Anal. Calcd. for C_7H_{14}: C, 85.63; H, 14.37. Found: C, 85.50; H, 14.31.

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EVANSTON, ILLINOIS

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

Decahydronaphthoic Acids and their Relationship to the Decalols and Decalylamines.[1] A Stereochemical Study of the Reaction of Nitrous Acid with Decalylamines

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The preparation of *cis–cis*-1-, *trans–trans*-1- and *trans–cis*-2-decahydronaphthoic acids in pure form has been achieved. The *cis*-decalyl derivative was obtained by catalytic hydrogenation and the *trans*-materials were prepared from the corresponding chlorides *via* carbonation of the Grignard reagent. The structures of the acids were assigned on the basis of stereospecific elimination reactions, conformational analysis as applied to reaction rates and by catalytic hydrogenation. The three acids were degraded, with stereochemical retention, to decalols and decalylamines. The steric courses of the deamination of decalylamines with nitrous acid has been re-examined and possible mechanisms of this reaction as applied to alicylic compounds have been discussed.

The reaction of aliphatic primary amines with nitrous acid to yield alcohols and olefins has been extensively investigated and in the acyclic series (containing no neighboring participating groups[2]) the stereochemical results can be adequately explained by assuming an SN1 type of reaction process[3] involving the intermediate formation of a diazonium ion. For example, it has been shown that when an optically active acyclic primary amine is allowed to react with nitrous acid, the products of

$$\text{L-RNH}_2 + \text{HONO} \longrightarrow \text{RN}_2^{\oplus}\text{OH}^{\ominus} \longrightarrow \text{D-ROH} + \text{DL-ROH} + \text{olefins}$$

the reaction are unsaturated hydrocarbons and an alcohol of inverted configuration. In the alicyclic series, however, such a reaction consistency is not to be found. In the simplest case, that is with *cis*- and *trans*-4-methylcyclohexylamine,[4] it has been reported that whereas the *cis*-amine yielded inverted alcohol and olefins, the *trans*-isomer gave rise to a single product, the *trans*-alcohol. This pattern of one isomer yielding only an alcohol with retention of configuration while its epimer gives largely inverted alcohol and olefin is the usual picture seen upon examination of the reaction of the other epimeric alicyclic amines with nitrous acid.[5] It is evident that in any two alicyclic epimers the conformation of the substituent is different and viewed in this manner various workers[6,7] have formulated the rule that when the amino group is in an equatorial conformation pure retention results while for an axial[8] conformation both inversion and elimination occur. Therefore, such a reaction as deamination is an example of conformational control.

In all of the cases cited by Mills[6] and Bose[7] in the cyclohexyl, menthyl and *trans*-decalyl series, the configurational relationship between the amine and the alcohol has been arbitrarily assigned. In order to utilize such data as an aid to the postulation of a mechanism of deamination, it is desirable to know these configurations with certainty. Accordingly, work was undertaken to establish firmly such relationship of epimers and the interest was centered on the decalin series since all 8 possible isomers of the 1- and 2-substituted decalins have been studied under deamination conditions by Hückel.[9] Also, it was noted that in this decalin series certain discrepancies existed which tended to cast doubt upon the generalized conformational postulates referred to above.[6,7]

The results obtained in the *cis*-2-decalin series have been reported earlier[1] and in such work the steric relationship between the alcohol and the amine was established by degradation of a common intermediate, the decahydro acid, by stereospecific processes. The methods utilized were to convert the acid to a methyl ketone with methyllithium followed by cleavage of the ketone with perbenzoic acid and degradation of the acid to an amine with hydrazoic acid. To employ these same methods

$$\text{RCOOH} \longrightarrow \text{RCOCH}_3 \longrightarrow \text{ROCOCH}_3$$
$$\text{RCOOH} \longrightarrow \text{RNH}_2$$

in the *cis*-1, *trans*-1 and *trans*-2 series necessitated the preparation of pure isomeric acids in each series.

Preparation of Decahydronaphthoic Acids.—Previous investigators have reported the preparation of several isomeric decahydronaphthoic acids

(1) For the previous paper in this series, see THIS JOURNAL, **73**, 1504 (1951).

(2) For a detailed discussion of such a series of compounds, see M. Mousseron, M. Mousseron-Canet and R. Jacquier, *Ann. chim.* (*Paris*), [12] **8**, 5 (1953).

(3) P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold and P. A. D. Rao, *Nature*, **166**, 178 (1950); C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1950, p. 395.

(4) M. M. Claudon, *Bull. soc. chim. France*, 627 (1950).

(5) Examples of such reactions are: menthyl and neomenthylamine, isomenthyl and neoisomenthylamine (J. Read, A. M. R. Cook and M. I. Shannon, *J. Chem. Soc.*, 2223 (1926); J. Read and G. J. Robertson, *ibid.*, 2168 (1927)), carvomenthyl and neocarvomenthylamine (R. G. Johnston and J. Read, *ibid.*, 1138 (1935); and A. K. Bose, *Experientia*, **8**, 458 (1952)).

(6) J. A. Mills, *J. Chem. Soc.*, 260 (1953).

(7) A. K. Bose, *Experientia*, **9**, 256 (1953).

(8) The term *axial* is employed here in place of *polar* in conformity with the recent suggestion of D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog (*Science*, **119**, 49 (1954)) with regard to those bonds in a cyclohexyl ring which are parallel to the axis of threefold symmetry.

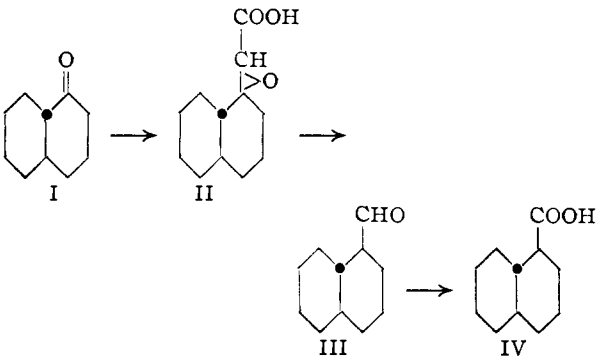
(9) W. Hückel, *Ann.*, **533**, 1 (1938).

and recently Dauben and Hoerger have reinvestigated the *cis*-2-decalyl series. From their work the assignment of physical properties to the *cis-cis*-2 and *cis-trans*-2 isomer[10] is possible. One isomer of the *trans*-2 series has been prepared from *trans*-2-decalol by proceeding through the chloride and Grignard reagent.[11,12] The same material also has been obtained, this time in pure form, by a similar procedure except the *trans*-2-decalyl chloride was obtained by chlorination of *trans*-decalin.[12,13]

In the decahydro-1-naphthoic acid series, one acid in the *cis* and none in the *trans* series has been reported. Ranedo and Leon[14] found that when 1-naphthoic acid was hydrogenated over platinum in dilute acetic acid, a pure decahydro-1-naphthoic acid was obtained and the material was arbitrarily assigned a *cis* configuration. In this acid, although the ring juncture configuration was known or could be assigned with a degree of surety, the configuration of the carboxyl group with relation to the nearest ring juncture hydrogen atom was unknown.

Several of these methods of preparation were repeated in order to obtain sufficient material so that their conversion to a decalol and decalylamine could be undertaken and so that the degree of homogeneity could be verified. It was found that when 1-naphthoic acid was hydrogenated over platinum in acetic acid at atmospheric pressure, one pure isomer could be obtained in 85% yield. It was important to make sure perhydrogenation had occurred since small amounts of 5,6,7,8-tetrahydro-1-naphthoic acid could not be removed readily by recrystallization and a preparation containing such tetrahydro material would melt quite low and over a wide range. In one case, the product obtained by incomplete hydrogenation was separated by partition chromatography[13] and both components isolated. The properties of the perhydrogenated material agreed with those reported by Ranedo and Leon[14] except the amide was found to melt 40° higher. A similar situation had previously been reported in the *cis*-2 series[1] and it was found that unless care was taken in the preparation of the amide, extensive isomerization could occur, giving rise to a mixture of amides. The procedure employed was to prepare the acid chloride at 40° or less and add, with stirring, to ammonia at 0°.

The preparation of a *trans*-1-acid utilized *trans*-1-chlorodecalin which had been obtained by chlorination of decalin. As has been shown by Dauben and Tweit,[13] such a method of preparation gave rise to both *trans*-1- and *trans*-2-chlorodecalin and the mixture of acids received from the chlorides could readily be separated by partition chromatography. The *trans*-1-acid, so obtained, was identical with that reported earlier.[12] Since it was inconvenient to prepare large amounts of acids by this chromatographic technique, two other methods were investigated. First, *trans*-1-decalyl chloride, prepared from *trans*-1-decalol, was converted to the Grignard and then carbonated. The product obtained melted over a range but when the acid was converted to acid chloride by heating for several hours with thionyl chloride, equilibration of the isomers was obtained and upon addition to ammonia, a sharp melting amide was received. The acid was regenerated from the pure amide by cold concentrated sulfuric acid and sodium nitrite. The acid was identical with that obtained from the mixed chlorides above. A second method proceeded from *trans*-1-decalone (I). The ketone was converted into 1,α-epoxy-(*trans*-1-decalyl)-acetic acid (II) in 48% yield by a Darzens reaction[15] with ethyl chloroacetate. The glycidic acid could be decomposed in one of two ways. When first allowed to react with hydrogen chloride in ether, the generated chlorohydrin was treated



with semicarbazide hydrochloride[16,17] and the semicarbazone of *trans*-1-decalylaldehyde isolated. The solid derivative was converted to an oily aldehyde (III) by reaction with 50% pyruvic acid[18] and the crude product oxidized with oxygen. The acid IV was obtained in an over-all yield of 37% from the glycidic acid and 18% from the starting *trans*-1-decalone.

If the glycidic acid was pyrolyzed at 150° and the pyrolyzate oxidized with alkaline hydrogen peroxide,[19] only a small amount of acid could be isolated. The aldehyde as received from the pyrolysis was found to be identical with that formed in the hydrogen chloride method by comparison of their dinitrophenylhydrazones; the aldehyde recovered after alkaline hydrogen peroxide treatment yielded a second dinitrophenylhydrazone. Although no proof has been obtained concerning the configuration, it might be assumed that the product from the alkaline hydrogen peroxide treatment is the more thermodynamically stable and should be assigned a *trans-trans* configuration.

The *trans*-2-acid could be obtained in pure form and large amounts from the mixed *trans*-chlorodec-

(10) All configurational assignments are in terms of the relative positions of the hydrogen atoms at C_8, C_{10} and C_9, C_2. The positions of the hydrogen atoms are represented in the formulas by black dots, a dot indicating that a hydrogen atom is above the plane of the molecule. A dot is always placed at C_9.

(11) W. Borsche and E. Lange, *Ann.*, **434**, 219 (1923).

(12) G. Tsatsas, *Ann. chim. (Paris)*, [11] **19**, 217 (1944).

(13) W. G. Dauben and R. C. Tweit, THIS JOURNAL, **76**, 3197 (1954).

(14) J. Ranedo and A. Leon, *Anal. soc. espan. fis. quim.*, **25**, 421 (1927).

(15) M. S. Newman and B. J. Magerlein, in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 413.

(16) W. A. Yarnall and E. S. Wallis, *J. Org. Chem.*, **4**, 270 (1939).

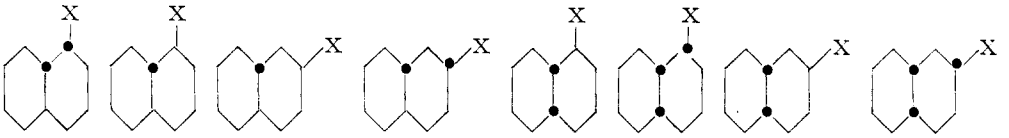
(17) W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, THIS JOURNAL, **75**, 4995 (1953).

(18) E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948).

(19) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd. Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

TABLE I

CONFIGURATION AND MELTING POINT OF SUBSTITUTED DECALINS



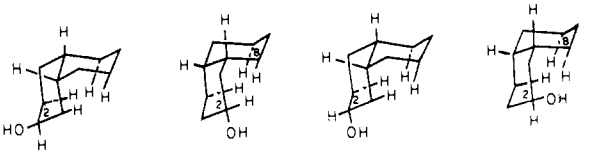
Conformation of substituent	a	e	a	e	ea	e	ea	e
Alcohol (X = OH)	49	63	53	75	55	93	18(30)	105
p-Nitrobenzoate	116	86	112	141	86	83	77	
Acid phthalate	121	168	108	180	142	176	153	116
Amine (X = NH_2)	−18	−1	−47	15	−2	−18	14	≤20
Acetamide	130	182	130	163	141	181	154	88
Benzamide	112	195	177	176	193	206	204	128
Acid (X = COOH)		102		106		125	98	81
Amide		223		205		238	187	180

alins as described earlier.[13] The amide was found to melt 12° higher than that previously reported by Borsche and Lange.[11] The properties of all of the acids and their amides prepared under non-equilibrating conditions are summarized in Table I.[20]

Steric Configuration and Relationship of the Decahydronaphthoic Acids, Decalols and Decalylamines.—With the preparation of at least one pure isomer of each epimeric pair of decahydronaphthoic acids, it next was necessary to relate the acids to amines and alcohols by the stereospecific processes discussed earlier and such was done. It was also necessary to assign steric configurations to each series. By determination of the stereochemistry of either the decalol, decalylamine or the perhydro-acid, all three could be assigned.

The first method utilized to determine the configurations depended upon the stereospecific Tschugaeff elimination reaction which has been shown to involve *cis*-related groups[21,22] with the additional preference of a tertiary hydrogen over a secondary hydrogen atom. Such a process is of use only in the 1-decalol series where the preferential direction of elimination can be obliterated by steric control. Hückel[23] has studied this reaction with the *cis*- and *trans*-1-decalols and from his results one can assign the configuration of the hydroxyl group with respect to the nearest ring juncture hydrogen atom. For example, the *trans*-1-decalol, m.p. 63°, yielded mainly $\Delta^{1,9}$-octalin while its epimer, m.p. 49°, gave rise mainly to $\Delta^{1,2}$-octalin. Accordingly, one can assign a *trans-trans* configuration to the former and a *trans-cis* to the latter.

The second method was that of conformational analysis as developed by Barton[24] and as such was applicable to both 1- and 2-decalols. From his concepts, it can be stated that of any epimeric pair, the isomer which has the hydroxyl group in an equatorial conformation is the more stable and should predominate at equilibrium and this same isomer should be esterified and saponified more rapidly. Again, Hückel[25–27] has accumulated such data and thus configurations can be assigned. For example, the *trans*-2-decalol, m.p. 75°, was found to predominate when the alcohols were equilibrated with sodium in xylene and also its acid phthalate is saponified 6.9 times more rapidly than the isomer, m.p. 53°. Thus, one can allocate a *trans-cis* structure to the former and a *trans-trans* to the latter. In the case of the *cis*-decalins, due to the flexibility of the ring system, a substituent of any relative configuration can occupy either an equatorial or axial conformation since this decalin isomer can exist in two equivalent chair–chair conformations[28] (V–VI and VII–VIII) interconvertible by transformation of all equatorial directed bonds to axial and *vice versa*. Nevertheless, it is seen that in the conformation VIII where the substituent is axial and *trans* to the ring juncture hydrogen atom, a marked steric interaction exists between the substituent and the axial directed hydrogen atom on C_8.[6] In conformation VII of this isomer, this steric interference is absent. In the isomer in which the substituent is *cis* to the ring juncture hydrogen atoms, the hydroxyl group can take either an equatorial VI or axial conformation V without this added steric interaction. Thus, in the isomer of a *cis*-2-decalyl derivative in which the substituent is *cis* to the ring juncture the number of molecules in conformation VI as compared to V will be a function only of the relative energy difference between an equator-



V VI VII VIII

(20) F. W. Kay and N. Stuart (*J. Chem. Soc.*, 3038 (1926)) have reported the reduction of 5,6,7,8-tetrahydro-2-naphthoic acid with both sodium and ethanol and sodium and amyl alcohol. They assumed the former gave rise to a "*cis*"-decalin and the latter to a "*trans*"-decalin. From each reduction they obtained a mixture of acids which were separated as amides. In the "*cis*"-series they reported two amide values of 140° and 171° while in the "*trans*"-series 174° and 196°. No criterion of purity was presented and from Table I it is obvious that they were, for the most part, dealing with mixtures.

(21) D. H. R. Barton, *J. Chem. Soc.*, 2174 (1949).

(22) E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810 (1950).

(23) W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(24) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(25) W. Hückel, H. Havekoss, K. Kumstat, D. Ullmann and W. Doll, *Ann.*, **533**, 128 (1938).

(26) W. Hückel, *Ber.*, **67**, 129 (1934).

(27) W. Hückel and H. Naab, *ibid.*, **64**, 2137 (1931).

(28) O. Bastiansen and O. Hassel, *Nature*, **157**, 765 (1946); O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947).

ial and an axial bond. With the isomer in which the substituent is *trans* to the ring juncture, there will be imposed on top of this energy difference the steric interaction and this should greatly increase the number of molecules in conformation VII as compared to VIII. On the basis of such an interpretation it would be predicted that the *cis-cis* isomer of conformation VII should possess a more equatorial character than the epimeric *cis-trans* (VI). Of the two *cis*-2-decalols, Hückel[25] has found that the acid phthalate of the isomer, m.p. 105°, saponified 1.5 times more rapidly than the 18° epimer. Accordingly, the former should be assigned the *cis-cis* configuration.[29] When similar reasoning is applied to the *cis*-1-series, stereochemical assignments are obtained which are in agreement with those previously derived by *cis*-elimination studies.

Further substantiation of these latter assignments can be gained by utilizing a third method for the determination of stereochemistry. Linstead and his co-workers[30] have shown that the predominate product (>75%) formed by catalytic hydrogenation over platinum in acetic acid of an aromatic acid has an all *cis* configuration. The acid so obtained from the hydrogenation of 1- and 2-naphthoic acid under such conditions can be assigned the *cis-cis* configuration. In the 1-series, the decalol related to such an acid has also been shown to possess a *cis-cis* configuration by elimination studies. Also, in the 2-series, agreement was reached with the configuration assigned on the basis of conformational analysis.

Thus, by application of these three methods, the configurations of all eight decalin isomers can be assigned. Table I summarizes the physical properties[9] of all of the decalols, decalylamines and perhydro-acids based on the steric relationships arrived at above.

Reaction of Decalylamines with Nitrous Acid.—In view of the establishment of the relationship of the decalylamines and decalols by direct chemical means and the assignment of configuration (and conformation) of the various isomeric pairs, it is of interest to investigate the stereochemical aspects of the reaction of nitrous acid with these decalylamines. Hückel[9] has reported such a study and his results (based upon the correct stereochemical relationships arrived at in the present work) are summarized in Table II. It is seen that in all of the decalin compounds, the data are in agreement with the conformational generalizations set forth by Mills[6] and Bose[7] for such a deamination reaction. Of particular interest are the amines of the *cis*-series. It is to be noted that the epimers assigned an equatorial conformation yield only alcohols of retained configuration whereas the epimers given an equatorial–axial conformation produce mainly retained alcohol but some elimination and inversion does occur and this might be attributed to the partial axial character of the amines. Thus, as has been pointed out by Mills,[6] such results strongly support the conformations assigned to the *cis*-series based upon steric interaction considerations and illustrates the importance of conformational control for this deamination reaction.

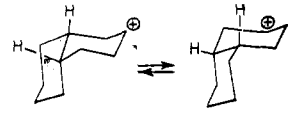
TABLE II

REACTION OF DECALYLAMINES WITH NITROUS ACID

Starting Amine	Amine Conformation	% Decalol		% Octalin	
	a	 27	 3	 35	 35
	e	 100			
	a	 27	 3	 20	 50
	e	 100			
	e a①	 68	 7	 3	 22
	e	 100			
	e a①	 63	 7	 9	 21
	e	 100			

① See text for explanation.

Although such steric generalizations as to the course of the reaction of alicyclic amines have been brought forth, the possible reasons as to why acyclic and alicyclic amines differ in their reaction with nitrous acid has not been thoroughly explored. The work of Ingold[3] on acyclic amines strongly indicates that such compounds react *via* a carbonium ion type intermediate which can give rise to inversion and racemization. It has been postulated by Mills[6] that this is not the case for the alicyclic amines of an equatorial conformation. Such a conclusion was arrived at by consideration of the almost complete retention of configuration of the epimeric *cis*-2-decalylamines. This evidence was taken to exclude a "true carbonium ion" as an intermediate because steric differences between the epimeric amines would disappear at such a stage and the same mixture of products should result from each epimer. This concept assumes that the change in ring juncture conformation of the two initially unlike intermediates from the two *cis*-isomers can compete with direct reaction of the initial intermediates with solvent. Some insight into the validity and utility of these concepts can be gained by evaluation of the steric differences of an equatorial and an axial isomer.



(29) It should be pointed out that, at equilibrium, the number of molecules of *cis–trans* configuration should be in excess since conformations VI and VII, being of the same energy, should be present in equal amounts and conformation V being of lower energy than VIII should be in excess. Hence, even though the *cis-cis* shows more equatorial character, the *cis-trans* should be more stable. Such a prediction is not in accord with the equilibrium studies of Hückel and this point is being examined in more detail.

(30) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. Whetstone, THIS JOURNAL, **64**, 1985 (1942), and subsequent papers; also *J. Chem. Soc.*, 1423 (1950).

From examination of models, it can be readily seen that, in general, the backside of the carbon atom holding a substituent in either an equatorial or axial conformation is quite hindered due to the body of the cyclic ring itself and to the various axially placed hydrogen atoms on the ring. Such types of hindrance have been suggested by various workers[31,32] to be one of the important factors contributing to the low reactivity of the cyclic system in bimolecular displacement reactions (SN2). In contradistinction, it can be noted that a substituent in an equatorial conformation is more open to frontal attack than when in an axial conformation, a consideration which has led Barton[24] to suggest a correlation between the rates of many reactions and the conformation of the compound (for example, ester saponification). Thus, any reaction in which frontal attack can occur should proceed more readily with an equatorially placed group.

Returning to the nitrous acid reaction, it is fairly well established that the reaction proceeds through the intermediate formation of a diazonium ion.[3,33,34] In the decomposition of such an ion, nitrogen, a neutral, thermodynamically-stable species, is evolved and as such suggests the first differentiation from the normal SN1 reaction which involves separation of ions and participation of solvent from the rearward side of the reacting carbon atom.[35] It seems reasonable to assume that such a decomposition of a solvated diazonium ion should be facile and give rise to a reactive species and such an ion when initially formed should be predominately solvated from the front side due to the rearward hindrance characteristic of the cyclic system. At least three reaction sequences are available to this intermediate; first, direct reaction with the solvent of the surrounding cage to yield a product of retained configuration, second, further non-specific equilibration with solvent to yield a symmetrically solvated intermediate which would react to form the isomer of lesser steric hindrance (equatorial) in predominance and third, conformational changes before either or both reactions. This last possibility can be assumed to be the slowest of the three pathways since it would require a fairly high activation energy arising from hydrogen–hydrogen interactions in the transition state. Direct reaction with solvent, on the other hand, should proceed with negligible activation energy.

The initial species from an equatorial amine, due to the lesser frontal hindrance of such a conformation, should react with solvent with a minimum of steric interference and be rapid and thus follow the first pathway to yield an alcohol of equatorial conformation. With an isomer of axial conformation, the reaction with solvent should not be so energetically favored since the solvent must be in an axial-like surrounding and accordingly the reaction should be less rapid, allowing time for equilibration with solvent and thus should follow the second pathway to yield a mixture of alcohols in which the less hindered equatorial isomer is in predominance. The greater rapidity of reaction as compared to conformational change of the whole molecule is important when considering the isomeric *cis* compounds since a conformational change prior to reaction could result in inversion. Thus, these concepts when applied to alicyclic amines adequately account for the complete retention found with equatorial amines and the formation of largely equatorial alcohol from axial isomers.[36]

The occurrence of elimination with only the axial amines and the preferred *trans* elimination found with the *cis-trans*-1-decalylamine strongly suggests the involvement of an axial–axial planar four centered transition state as has been postulated by Mills.[6] It would thus appear that only when this stereochemical specificity is met can elimination compete with substitution in the deamination reaction.

Experimental[37]

cis-cis-Decahydro-1-naphthoic Acid.—A mixture of 15 g. of 1-naphthoic acid (m.p. 162.5–163°), 1.0 g. of platinum oxide and 200 ml. of glacial acetic acid was hydrogenated at room temperature and 45 p.s.i. After the theoretical amount of hydrogen had been absorbed, the catalyst was filtered, the solvent removed under reduced pressure and the residual material recrystallized from aqueous ethanol, yield 13.5 g. (85%), m.p. 121–123°. One further recrystallization raised the m.p. to 123.5–124.0° (lit.[14] 126°).

The amide was prepared by allowing 2.0 g. of the acid to react with 6.5 ml. of thionyl chloride in 5 ml. of anhydrous benzene (1 drop of pyridine) for 30 minutes at 40°. The benzene and excess thionyl chloride were removed under reduced pressure (bath at 50°). The crude acid chloride then was added dropwise, with stirring, to 20 ml. of ammonia cooled in an ice-bath. The amide was recrystallized from ethanol, m.p. 237–238° (lit.[14] 198°). A small amount of acid was recovered from the ammonia solution and melts 120–121°.

Hydrogenation of 1-Naphthol.—1-Naphthol was vacuum distilled and recrystallized from aqueous ethanol, m.p. 94–96°. A solution of 72.1 g. (0.5 mole) of 1-naphthol in 144 ml. of glacial acetic acid was hydrogenated at low pressure over 0.7 g. of platinum oxide. During 72 hours, 3 additional 0.5-g. portions of catalyst were added. The catalyst was filtered and the solvent removed by distillation. The residue was dissolved in benzene, washed with base, dried and concentrated. During this last operation, 2 crops of crystals were obtained, 32.0 g., m.p. 89–91.5° (*cis-cis*-1-decalol, m.p. 93°[38]). The residue from the concentration was distilled and after 5.5 g. of decalin, 19.3 g. of mixed decalols, b.p. 119–127° (13 mm.), $n^{25}D$ 1.4882, was obtained. The total yield of decalols was 51.3 g. (67%).

trans-1-Decalone.—Potassium dichromate (26.4 g., 0.09 mole) was dissolved in 13.5 ml. of water and 20.0 g. (0.13 mole) of the mixed 1-decalols was added. Concentrated sulfuric acid (12.2 ml.) then was added, dropwise, to the stirred mixture and the stirring continued for 11 hours. The solution was extracted 3 times with ether, the ethereal

(31) S. J. Angyal and J. A. Mills, *Revs. Pure Appl. Chem.*, **2**, 185 (1952).

(32) See comments of M. J. S. Dewar and E. D. Hughes in *Bull. soc. chim. France*, C-85 (1951).

(33) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 295.

(34) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 181.

(35) W. E. Doering and H. H. Zeiss, THIS JOURNAL, **75**, 4733 (1953).

(36) Various minor modifications of these postulates also adequately account for the results. For example, Dr. W. H. Saunders, Jr., (private communication) has pictured the reaction as proceeding through a similar reactive intermediate and has further assumed that all reaction with solvent is by an equatorial pathway. The small amount of axial isomer formed from an axial amine may then be due to the participation of a hydrogen-bridge "non-classical" carbonium ion. The postulates also differ to a degree from the classical non-ionic SNi reaction suggested by Bartlett for apocamphylamine (P. D. Bartlett in Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 45).

(37) Analyses by the Microanalytical Laboratory, Department of Chemistry, University of California. All melting points are corrected.

(38) W. Hückel, R. Danneel, A. Gross and H. Naab, *Ann.*, **502**, 99 (1933).

solution washed with base, dried and the ether evaporated. The residue was distilled, b.p. 80–85° (3 mm.), yield 17.3 g. (88%).

trans-trans-1-**Decalol.**—*trans*-1-Decalone (14.8 g., 0.097 mole) was dissolved in 200 ml. of absolute ethanol and 9.2 g. (0.4 mole) of sodium added in small pieces to the stirred solution over a period of several hours. The solution was diluted with 750 ml. of water and extracted with ether–hexane. The solvent was removed and the residue distilled, b.p. 89–99° (4 mm.), yield 13.1 g. (88%). The product solidified on standing and was recrystallized from pentane, m.p. 58.0–59.5° (lit.[39] 63°).

trans-trans-1-**Decalyl Chloride.**—*trans-trans*-1-Decalol (25 g., 0.16 mole) was dissolved in 57 ml. of purified thionyl chloride and allowed to stand for 12 hours at room temperature. The solution was then warmed to 70° for several hours and poured into 4 *N* sodium hydroxide. The organic layer was separated and the alkaline layer extracted with hexane. The extracts were combined, dried and the product distilled, b.p. 105–109° (17 mm.), yield 19.2 g. (69%).

trans-trans-**Decahydro-1-naphthoic Acid.** (a) **From** *trans-trans*-1-**Decalyl Chloride.**—Magnesium turnings (2.96 g., 0.122 mole) were placed in a 3-necked flask under a nitrogen atmosphere and 75 ml. of dry ether and 1 ml. of ethyl iodide added. After the reaction had started, 19.2 g. (0.11 mole) of the chloride dissolved in 100 ml. of dry ether was added, with stirring, over a period of 40 minutes. The Grignard solution was cooled to −10°, carbon dioxide passed in for 6 hours and the solution then allowed to stand at room temperature, under carbon dioxide, for an additional 16 hours. After processing, 11.6 g. (58%) of an acid was obtained, m.p. 78–100°.

The crude acid (0.79 g.) was refluxed for several hours with excess thionyl chloride in benzene containing a drop of pyridine. The benzene and thionyl chloride were removed under reduced pressure and the crude acid chloride added to concentrated aqueous ammonia. The amide was recrystallized from ethanol–carbon tetrachloride, m.p. 222.4–222.9°, yield 0.47 g. (30%). *Anal.* Calcd. for $C_{11}H_{19}ON$: C, 72.88; H, 10.56. Found: C, 73.04; H, 10.33.

The pure amide (0.47 g.) was dissolved in 8 ml. of concentrated sulfuric acid, the solution cooled to 0° and to it a solution of 1.6 g. of sodium nitrite in 8 ml. of water was added, with stirring. The suspension of solid was heated on a steam-bath until colorless, diluted with water and filtered. The product was dissolved in base, filtered and precipitated with acid, m.p. 99.5–100.4° (lit.[13] 102.2–103.6°), yield 0.43 g. (91%).

(b) **From** *trans*-1-**Decalone.** 1,α-**Epoxy-(***trans*-1-**decalyl)-acetic Acid.**—A mixture of the ketone (20 g., 0.13 mole) and 22.8 g. (0.21 mole) of methyl chloroacetate was mixed with 7 ml. of ether and cooled to 0°. Freshly prepared solid sodium methoxide, from 5.2 g. of sodium, was added in portions in one hour with frequent shaking. Since the addition of the base induced a strongly exothermic reaction, the mixture was cooled to −80° after each addition and then allowed to rise to 0°. After the addition was complete, the reaction mixture was allowed to stand at room temperature for 18 hours and then finally heated at 100° for 6 hours. The reaction mixture was poured into ice-water and extracted with ether. The ethereal layer was washed with aqueous sodium carbonate solution, dried, the solvent and unreacted starting ester removed by distillation. The residual material then was stirred with a solution of 17 g. of sodium hydroxide in 60 ml. of water and after one hour the mixture had set to a thick gel which was allowed to stand for an additional 36 hours. On acidification and addition of hexane, a yellow solid precipitated and was filtered and recrystallized from ether–hexane to yield 8.62 g. of a white solid. The mother liquor and the original hexane extract were concentrated and resaponified. On acidification and extraction with hexane, an additional 2.13 g. of product was obtained. The remaining oil was separated into neutral and acidic material and the neutral fraction yielded 3.92 g. of starting ketone. The total yield of 1,α-**epoxy-(***trans*-1-**decalyl)-acetic acid** was 10.75 g. (48% based on recovered ketone) which was recrystallized from ether–pentane, m.p. 107–108.5°.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.45; H, 8.63.

(39) W. Hückel, *Ann.*, **441**, 1 (1925).

Decomposition of the Glycidic Acid. (1) **Semicarbazide Method.**[16,17]—The acid (1.0 g.) was dissolved in ether and dry hydrogen chloride bubbled into the solution for several hours. The ether was removed and the residue dissolved in 25 ml. of pyridine. A solution of 1.0 g. of semicarbazide hydrochloride in a minimum volume of water was added and the solution refluxed for one hour. After dilution with water, the mixture was cooled and filtered and the precipitate was recrystallized from aqueous ethanol, m.p. 176.2–176.6° (dec.). The yield of *trans-cis*-decahydro-1-naphthyl carboxaldehyde semicarbazone was 0.73 g. (69%).

Anal. Calcd. for $C_{12}H_{14}ON_3$: C, 64.54; H, 9.48; N, 18.82. Found: C, 64.88; H, 9.48; N, 18.57.

The semicarbazone (0.5 g.) was dissolved in 6 ml. of 67% acetic acid and refluxed with 0.7 ml. of 50% pyruvic acid.[18] After the solution was diluted with water, the product was extracted with hexane and the solvent removed by a stream of oxygen. The residue was only partially soluble in base and so the process was repeated. The *trans-trans*-decahydro-1-naphthoic acid was isolated and recrystallized, yield 0.22 g. (50%).

A small amount of the aldehyde was directly converted to a 2,4-dinitrophenylhydrazone in the usual fashion and a yellow product was obtained. After recrystallization from aqueous ethanol, it melts 158–160°.

Anal. Calcd. for $C_{17}H_{21}O_4N_4$: C, 59.12; H, 6.13. Found: C, 59.27; H, 6.43.

(2) **Thermal Method.**—The acid (1.0 g.) was placed in a small sublimer and heated to 160° at 1 mm. and 0.47 g. (58%) of a viscous oil was obtained. The material was oxidized with alkaline hydrogen peroxide,[19] the acidic fraction removed and a small yield of the *trans-trans*-1-acid obtained. The neutral portion was converted to the 2,4-dinitrophenylhydrazone and the dark red derivative of the *trans-trans*-decahydro-1-naphthyl carboxaldehyde obtained, m.p. 203–204°.

Anal. Calcd. for $C_{17}H_{21}O_4N_4$: C, 59.12; H, 6.13. Found: C, 59.24; H, 6.30.

When the aldehyde isolated directly from the pyrolysis (no alkaline treatment) was converted to the 2,4-dinitrophenylhydrazone, the yellow product melts 155–156° and shows no depression with the similar derivative prepared from the aldehyde in the semicarbazone method.

Schmidt Reaction of Acids.[1] (a) *cis-cis*-**Decahydro-1-naphthylamine.**—The *cis-cis*-acid (1.82 g., 0.01 mole, m.p. 123–124°) was dissolved in 50 ml. of chloroform and 20 ml. of concentrated sulfuric acid added. The mixture was stirred at 40° and 0.98 g. (0.015 mole) of sodium azide was added in small portions. The temperature then was raised to 50°, the mixture stirred for one hour and poured onto ice. The chloroform layer was separated and the aqueous layer washed with ether. The acidic solution was made alkaline and extracted 3 times with ether, the ethereal solution dried and the solvent distilled. The residual amine was benzoylated with 2 ml. of benzoyl chloride in the presence of 5% sodium hydroxide solution. The crystalline N-(*cis-cis*-decahydro-1-naphthyl)-benzamide was washed with water and recrystallized from aqueous ethanol, yield 1.40 g. (54%), m.p. 204–206° (lit.[38,39] 206°).

(b) *trans-trans*-**Decahydro-1-naphthylamine.**—As described above, 18 mg. (0.1 mmole, m.p. 102°) was degraded with hydrazoic acid and the crude amine acetylated with acetic anhydride in benzene. The crude acetyl derivative was recrystallized from pentane and 10.9 mg. (56%) of N-(*trans-trans*-decahydro-1-naphthyl)-acetamide was obtained, m.p. 183.8–184.2° (lit.[38] 182°).

When the same reaction was repeated with 18 mg. of acid and the amine benzoylated, the N-(*trans-trans*-decahydro-1-naphthyl)-benzamide was obtained, m.p. 195° (lit.[38] 195°).

(c) *trans-cis*-**Decahydro-2-naphthylamine.**—As described previously, 546 mg. (3 mmoles) of *trans-cis*-2-acid (m.p. 104–105°) was degraded with hydrazoic acid and the crude amine acetylated. The N-(*trans-cis*-decahydro-1-naphthyl)-acetamide was recrystallized from dilute aqueous ethanol, yield 232 g. (42%), m.p. 161.5–162.5° (lit.[9] 163°).

Acetyldecalins.[1] (a) *cis-cis*-1-**Ketone.**—A solution of 1.0 g. (5.5 mmoles, m.p. 123–124°) of the *cis-cis*-1-acid was dissolved in 50 ml. of dry ether and 50 ml. of a 0.4 *M* solution of methyl lithium (20 mmoles) was added and the reaction allowed to proceed for 30 minutes. The reaction mixture

was poured onto ice, the ether layer separated and washed. After drying, the ether was distilled leaving 916 mg. (93%) of crude ketone which was used directly in the perbenzoic acid reaction. A small sample was converted to a 2,4-dinitrophenylhydrazone which was recrystallized from ethanol, m.p. 160.5–160.9°.

(b) *trans-trans*-1-**Ketone.**—Due to the insolubility of the lithium salt of this acid, the methyl ketone was prepared by means of the acid chloride and dimethylcadmium. Such a reaction has been shown to be stereospecific.[40] The acid (2.74 g., m.p. 99°) was dissolved in 10 ml. of dry benzene and 3 ml. of thionyl chloride was allowed to stand at room temperature for 36 hours. The solvent was removed, additional benzene added and the process repeated. The crude acid chloride was dissolved in anhydrous ether and added to a solution of dimethylcadmium prepared from methylmagnesium bromide and 1.84 g. of anhydrous cadmium chloride. The reaction was heated under reflux for 3 hours and processed in the usual manner; 0.6 g. of acid was recovered and 0.89 g. (42%) of the ketone obtained, b.p. 125–130° (11 mm.), $n^{25}D$ 1.4822.

(c) *trans-cis*-2-**Ketone.**—Using the methyllithium procedure, 7.2 g. (0.04 mole) of the *trans-cis*-2-acid (m.p. 103.5–105°) was converted to the methyl ketone and the product distilled, b.p. 132–137° (10 mm.), $n^{23}D$ 1.4815, yield 6.4 g. (90%). The yellow 2,4-dinitrophenylhydrazone melts 134–135°.

Perbenzoic Acid Oxidation of Ketones.[1] (a) *cis-cis*-1-**Decalol.**—*cis-cis*-1-Acetyldecalin (0.84 g., 4.7 mmoles) was dissolved in chloroform and allowed to react for 12 days with 935 mg. of 77% perbenzoic acid (5.2 mmoles). The solution then was diluted with ether and washed with base until neutral. The solvents were distilled and the residue saponified by refluxing with 1 *N* sodium hydroxide in methanol for 2 hours. The solution was diluted with water, extracted 2 times with ether and the crude decalol obtained upon evaporation of the ether. The product was recrystallized from pentane, m.p. 89.9–91.4° (lit.[38] 93°), yield 392 mg. (55%).

(b) *trans-trans*-1-**Decalol.**—The *trans-trans*-1-acetyldecalin (0.68 g., 3.78 mmoles) was treated with perbenzoic acid and the crude reaction mixture treated with Girard's reagent T and the non-ketonic fraction isolated. It was found that this ester was quite resistant to saponification and the reflux period was extended to 18 hours. After dilution of the saponification mixture, the decalol was isolated by ether extraction and the solvent removed. The crude decalol (490 mg., 72%) was allowed to react with 750 mg. of *p*-nitrobenzoyl chloride in 4 ml. of dry pyridine for 24 hours at room temperature. After the usual processing procedure, the ester was recrystallized, yield 347 mg. (42%), m.p. 83.5–85° (lit.[38] 86°).

(c) *trans-cis*-2-**Decalol.**—The *trans-cis*-2-acetyldecalin (6.0 g., 0.033 mole) was degraded as described for the 1-isomers and the crude decalol recrystallized from hexane, yield 2.85 g. (55%), m.p. 72.1–74.8° (lit.[39] 76°).

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

The Stereochemistry and Reactivity of the *cis*-5-Hydrindanyl Derivatives[1]

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The stereochemistry of the epimeric *cis*-5-hydrindanyl derivatives has been investigated and it has been found that the previously assigned steric relationships of the amines and alcohols were inverted. The steric course of the deamination of the amines has been shown to follow the general pattern developed in the *cis*-decalin series. Extension of these concepts to the epimeric *cis*-4-hydrindanyl compounds have been discussed.

The recent interest in the stereochemical aspects of the reaction of nitrous acid with alicyclic amines has brought forth certain generalizations which have been shown to be useful in elaboration of the steric configuration (and conformation) of the amines and the alcohols produced from them.[1-3] It has been found that when an amine of an equatorial conformation is deaminated with nitrous acid, the reaction yields practically a single product and this material is an alcohol of the same steric configuration as the original amine. With compounds which possess the amino grouping in an axial conformation, however, the reaction produces both olefins and alcohols, and these alcohols are composed of a predominant amount of the epimer of inverted (or equatorial) configuration. Special attention has been given to the amines derived from *cis*-decalin since in such compounds both of the epimeric amines can exist in an equatorial conformation. In such a series, Hückel[4] had reported the interesting results that deamination of the *cis*-1-decalylamines proceeded with retention while the *cis*-2-decalylamines gave rise to inverted products. Dauben and Hoerger[5] reinvestigated this anomaly to the above generalizations and found that the relationship between *cis*-2-decalylamines and *cis*-2-decalols had been incorrectly assigned and by correcting such steric configurations, a consistent pathway of reaction in the deamination was followed.

Hückel[4,6] also has reported a detailed investigation of the aminohydrindanes substituted on either the 5- or 6-membered ring. In the latter series, direct analogy to the previous work in the decalin field was to be found and it was noted that here again, the *cis*-4-hydrindanylamines underwent deamination with retention of configuration and the *cis*-5-hydrindanylamines followed the inversion pathway. In order to ascertain whether such results were due to incorrect configurational assignments or whether a true anomaly existed from the conformational concepts of deamination, the steric relationship between the *cis*-5-hydrindanyl derivatives was investigated as previously described[5] for the *cis*-2-decalin compounds.

(1) For the previous paper in this series, see W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954).

(2) J. A. Mills, *J. Chem. Soc.*, 260 (1953).

(3) A. K. Bose, *Experientia*, **9**, 256 (1953).

(4) W. Hückel, *Ann.*, **533**, 1 (1937).

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

(6) W. Hückel, R. Schlüter, W. Doll and F. Reimer, *Ann.*, **530**, 166 (1937).