

TABLE II
SEPARATION OF MIXTURES OF AROMATIC ACIDS ON SILICIC ACID COLUMNS

Acids	Mg. put on column	State in which applied to the column	Length of column, cm.	Fractions in which eluted ^a	Peak fraction	Recovery, %
5,6,7,8-Tetrahydro-2-naphthoic,	2.96			6-13(8)	8	102.3
2-naphthoic and salicylic	2.87	Suspension	23	14-23(10)	16	102.8
	3.02			27-41(15)	31	96.2
2-Naphthoic and benzoic	2.50	Suspension		37-50(14)	40	96.8
	3.40		50	57-77(21)	62	95.3
<i>cis,trans</i> -Decahydro-2-naphthoic ^b	3.50			14-17(4)	15	Total:
and <i>cis,cis</i> -decahydro-2-naphthoic ^b	3.42	Solution	53.5	18-24(7)	19	53.8
3-Hydroxy-2-naphthoic and 2-naphthoic ^c	..	Suspension	48	43-54(12)	46	...
	..			58-77(20)	66	...

^a Same as footnote *b* for Table I. ^b W. G. Dauben and E. Hoerger, *THIS JOURNAL*, **73**, 1505 (1951); the gift of these acids from Dr. Dauben is gratefully acknowledged; the chromatographic positions assigned to these acids are arbitrary. ^c These acids cannot be separated on a 23-cm. column (see Table I); the weight and recovery were not determined in this experiment.

methanol (90%)—0.5 *N* sulfuric acid; the upper layer was used as the mobile phase and the lower layer as the stationary phase.

Silicic Acid.—Mallinckrodt analytical reagent grade, 100-mesh silicic acid was used. Fine particles were removed by repeated (5–6 times) suspensions in an excess of distilled water and decantation after an hour. The jelly-like, fully hydrated, acid was then filtered under suction, dried overnight at 120°, and stored in a desiccator.

Preparation of the Column.—Ten grams of silicic acid was ground thoroughly in a mortar with 7 ml. of the stationary phase, added in 2–3 lots; the acid appeared completely *dry* after this treatment. To this was added 25–30 ml. of the mobile phase and the mixture ground into a *uniform* slurry, which was poured from a 50-ml. beaker into a Pyrex column, 35 cm. (or 75 cm., if the height of the packed column was to be about 50 cm.) long and of 1 cm. internal diameter. The glass column had a small constriction, 5 cm. from the bottom, which supported a closely fitting, detachable sintered-glass plate, kept in position by a thick filter paper disc. It is very important that no air bubbles remain trapped in the slurry inside the column as they were found to cause eventual coagulation of the column. Extensive coagulation (beyond 1–2 cm. at the bottom) during the run was found to affect the chromatographic separation adversely. To avoid this, the silicic acid slurry was poured into the column gently, in small lots, and the column tapped after each addition until air bubbles no longer escaped from the top. Five-lb. pressure was applied to pack the column to the desired length, care being taken that the level of the solvent did not drain below that of the silicic acid at any time.

Application of the Acid and Collection of Fractions.—The organic acid was dissolved in 0.2 ml. of reagent grade ethyl acetate and 2 ml. of the equilibrated ligroin; when large quantities of the acid were used, and in case of some less soluble acids, a suspension was obtained. The solution or suspension of the acid was gently transferred, with a dropper, to the column, in which the solvent had been allowed to run down *almost* to the level of the silicic acid; the solvent was again allowed to drain similarly, with the application of pressure (5 lb.). The above process was repeated three times with the addition of 1 ml. of the mobile phase solvent to the column each time. The silicic acid in the column was finally covered with 3–4 ml. of the ligroin, the column immediately attached to an automatic fraction collector (a model manufactured by Gilson Medical Electronics Co., Madison, Wisconsin, was used) and the chromatogram developed with the mobile phase solvent at a pressure of 5 lb. Two-ml. fractions were collected.

The use of 0.2 ml. of ethyl acetate to dissolve the acid(s) before application to the column, was not found to affect the results significantly (see Table I); its use, however, greatly facilitated solution of the acids in the mobile phase.

Treatment of Fractions.—Two ml. of distilled water, 0.2–0.3 ml. of butanol and one drop of phenol red indicator (*pH* 7.4) were added to all the fractions, which were then titrated with 0.006–0.012 *N* sodium hydroxide, added from a microburet. The two-phase mixture was continuously

stirred with a stream of carbon dioxide-free air. The end-points were very sharp and could be read accurately to ± 0.005 ml. of alkali.

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The Stereochemistry of Some Derivatives of Decalin with Angular Substituents¹

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Hussey, Liao and Baker² recently described the synthesis of a new isomer of 10-methyl-2-decalol (IIIA) by a novel approach to bicyclic compounds with angular methyl groups. The procedure involved catalytic hydrogenation of 10-carbethoxy- $\Delta^{1,9}$ -2-octalone (IB) and the transformation of the angular carbethoxy group in the product (IIB) into a methyl group. The authors concluded that the 10-carbethoxy-2-decalone (IIB) and all compounds derived from it, including the alcohol IIIA, had the *cis*-configuration at the ring juncture on the basis of the following evidence.

A series of operations converted the 10-carbethoxy-2-decalone (IIB) to a 9-methyldecalin IVA with a refractive index (n_D^{25} 1.4802) similar to that of two samples of 9-methyldecalin to which Hibbit and Linstead³ and Linstead, Millidge and Walpole⁴ had assigned the *cis*-configuration. Moreover, this hydrocarbon was isomerized in the presence of aluminum chloride, as had also been observed by Hibbit and Linstead with their sample,³ to a product with a lower refractive index (n_D^{25} 1.4667). This value was similar to one reported by Ruzicka,

(1) This work was supported by institutional grants to the Detroit Institute of Cancer Research from the American Cancer Society, Inc., The American Cancer Society, Southeastern Michigan Division and The Kresge Foundation.

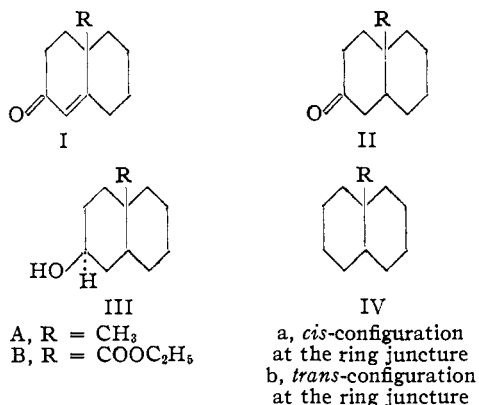
(2) A. S. Hussey, H. P. Liao and R. H. Baker, *THIS JOURNAL*, **75**, 4727 (1953).

(3) D. C. Hibbit and R. P. Linstead, *J. Chem. Soc.*, 470 (1936). This sample (n_D^{16} 1.4813) was prepared by the catalytic hydrogenation of a 9-methyloctalin.

(4) R. P. Linstead, A. F. Millidge and A. L. Walpole, *ibid.*, 1140 (1937). In this work the hydrocarbon (n_D^{16} 1.4844) was prepared by a Clemmensen reduction of a pure sample of 9-methyl-2-decalone the *cis*-configuration of which was proven by degradation.

Koolhaas and Wind⁵ for a 9-methyldecalin which was thought to have the *trans*-configuration.

More recently it was shown⁶ that some heterobicyclic six-membered ring systems with angular methyl groups are slightly more stable in the *cis*-configuration. It was suggested, by re-interpretation of the available degradational evidence,⁶ that the sample which Hibbit and Linstead used in the isomerization⁸ may actually have consisted predominantly of *trans*-9-methyldecalin and that the isomerization may, at least to some extent, have taken place in the opposite direction.



This interpretation cast doubt on the main basis for Hussey, Liao and Baker's configurational assignment and opened up the possibility that their angularly substituted decalin derivatives might have the *trans*-configuration at the ring juncture. This has now been substantiated by demonstrating that the alcohol, which Hussey, Liao and Baker had called *cis*-10-methyl-2-*cis*-decalol (IIIa) actually is *cis*-10-methyl-2-*trans*-decalol (IIIb).⁷ An alcohol, identical with it, was produced in a lithium aluminum hydride reduction of *trans*-10-methyl-2-decalone (IIAb).^{8,9} Moreover, the oxidation of Hussey, Liao and Baker's sample of the alcohol IIIA yielded a ketone, the 2,4-dinitrophenylhydrazone of which was identical with this derivative of an authentic sample of *trans*-10-methyl-2-decalone (IIAb).

These reactions prove that the 10-carbethoxy-2-decalone (IIB) obtained in the catalytic hydrogenation of 10-carbethoxy- $\Delta^{1:9}$ -2-octalone (IB),² as well as all the compounds derived from it,² should be assigned the *trans*-configuration at the ring juncture. This is particularly interesting because the closely related 10-methyl- $\Delta^{1:9}$ -2-octalone (IA) is reduced under almost the same conditions to give 10-methyl-

2-decalone consisting primarily of the *cis*-isomer IIAa.^{8,10}

Hussey, Liao and Baker prepared their 9-methyldecalin by a lithium aluminum hydride reduction of the crystalline *p*-toluenesulfonate of a 9-hydroxy-methyldecalin. Since the present work shows that this intermediate is the *trans*-isomer, it is evident the 9-methyldecalin also belongs to the *trans*-series. This is worthy of special mention since its refractive index (n^{25}_D 1.4802)² differs considerably from those of the other two samples to which a *trans*-configuration had been assigned previously, namely the aluminum chloride isomerized sample of Hibbit and Linstead (n^{17}_D 1.4697)⁸ and the hydrocarbon prepared by Ruzicka, Koolhaas and Wind (n^{20}_D 1.4631),⁵ while it is quite similar to that of a sample of *cis*-9-methyldecalin (n^{12}_D 1.4844)⁴ the authenticity of which could be questioned only on the basis of the possibility of a partial isomerization during the Clemmensen reduction.

In conclusion, a remark should be made on the configuration of the hydroxyl group in the 10-methyl-2-*cis*-decalol, produced in the catalytic hydrogenation of *cis*-10-methyl-2-decalone (IIAa).^{11,12} Hussey, Liao and Baker² concluded that this alcohol had the *trans*-configuration of hydroxyl-to-methyl group because it differed from the 10-methyl-2-decalol prepared from 10-carbethoxy-2-decalone, which they considered also to have the *cis*-configuration at the ring juncture, and for which they demonstrated the *cis*-relationship of hydroxyl- and methyl-groups. Since the present work shows that the latter alcohol is, in fact, a derivative of *trans*-9-methyldecalin, this argument is invalid and the configuration of the hydroxyl group in the hydrogenation product is still unknown.

Experimental

***cis*-10-Methyl-2-*trans*-decalol (IIIb).**—The decarboxylation of 175 mg. of *trans*-3-carboxy-10-methyl-2-decalone, m.p. 129–130°, was carried out at 130–140° for 5 minutes. The residual oily *trans*-10-methyl-2-decalone (IIAb) was taken up in ether and heated with 10 cc. of a 2% solution of lithium aluminum hydride in ether for 30 minutes. The excess reagent was decomposed with dilute hydrochloric acid and the product was isolated in the usual manner. By crystallization from petroleum ether at –60°, 51 mg. (36%) of *cis*-10-methyl-2-*trans*-decalol (IIIb) was obtained, m.p. 66–70°. The m.p. was raised to 69–70° by recrystallization from the same solvent and was not depressed on admixture of the "*cis*-10-methyl-2-*cis*-decalol" of Hussey, Liao and Baker.^{2,13}

The material in the mother liquor was converted to the 3,5-dinitrobenzoate, yield 82 mg. (27%), m.p. 100–102°. Three recrystallizations from petroleum ether brought the m.p. to 110–111° alone and when mixed with this derivative of "*cis*-10-methyl-2-*cis*-decalol."^{2,13}

***trans*-10-Methyl-2-decalone (IIAb).**¹⁴—A solution of 88.0 mg. (0.880 mole) of chromic anhydride in 8.0 cc. of glacial acetic acid and 2.0 cc. of water was added dropwise over 35 minutes to a solution of 212.3 mg. (1.26 moles) of "*cis*-10-methyl-2-*cis*-decalol," m.p. 67.4–68.5°,² in acetic acid at

(10) E. C. duFeu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).

(11) V. C. E. Burnop and R. P. Linstead, *J. Chem. Soc.*, 720 (1940).

(12) R. B. Woodward, *THIS JOURNAL*, 62, 1208 (1940); M. Yanagita and A. Tahara, *J. Org. Chem.*, 18, 792 (1953).

(13) We are grateful to Dr. Allen S. Hussey for comparing the two samples of the alcohol and the 3,5-dinitrobenzoate and reporting that the mixture m.p.'s were not depressed.

(14) This preparation of 10-methyl-2-decalone was carried out by Dr. Allen S. Hussey at Northwestern University who kindly furnished us with samples of the ketone and its 2,4-dinitrophenylhydrazone.

(5) L. Ruzicka, D. R. Koolhaas and A. H. Wind, *Helv. Chim. Acta*, 14, 1151 (1931). This hydrocarbon (n^{20}_D 1.4631) was obtained from a Clemmensen reduction of 10-methyldecalin-1,3-dione.

(6) W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. S. Smith, *J. Org. Chem.*, 19, 222 (1954).

(7) For an explanation of this nomenclature see footnote 3 in reference 2. An alternative designation for compounds of this type could be modeled after the one used for steroids (Cf. L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd ed., Reinhold Publ. Corp., New York, N. Y., 1949). According to it, IIIAa would be called *cis*-10-methyldecalin-2 β -ol, while IIIAb would be *trans*-10-methyldecalin-2 β -ol.

(8) R. B. Woodward, F. Sondheimer, K. Taub, K. Heusler and W. M. McLamore, *THIS JOURNAL*, 74, 4223 (1952).

(9) A. S. Dreiding and A. J. Tomaszewski, *J. Org. Chem.*, 19, 241 (1954).

45 ± 5°. After standing for 15 minutes the mixture was poured onto 50 cc. of ice-water. The acid was neutralized by adding 12 g. of KOH, then NaHCO₃ and the product was extracted with ether. The crude ketone weighed 208.1 mg. A chromatographic procedure on alumina in pentane gave 187.2 mg. (89%) of 10-methyl-2-decalone which could not be crystallized.

The 2,4-dinitrophenylhydrazone was prepared from 163.0 mg. of ketone and 220 mg. of 2,4-dinitrophenylhydrazine in 25 cc. of ethanol with 1 cc. of H₂SO₄; yield 320 mg. (94%), m.p. 130–147°. When recrystallized from ethanol or ethanol-pyridine, a crystalline form melting at 125–128° mixed with higher melting material (148–154°) was observed. Several crystallizations from ethanol and from ether raised the m.p. to 174–176°; yield 220 mg. (64%). When this sample was mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of *trans*-10-methyl-2-decalone, m.p. 173–175°, it melted at 172–175°. Mixture of the present sample with the 2,4-dinitrophenylhydrazone of *cis*-10-methyl-2-decalone, m.p. 175–177°,^{8,9} produced a m.p. of 150–158°.

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Tetrakis-(trimethylsiloxy)-titane¹

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In the work published by various authors² about trimethylsilanol, the only esters of this compound with inorganic acids reported were the phosphate,^{2a} the sulfate,^{2b,c,3} the silicate^{2d,4} and the borate.⁵ Perhaps the lead derivative,^{2b} (Me₃SiO)₂Pb should also be mentioned. Because of reports that titanium alkoxides form heat-resistant materials⁶ and because of the well-known thermal stability of organosiloxanes, we became interested in a molecule which combined both structures.

We have synthesized trimethylsilyl titanate (or *tetrakis*-(trimethylsiloxy)-titane) from trimethylsilanol and titanium tetrachloride in the presence of ammonia.⁷ This siloxy titane is a water-white, mobile liquid which boils at 106° at 7 mm., almost the same boiling point as *t*-butoxy titanate, 108° at 10 mm.⁸ In this connection it is interesting to note that hexamethyldisiloxane boils at 100°⁹ and di-*t*-butyl ether boils at 101°,¹⁰ both at atmospheric pressure.

Trimethylsilyl titanate resembles the alkyl titanates but does not hydrolyze as vigorously. A

(1) Paper 45 in a series on organosilicon chemistry. For paper 44 see *THIS JOURNAL*, **76**, 5002 (1954).

(2) (a) R. O. Sauer, *ibid.*, **66**, 1707 (1944); (b) W. J. Patnode and F. C. Schmidt, *ibid.*, **67**, 2272 (1945); (c) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **68**, 2282 (1946); (d) L. H. Sommer, L. Q. Green and F. C. Whitmore, *ibid.*, **71**, 3253 (1949).

(3) L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, *ibid.*, **68**, 156 (1946); L. H. Sommer, G. T. Kerr and F. C. Whitmore, *ibid.*, **70**, 445 (1948); L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

(4) N. Wright and M. J. Hunter, *ibid.*, **69**, 803 (1947).

(5) R. H. Kriebel, U. S. Patent 2,440,101 (Apr. 20, 1948) (C. A., **42**, 6376 (1948)).

(6) For a review of the work on preparing and formulating titanium alkoxides, see M. Kronstein, *Paint and Varnish Production*, **30**, [No. 8] 10, 20 (1950).

(7) J. Nelles, U. S. Patent 2,187,821 (Jan. 23, 1940) (from C. A., **34**, 3764 (1940)); D. C. Bradley and W. Wardlaw, *J. Chem. Soc.*, 280 (1951).

(8) R. J. Speer, *J. Org. Chem.*, **14**, 655 (1949).

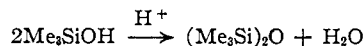
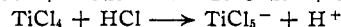
(9) E. G. Rochow, "An Introduction to the Chemistry of the Silicons," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 184.

(10) Boiling point given as 214°F., H. E. Alquist and L. K. Tower, *Natl. Adv. Comm. Aeronaut.*, Wartime Report M. R. No. E5A04 (from C. A., **42**, 4736 (1948)).

film formed by baking trimethylsilyl titanate on steel appeared to have interesting properties.

Experimental

Synthesis of Trimethylsilyl Titanate.—Gaseous NH₃ was bubbled through a solution of 80 g. (0.89 mole) of trimethylsilanol¹¹ in 50 ml. of dry benzene in a 3-liter flask fitted with a reflux condenser. From a dropping funnel was slowly added 24 g. (0.125 mole) of TiCl₄ in 50 ml. of benzene.¹²



The reaction was vigorous. It evolved white fumes and a white precipitate formed. When the reaction mixture became too thick, 100 ml. more of benzene was added. Toward the end of the addition of TiCl₄, the white precipitate turned yellow. After addition was complete, the reaction mixture was heated at reflux for one hour, maintaining the flow of NH₃. The mixture was then cooled, the gas stream turned off, and the precipitate filtered out, rinsed with benzene and the benzene solutions combined.

Benzene and unreacted trimethylsilanol were fractionated from the mixture at atmospheric pressure, then the residual liquid was fractionated at reduced pressure. The yield was 9.2 g. (18% based on Ti) of a pale yellow-green liquid boiling at 106° at 7 mm. On standing for a short time the liquid became colorless; properties: *n*_D²⁰ 1.4278, *d*₄²⁰ 0.9078, *M*_{RD} 114.6.

Anal. Calcd. for C₁₂Si₄TiH₃₆O₄: Si, 27.8; Ti, 11.8. Found: Si, 28.1, 28.0; Ti, 11.6, 11.9.

There are no bond refractions for Ti–O in the literature, so calculation of the molecular refraction was impossible. Instead, the bond refraction was calculated from the observed molecular refraction; bond ref. Ti–O, 4.02.

Reactions and Properties of Trimethylsilyl Titanate.—This compound is soluble in ether, acetone and benzene. It is insoluble in water. Samples of trimethylsilyl titanate were dropped onto water, 0.1 N NaOH and dilute HCl. The liquids lay quietly with no signs of reaction even at the interfaces. Mixing the liquids by shaking produced immediate reaction in each case, but the reaction was mild with no noticeable heat effect or gas evolution. In water and base a curdy, white precipitate formed. In acid a layer of oil formed on the surface, smaller in volume than the layer of titanate had been. No odor of silanol was noticeable from any of the three.

The steel blade of a spatula was carefully cleaned with steel wool and a few drops of trimethylsilyl titanate placed on it. The blade was held high over the flame of a Meker burner and then slowly brought closer to the flame in order to bake the titanate onto the blade without igniting it. A colorless, smooth and apparently continuous film was produced. When the spatula blade and film were subsequently heated to bright red heat several times at the maximum temperature of the burner there was no apparent change in the film.

(11) Prepared from trimethylfluorosilane in 94% yield by the method of L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, reference 2c.

(12) The TiCl₄ and silanol cannot be mixed and then the NH₃ bubbled through because acid released would cause the condensation of the silanol to hexamethyldisiloxane.

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Reaction of Methanesulfonic Anhydride with Hydrogen Halides¹

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Proell recently disclosed that a mixture of *n*-butanesulfonic anhydride and *n*-butanesulfonic

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