted to a *p*-nitrobenzoate ester and the only pure isomer which could be isolated was a *trans*-1-decalol ester (Hückel[11,14,15] *trans*-1-II-decalol, m.p. 63°, *p*-nitrobenzoate, m.p. 86°). Saponification of the petroleum ether soluble fraction followed by conversion of the decalols to *p*-nitrobenzoate esters and extensive fractional crystallization yielded a small amount of the other *trans*-1-decalol ester (Hückel[11,14,15] *trans*-1-I-decalol, m.p. 49°, *p*-nitrobenzoate, m.p. 116°) as the only pure compound.

In order to obtain a more accurate estimation as to the relative amounts of the 1- and 2-isomers in the original mixture, a sample of the decalol mixture was oxidized and the resulting ketones converted into 2,4-dinitrophenylhydrazones. These derivatives were separated by a combination of crystallization and chromatography and the results indicated about equal amounts of the 1- and 2-decalyl series.

The over-looking of the 1-isomer in the direct chlorination mixture by previous workers can most likely be ascribed to incomplete separation of the products of their subsequent reactions. For example, the remarkable stereospecificity observed by Zlatkis and Smith[9] in the conversions of the "apparent" isomeric 2-decalyl chlorides *via* the Grignard reagent could adequately be explained by assuming that one of their isomers was rich in 1-chlorodecalin and the reported *trans*-2-decalol, m.p. 53.5°, was actually a mixture of the *trans*-1-decalols, m.p. 63° and 49°, respectively.

No conclusion can be drawn as to whether chlorination occurred at the 9-position, the carbon atom at which nitration is reported to preferentially take place.[16] That the 9-position can be chlorinated was demonstrated by Bartlett, Condon and Schneider[17] who prepared a chlorodecalin mixture by an exchange reaction using decalin, *t*-butyl chloride and aluminum chloride. They established the presence of the 9-isomer by dehydrochlorination to Δ^9-octalin and the 1-isomer by conversion of the mixture to ketones and the isolation of the *trans*-1-decalone, as a 2,4-dinitrophenylhydrazone. From our work, it is evident that if about equal amounts of the 1- and 2-chloride were present, only the 1-isomer would be readily isolated by direct crystallization. Bartlett and his associates also prepared a mixture of carboxylic acids from their material and isolated one pure compound (m.p. 103.8–105.6°). Although no structure was suggested for the acid, it would appear from the present work that in a direct isolation only a *trans*-2-acid is readily freed from a mixture and the properties of their material agree well with the known *trans*-2-acid, m.p. 105–106°.

Experimental[18]

trans-Decalin.—"Practical" grade decalin was stirred with concentrated sulfuric acid for three hours and then the organic layer separated, washed with water, saturated aqueous sodium carbonate, water and then dried and distilled, b.p. 192–194°. This material, 768 g., was stirred with 343 g. of anhydrous aluminum chloride for 48 hours at room temperature, the mixture filtered and distilled, b.p. 186–187.5°, n^{20}_{D} 1.4696, yield 689 g. (90%) (reported[19] b.p. 185.5°, n^{20}_{D} 1.4697).

Chlorination of *trans*-Decalin.[8]—*trans*-Decalin (689 g.) was placed in a wide-mouth flask fitted with a stirrer and a gas inlet tube extending below the surface of the liquid. A solution of 1 g. of iodine in 15 ml. of ethanol was added, the mixture cooled with stirring to −5° and chlorine bubbled in slowly. At intervals the flask was removed, allowed to warm to room temperature, weighed and then cooled to −5° again. After 14 days the weight increase of the solution was 175 g. (theory 177 g.). The organic material was dissolved in ether, washed with 15% sodium bicarbonate and then sodium bisulfite, dried and the ether removed. Distillation in vacuum yielded 274 g. of unreacted *trans*-decalin (n^{20}_{D} 1.4696) and 302 g. (58% based upon recovered decalin) of mixed *trans*-chlorodecalins, b.p. 100–115° (12 mm.), n^{24}_{D} 1.4916, d^{16}_{4} 1.0253 (lit.[8] b.p. 108–115° (13 mm.), n^{25}_{D} 1.4939, d^{25}_{4} 1.0231).

***trans*-Decahydronaphthoic Acids.**[8]—The Grignard reagent prepared from 9.7 g. (0.4 mole) of magnesium and 52.3 g. (0.3 mole) of mixed *trans*-chlorodecalins in 300 ml. of dry ether was carbonated by bubbling carbon dioxide into the stirred solution for 2 hours at −5°. The mixture was decomposed with acid and the decahydronaphthoic acids isolated by extraction with 25% sodium hydroxide. The product was obtained as a sirup which solidified on cooling, 22.5 g. (44%). The crude acid was recrystallized from hexane, the first crop amounted to 6.0 g., m.p. 102–104°. Further recrystallization of the first fraction gave a pure *trans*-decahydro-2-naphthoic acid, m.p. 105–106° (lit.[8] 109°). Attempts to obtain other pure materials were unsuccessful.

Separation of Decahydronaphthoic Acids.—The crude acid mixture (see above) remaining after removal of some of the *trans*-2-acid was separated utilizing the method of Ramsey and Patterson.[13] Silicic acid (400 g., Mallinckrodt No. 2847) was mixed in two portions in a mortar with totally 325 ml. of methanol, 2 ml. of brom cresol green solution, 25 ml. of water and 10 ml. of 1 *N* ammonium hydroxide. The resulting powder was slurried with 1200 ml. of isoöctane saturated with 90% methanol and packed into a column 6.3 × 50 cm. The excess isoöctane was forced through the column and then a solution of 300 mg. of crude acid from the above crystallization mother liquors in 15 ml. of isoöctane was placed on the column. The column was developed with isoöctane and two bands appeared. The threshold volume of the first zone was about 1400 ml. and

---

[14] W. Hückel, *Ann.*, **441**, 1 (1925).

[15] W. Hückel, *ibid.*, **533**, 1 (1937). The Roman numeral in the name *trans*-2-II refers to the arbitrary assignment of Hückel of decalin derivatives into two series, I and II.

[16] S. Nametkin, *Ber.*, **59**, 370 (1926).

[17] P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1531 (1944).

[18] Analyses by the Microanalytical Laboratory of the Department of Chemistry, University of California. All melting points are corrected.

[19] W. F. Seyer and R. D. Walker, THIS JOURNAL, **60**, 2125 (1938).

when the solvent was removed from this fraction, slightly impure *trans*-2-acid was obtained. The second zone had a threshold volume of 1700 ml. and gave 57 g. of a new acid which after recrystallization from ethanol–water melts 102.0–102.8°.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.35; H, 10.07.

trans-**Decalylamines.** (a) **From** *trans*-**1-Acid (III).**—The acid (18 mg., 0.1 mmole) was dissolved in a mixture of 1 ml. of concentrated sulfuric acid and 2 ml. of chloroform. Approximately 10 mg. (0.15 mmole) of sodium azide was added slowly and the stirring continued at 30° for 3 hours. The mixture was poured onto ice, the chloroform layer separated and the aqueous layer made alkaline and extracted with ether. Benzene and acetic anhydride were added to the ethereal solution and the ether distilled and the residue refluxed for 10 minutes. The solution was then washed with dilute sodium hydroxide and water until neutral, concentrated and pentane added. The amide crystallized on cooling; yield 10.9 mg. (56%), m.p. 183.8–184.2° (lit.[11] 182° for N-(*trans*-1-decalyl)-acetamide).

The reaction was repeated on 14 mg. (0.77 mmole) of acid and the amine benzoylated with benzoyl chloride and sodium hydroxide, m.p. 195° (lit.[11] 195° for N-(*trans*-1-decalyl)-benzamide).

(b) **From** *trans*-**2-Acid (II).**—Starting with 546 mg. (3.0 mmoles) of the acid and proceeding as above, there was obtained 232 mg. (40%) of the acetamide, m.p. 161.5–162.5° (lit.[10] 163° for N-(*trans*-2-decalyl)-acetamide).

trans-**Decalols.**—The Grignard reagent prepared as above from 7.0 g. (0.29 mole) of magnesium and 50 g. (0.29 mole) of mixed *trans*-chlorodecalins, except that the total reaction time was extended to 17 hours to ensure completion, was oxidized at −5° by passing oxygen through the solution for 12 hours. The product was decomposed with hydrogen peroxide and ice. After separation of the ethereal layer, it was washed with sodium thiosulfate, dried and the solvent removed. The residue was distilled at 13 mm. pressure through a Podbielniak type spiral band column, b.p. 68–111°, 10.8 g. (27%) of *trans*-decalin, b.p. 111–120°, 24.7 g. (55%) of *trans*-decalols and 4.6 g. of residue.

The decalol fraction partially crystallized upon standing and from it 2.3 g. of *trans*-2-decalol (IV), m.p. 74.0–75.5° (lit.[10] 75°) was obtained.

(a) **Separation of Decalols as Acid Phthalate Esters.**—The remaining mixture of decalols was partially separated following the procedure of Tsatsas.[8] After converting the decalols to acid phthalates by heating with phthalic anhydride, the oily esters were extracted with hexane in a Soxhlet apparatus. Both the soluble and insoluble fractions were oily and obviously not pure compounds. Both fractions were saponified with base and from the hexane-insoluble fraction there was obtained a small quantity of *trans*-2-decalol (IV), m.p. 74–76° (lit.[10] 75°) after repeated recrystallization from hexane. When the residue from the mother liquors of these recrystallizations was converted to the *p*-nitrobenzoate ester and the product recrystallized from ethanol–water, *trans*-1-decalyl *p*-nitrobenzoate (V), m.p. 84–86° (lit.[11] 86°) was obtained.

The hexane-soluble fraction also was converted to the *p*-nitrobenzoate ester which on recrystallization from ethanol yielded a small quantity of *trans*-1-decalyl *p*-nitrobenzoate (VI), m.p. 115.0–115.5° (lit.[11] 116°). The remaining material melted over a wide range and could not be purified by further recrystallization although Tsatsas[8] reported the isolation of a 2-decalol from this fraction. Only a small fraction of the crude decalol mixture was recovered as pure isomers.

(b) **Separation as 2,4-Dinitrophenylhydrazones.**—The mixed decalols (after removal of 9% of *trans*-2-decalol), 1 g., were oxidized with 1.3 g. of potassium dichromate in aqueous solution. Sulfuric acid (0.6 ml.) was dropped slowly into the stirred solution and then the reaction mixture extracted three times with ether. The ethereal solution was washed with base, dried and the ether removed. The residue was converted to a mixture of dinitrophenylhydrazones by the usual method,[20] yield 1.40 g. (65%). The mixture was recrystallized first from benzene–hexane and then from ethyl acetate–ethanol, yield 0.50 g. of *trans*-1-decalone 2,4-dinitrophenylhydrazone, m.p. 225.2–227.8° (lit.[21] 222–222.5°). The residual material from the mother liquors was dissolved in 50 ml. of benzene and a 5-ml. aliquot removed for chromatography. The benzene aliquot was diluted with 10 ml. of hexane and chromatographed as described by Roberts and Green[22]; development with hexane–ether (20:1) separated the mixture into two zones which were extruded, sectioned and eluted. The first zone gave 21 mg. of crude *trans*-1-decalone derivative (equivalent to 0.21 g. in original mixture) and the second zone gave 61 mg. (equivalent to 0.61 g.) of material which was rechromatographed and recrystallized from ethanol–water to yield *trans*-2-decalone 2,4-dinitrophenylhydrazone, m.p. 159–160° (for comparison with authentic sample see below).

The total yield of the *trans*-1-decalone derivative was 0.71 g. (54%) and of the *trans*-2-decalone derivative was 0.61 g. (46%). Since 9% of the starting decalol mixture has been removed as crystalline *trans*-2-decalol before oxidation, the amounts of the two isomers present in the original chloride mixture were about equal.

trans-2-Decalol, m.p. 74.0–75.5°, was oxidized to *trans*-2-decalone as described above. The ketone was purified through the bisulfite addition product and then converted to the 2,4-dinitrophenylhydrazone. The derivative was recrystallized from hexane–benzene and ethanol–water, the yellow prisms melt 164.7–165.2°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.58; H, 6.09; N, 17.10.

BERKELEY 4, CALIFORNIA

---

[20] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

[21] J. W. Cook and G. A. Lawrence, *J. Chem. Soc.*, 817 (1937).

[22] J. D. Roberts and C. Green, *Anal. Chem.*, **18**, 335 (1946).