authentic sample[14]; b.p. 81–82° (2 mm.), $n^{25}D$ 1.4369, $d^{25}{}_4$ 0.8705.

Anal. Calcd. for $C_9H_{18}N_2$: C, 70.08; H, 11.76; N, 18.16. Found: C, 70.06, 70.01; H, 11.60, 11.89; N, 18.02, 18.17.

Attempted Catalytic Reduction of *s*-Triazine. (A) With Palladium-on-charcoal Catalyst.—After being found active on maleic anhydride, the 16.6% palladium-on-charcoal catalyst (0.1 g.) was added to a solution of 2 g. of *s*-triazine in 20 ml. of cyclohexane and the mixture shaken with hydrogen for 2 hours at room temperature and thereafter for 2 additional hours at 70–75°. However, no absorption of hydrogen occurred.

(B) With Platinum Catalyst.—The attempted hydrogenation of 2 g. of *s*-triazine, using 0.08 g. of platinum from platinum dioxide in 25 ml. of cyclohexane also was unsuccessful both at room temperature and at an elevated temperature of 70–75°.

Cyclohexene (1.0 g.) in 30 ml. of decalin was completely hydrogenated with 0.17 g. of the same catalyst in 45 minutes. After adding 0.1 g. of *s*-triazine to such a run, no adsorption of hydrogen took place in 5 hours. The presence of 0.01 g. of *s*-triazine stopped the hydrogenation after 25% of the required hydrogen had been taken up in 3 hours.

Friedel–Crafts Reaction of 2,4,6-Trichlorohexahydro-1,3,5-triazine Sesquihydrochloride (I) with Benzene.—A vigorous reaction occurred when 7 g. of aluminum chloride was added in small portions to a stirred suspension of 10 g. of I in 11 g. of benzene. The reaction, when ceasing, was completed by heating the mixture for 1 hour on the steam-bath; the evolution of hydrogen chloride, noticed at the beginning of the heating, slackened after 0.5 hour. The reaction mixture, after cooling, was poured into 150 g. of ice-water slightly acidified by hydrochloric acid. The addition of more concentrated hydrochloric acid precipitated XV as a white solid which after separation and drying amounted to 8.1 g.

COLUMBUS, OHIO

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[14] E. B. Vliet, THIS JOURNAL, **46**, 1306 (1924).

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

The Configuration and Reactivity of 9-Substituted Decalins

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

RECEIVED MARCH 15, 1954

trans-9-Decalincarboxylic acid has been prepared from 2-keto-10-carbethoxy-$\Delta^{1(9)}$-octahydronaphthalene and its stereo chemistry established by conversion to *trans*-9-methyldecalin by way of the *trans*-9-decalylcarbinol and the tosylate. Previous workers had assigned a *cis* structure to this series of compounds. The acid also has been converted to *trans*-9-decalylamine and the material is in stereochemical agreement with the arbitrarily assigned structures. *trans*-9-Hydroxydecalin was prepared from Δ^9-octalin epoxide by lithium aluminum hydride reduction. The steric course of the reaction of the 9-aminodecalins with nitrous acid to yield 9-hydroxydecalins and octalins has been reinvestigated and the results discussed.

To date, various 9-substituted decalins have been prepared either by direct substitution on decalin itself or by proceeding from Δ^9-octalin by addition reactions. For example, nitration of *trans*-decalin has been reported[2,3] to yield only 9-nitrodecalin whereas the preparation of 9-chlorodecalin[4] by an exchange reaction with *t*-butyl chloride and aluminum chloride is accompanied by the simultaneous formation of lesser amounts of other isomers. Similarly, direct oxidation of decalin with oxygen gives rise to a 9-hydroperoxide[5] while ozone yields the 9-decalols.[6] In all of these compounds, the stereochemistry of the ring juncture has been arbitrarily assigned.[7] The preparation of 9-bromo- and 9-iododecalin[8] by addition of hydrogen bromide and hydrogen iodide to Δ^9-octalin, however, should yield *trans*-isomers while the stereochemistry of the products (*i.e.*, 9-nitroso, 9-amino and 9-hydroxy[3]) resulting from transformation of the addition compound obtained from this octalin and nitrosyl chloride again have been arbitrarily assigned.[7] The steric configuration of the isomeric 9-methyldecalins, on the other hand, is well established[9,10] and these compounds would serve as excellent reference points in a study pertaining to the 9-substituted decalins.

Before investigating the steric aspects of the reaction of nitrous acid with 9-aminodecalins, it was desirable to first establish with certainty, the configuration of the 9-amino- and 9-hydroxydecalins. A convenient procedure to accomplish such a correlation of configuration of amines and alcohols has been utilized in the *cis*-2-decalin series[11] where a carboxylic acid was degraded *via* stereospecific reactions to each type of compound. In order to employ a similar reaction sequence in the 9-decalin series, the preparation of a 9-decalincarboxylic acid was undertaken.

Preparation of *trans*-9-Decalincarboxylic Acid.—Recently, Hussey, Liao and Baker[12] reported the synthesis of a 9-decalincarboxylic acid by a sequence of reactions starting with 2-keto-10-carbethoxy-$\Delta^{1(9)}$-octahydronaphthalene (I), a compound previously prepared by DuFeu, McQuillin and Robinson[13] from 2-carbethoxycyclohexanone and 1,1-diethylamino-3-butanone methiodide. Hydrogenation of I followed by Wolff–Kishner reduction yielded a crystalline acid, the stereochemistry of which was stated to have been established by con-

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[1] United States Rubber Company Predoctoral Fellow in Chemistry, 1952–1953.

[2] S. Nemetkin and O. Madaeff-Ssitscheff, *Ber.*, **59**, 370 (1926).

[3] W. Hückel and M. Blohm, *Ann.*, **502**, 114 (1933).

[4] P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1351 (1944).

[5] R. Criegee, *Ber.*, **77**, 22, 722 (1944).

[6] H. R. Durland and H. Adkins, THIS JOURNAL, **61**, 429 (1939).

[7] W. Hückel, *Ann.*, **533**, 1 (1937).

[8] G. R. Clemo and J. Ormston, *J. Chem. Soc.*, 1778 (1932).

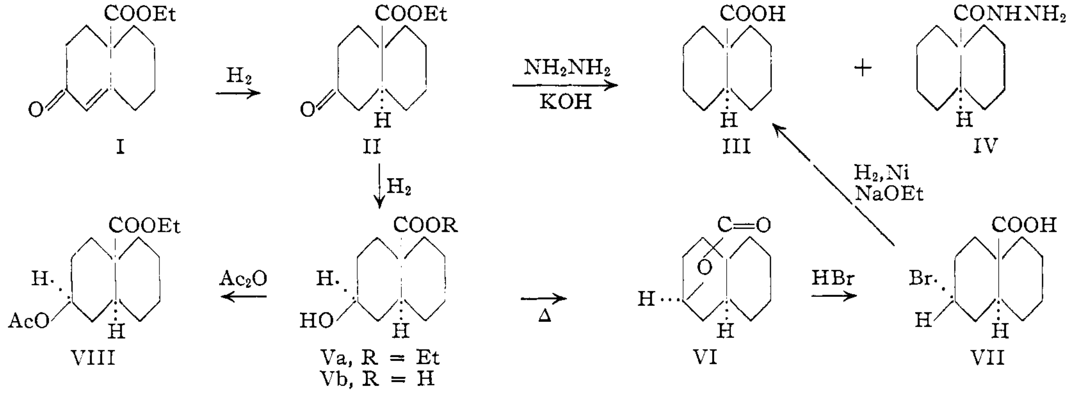
[9] W. G. Dauben, J. B. Rogan and E. J. Blanz, Jr., THIS JOURNAL, **76**, 6384 (1954).

[10] R. P. Linstead, A. F. Millidge and A. L. Walpole, *ibid.*, 1140 (1937); G. H. Elliott and R. P. Linstead, *ibid.*, 660 (1938); W. E. Bachmann and A. S. Dreiding, *J. Org. Chem.*, **13**, 317 (1948); A. Wilds, Abstracts of the 120th Meeting of the American Chemical Society, New York, N. Y., September, 1951, p. 120M; R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLemore, THIS JOURNAL, **74**, 4223 (1953).

[11] W. G. Dauben and E. Hoerger, *ibid.*, **73**, 1504 (1951).

[12] A. S. Hussey, H. O. Liao and R. H. Baker, *ibid.*, **75**, 4727 (1953).

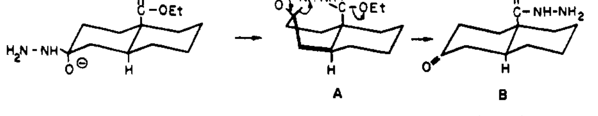
[13] E. C. DuFeu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).



version to *cis*-9-methyldecalin *via* 9-decalylcarbinol. Concurrent with the foregoing study, this same series of reactions was under investigation in this Laboratory and the results obtained contradict the stereochemical conclusion of Hussey, Liao and Baker.[12]

In our hands, the Wolff–Kishner reduction of the saturated ketone II yielded two products, the amounts of which varied with the quantity of hydrazine employed. The pure acid III was obtained in 30–55% yield and an acid soluble nitrogen-containing compound IV in 30–60% yield. This latter compound IV was proved to be the hydrazide of the acid III by preparation of an isopropylidene derivative with acetone and degradation to a known 9-aminodecalin by a Curtius reaction. Hussey, *et al.*,[12] reported an 82% yield of the crude acid but the amount of pure acid obtained was not specified. These workers also obtained the same nitrogeneous by-product but on the basis of a nitrogen analysis it was suggested that the material might be a product of intramolecular cyclization of the hydrazone, $C_{11}H_{16}ON_2$. The percentage of nitrogen in their formulation is 14.57% while in the hydrazide structure IV, $C_{11}H_{20}ON_2$, it is 14.27% and it is evident that such a single elementary analysis could not differentiate between these two formulas; carbon and hydrogen analysis readily separates the structures.

It is of further interest to note that the hydrazide when subjected to the alkaline saponification conditions similar to those obtained in the Huang-Minlon modification[14] of the Wolff–Kishner reaction the hydrazide was recovered unchanged. Furthermore, when the methyl ester of the acid III was allowed to react with anhydrous hydrazine at temperatures up to 180°, no hydrazide was formed. From such a non-reactivity of this 9-substituted decalin in intermolecular reactions, it would appear that the hydrazide formation proceeds through an intramolecular pathway involving an intermediate such as shown in (A) and the resulting keto hydrazide (B) then is reduced.



In addition to the large amount of hydrazide received and which could not be converted to the parent acid, a further disadvantage of the Wolff–Kishner procedure was the fact that the acid obtained had a slight melting range and required numerous crystallizations before a material of constant range (m.p. 133–134°) was obtained. From the mother liquors of this purification, an analytically pure acid melting from 85–105° could be isolated and such a material apparently is a mixture of the *cis*- and *trans*-9-acids.[15]

In view of these disadvantages, another route to the *trans*-9-decalincarboxylic acid was explored. It was found that if the hydrogenation of the unsaturated keto ester I in the presence of palladium-on-strontium carbonate was allowed to continue until 2 moles of hydrogen had been absorbed or if after one mole of hydrogen had been taken up (corresponding to the saturation of the carbon–carbon double bond), platinum oxide was added and the hydrogenation continued, the reaction product upon distillation gave rise to the lactone of *trans-cis*-2-hydroxy-10-decalincarboxylic acid (VI)[16] in 80–90% yield. This same lactone was prepared previously by Hussey, Liao and Baker[12] by the Meerwein–Pondorff reduction of the saturated ketone II. When the lactone VI was allowed to react with hydrogen bromide in acetic acid, a crystalline bromoacid VII was obtained which by hydrogenation over Raney nickel in the presence of base[17] yielded pure *trans*-9-decalincarboxylic acid (III) in 80% yield. Thus, this reaction scheme by proceeding through the lactone apparently eliminates the *cis* ring-juncture isomer in the lactonization step and suggests that the *cis* isomer must be hydrogenated to the non-lactonizable *cis-trans* compound.

When an attempt was made to aid the lactonization of the crude hydrogenation product by the addition of acetic anhydride, the acetate of the *trans-cis*-hydroxy ester VIII was formed. The acetate was stable to heating to 190° whereas the free hydroxy ester lactonized on being heated

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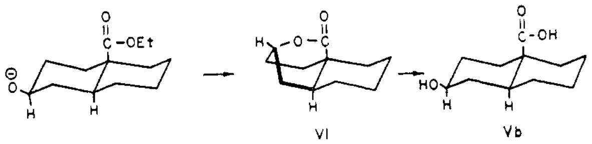
[14] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[15] A mixture of isomers also was obtained by Woodward and his co-workers (see ref. 10) in the reduction, under similar conditions, of 2-keto-10-methyl-$\Delta^{1(9)}$-octahydronaphthalene.

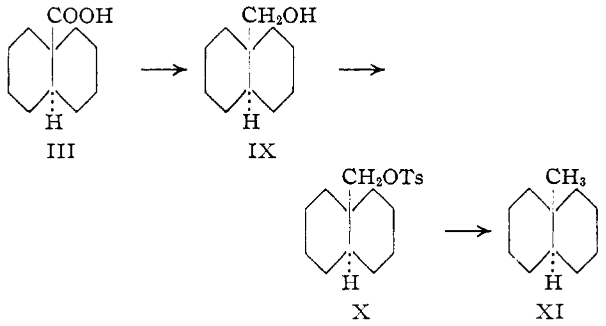
[16] The term *trans-cis* refers to the stereochemistry of the ring juncture at C_9 and C_{10} and of the substituent at C_2 with relation to C_{10}. The carboxyl group is always placed above the plane of the paper. This nomenclature is employed in preference to that suggested by Hussey, *et al.*, in view of its more direct simplicity.

[17] W. G. Dauben, C. F. Hiskey and A. H. Markhart, THIS JOURNAL, **73**, 1393 (1951).

to 120°. Also, the acetate could be saponified to a mixture of hydroxy acid Vb and lactone VI with 1 *N* potassium hydroxide in aqueous methanol while the ester of 9-decalincarboxylic acid required a temperature of 150° in order to bring about appreciable saponification. Such enhanced reactivity seems to be evidence for another intramolecular reaction, similar to the hydrazide formation in the Wolff–Kishner reduction. It is likely that the alkoxide ion, formed by rapid hydrolysis of the acetate, attacks the angular carbethoxy group giving rise to the lactone VI which in turn is hydrolyzed by base to the hydroxy acid Vb. Such a concept is supported by the direct isolation of both lactone and hydroxy acid from the saponification mixture and by the previous work of Hussey, *et al.*,[12] in which it was found that the lactone was readily hydrolyzed to Vb. The hydroxy acid was converted to the lactone upon distillation.



Conversion of *trans*-9-Decalincarboxylic Acid to *trans*-9-Methyldecalin.—The earlier work of Hussey and his collaborators[12] on this conversion led them to the conclusion that the acid was of the *cis* configuration and their method was to reduce the acid to the 9-decalylcarbinol (IX) by lithium aluminum hydride reduction. The carbinol, in turn, was converted to the *p*-toluenesulfonate ester (X) and the ester reduced with lithium aluminum hydride to yield a 9-methyldecalin. The stereochemistry of the hydrocarbon was established by comparison of the physical properties and the reactivity with aluminum chloride with the previously prepared *cis* hydrocarbon.[10]



This same sequence of reactions also was performed independently in this Laboratory and the properties of the alcohol IX and the tosylate X were in agreement with Hussey, Liao and Baker.[12] However, when the tosylate was converted to the 9-methyldecalin, a hydrocarbon of different physical properties was obtained and, in fact, the material appeared to be a mixture of *cis*- and *trans*-9-methyldecalin. In view of this result and the establishment of the chemical purity of all of the starting materials and the stereospecificity of the reactions employed, the properties of the 9-methyldecalins themselves were reinvestigated. As has been reported in an earlier paper,[9] it was found that the previous preparations of *trans*-9-methyldecalin (XI) led to impure materials and, in fact, the *trans* isomer when prepared in pure form agreed well in physical properties with the hydrocarbon derived from the 9-acid. The only explanation of the higher refractive index reported by Hussey, *et al.*,[12] appears to be that the hydrocarbon will contain the alcohol IX unless it has been distilled from sodium and such was not done by those workers. Further substantiation of this hypothesis can be gained from the fact that in the present work the alcohol was only readily separated from the reaction mixture when chromatographic separation or sodium treatment was employed.

The preparation of a *trans*-decalin derivative by hydrogenation of the $\Delta^{\alpha,\beta}$ unsaturated ketone II under neutral conditions is of interest since it has been found that when the angular substituent is a methyl group instead of a carbethoxyl group, a hydrogenation under similar conditions[9,10] gives rise to a *cis*-decalin compound. Furthermore, in the steroids it also has been shown that in the hydrogenation of a 3-keto-Δ^4-compound the usual result is a *cis*-product. In this decalin case no apparent explanation is at hand for the different steric results obtained with a 9-carbethoxyl and a 9-methyl substituent other than an increase in catalyst hindrance due to the larger carbethoxyl grouping.

In view of the establishment of the configuration of the *trans-cis*-hydroxy acid Vb, one is able to compare the stereochemical results obtained in this series with the configurations predicted by the application of the von Auwers–Skita rules.[18] Barton[19] recently has restated these rules utilizing conformational concepts. Thus, catalytic hydrogenation of unhindered ketones in neutral media (slow hydrogenation) normally yields an alcohol with the hydroxyl group in an equatorial conformation. With a 1,3-disubstituted cyclohexane derivative, as has been pointed out by Siegel,[20] this results in the formation of an isomer in which the hydroxyl group is *trans* to the hydrogen atom (or *cis* to the carbon substituent) and such a result was found in the present work. Currently, the effects of acidity are being investigated with regard to this steric control.

It was stated earlier in the utilization of this pure *trans-cis* material (Va) for the preparation of the 9-acid (III), the contaminating isomer containing a *cis* ring juncture was readily removed by the lactonization process and that such a result suggested a *cis-trans* configuration for the compound. It cannot be stated with certainty whether this is the isomer expected on the basis of the conformational predictions since in the case of a *cis*-decalin, due to the flexibility of the ring system, a substituent of any relative configuration can occupy either an equatorial or an axial conformation[21,22] and since

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[18] K. von Auwers, *Ann.*, **420**, 84 (1920); A. Skita, *Ber.*, **53**, 1792 (1920); A. Skita and W. Faust, *ibid.*, **64**, 2878 (1931).

[19] D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

[20] S. Siegel, THIS JOURNAL, **75**, 1317 (1953). In discussing the application of this concept to the steroids, the term *cis* has been used inadvertently in place of *trans*.

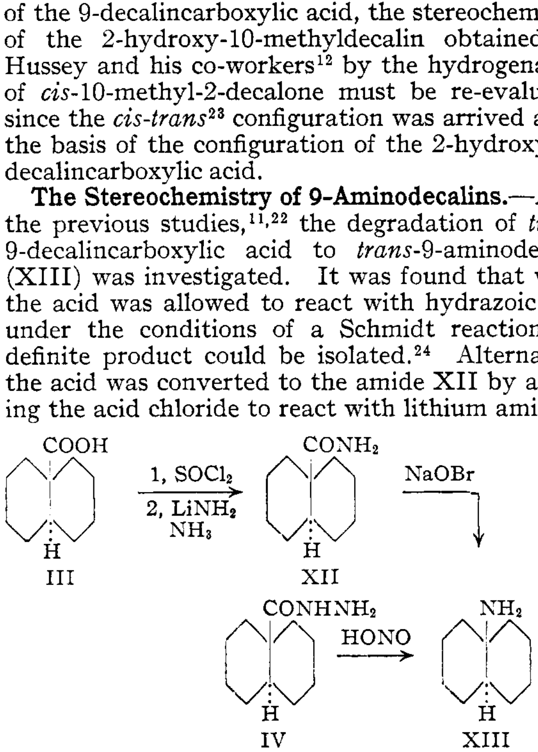
[21] J. A. Mills, *J. Chem. Soc.*, 260 (1953).

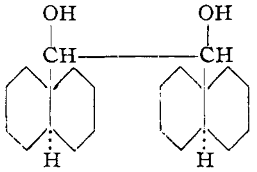
[22] W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954).

the conformational interpretation of the steric course of catalytic hydrogenation given by Barton[19] is, in general, synonymous to having the more stable isomer uniquely possess an equatorial conformation.

In view of the reassignment of the configuration of the 9-decalincarboxylic acid, the stereochemistry of the 2-hydroxy-10-methyldecalin obtained by Hussey and his co-workers[12] by the hydrogenation of *cis*-10-methyl-2-decalone must be re-evaluated since the *cis-trans*[23] configuration was arrived at on the basis of the configuration of the 2-hydroxy-10-decalincarboxylic acid.

The Stereochemistry of 9-Aminodecalins.—As in the previous studies,[11,22] the degradation of *trans*-9-decalincarboxylic acid to *trans*-9-aminodecalin (XIII) was investigated. It was found that when the acid was allowed to react with hydrazoic acid under the conditions of a Schmidt reaction, no definite product could be isolated.[24] Alternately, the acid was converted to the amide XII by allowing the acid chloride to react with lithium amide in liquid ammonia. It is of interest to note that when the acid chloride was allowed to react with aqueous ammonia for 10 minutes at 0° with stirring, only starting acid and unreacted acid chloride was isolated. Also, when the acid chloride was mixed with a solution of sodium (not $NaNH_2$) in liquid ammonia, the dimeric glycol XIV and the starting acid were obtained.





XIV

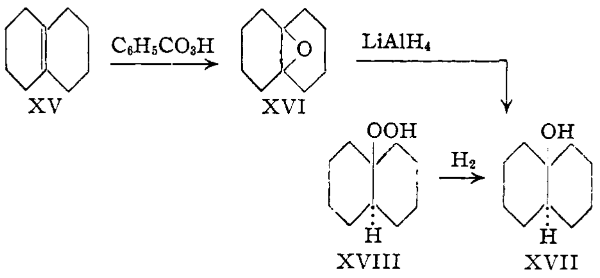
When the amide XII was treated with sodium hypobromide in methanol and the resulting methylurethan hydrolyzed, a 9-aminodecalin could be isolated as the crystalline acetyl derivative (m.p. 183°). Attempts to degrade the acid chloride directly following the Curtius procedure utilizing activated sodium azide failed and led only to recovery of the acid.

Since the hydrazide IV formed in the Wolff-Kishner reduction of the keto ester II had not been directly related to the acid obtained in the same reaction, the hydrazide was degraded by a Curtius reaction. It was found that the same amine XIII was obtained from it as from the amide and thus the identity of the ring juncture of these two compounds was established.

Hückel[3] has prepared the two isomeric 9-aminodecalins by reduction of the isomeric 9-nitro compounds.[2] One of the amines also could be prepared from Δ^9-octalin starting with the nitroso chloride addition product and transforming it to 9-amino-$\Delta^{4(10)}$-octalin which in turn was catalytically hydrogenated in acid solution to an amine (acetyl derivative, m.p. 127°). On the basis of this method of synthesis, the latter compound was assigned a *cis*-configuration and thus the isomeric amine (acetyl derivative, m.p. 183°) was given a *trans*-configuration. Since the latter amine (acetyl derivative, m.p. 183°) has been obtained from a *trans*-acid by reactions which have been shown to proceed stereospecifically with retention,[11] the assigned configurations of Hückel are proved.

The Stereochemistry of 9-Hydroxydecalins.—The stereoisomeric 9-hydroxydecalins previously have been prepared by two different methods. The first method was to allow nitrous acid to react with 9-aminodecalins and to isolate the alcoholic products.[3] The configuration of the two isomers was assigned by Hückel[3,7] on the basis of their physical properties and cryoscopic behavior in benzene and cyclohexane. The isomer which was assigned a *trans*-configuration was also reported to yield a solid chromate ester. A second method of preparation was reported by Durland and Adkins[6] who found that by allowing ozone to react with *cis*-decalin, the *cis*-alcohol was obtained and that the *trans*-alcohol was isolated from *trans*-decalin. Thus no rearrangement of ring juncture configuration occurred on oxidation. A further fact which supported the arbitrarily assigned configurations was the greater ease of dehydration of the *trans* isomer to Δ^9-octalin.

Since in our studies it was desired to firmly establish the configuration of the 9-decalols, the preparation of the *trans* isomer was undertaken in a stereospecific manner.



Δ^9-Octalin (XV), prepared according to the procedure of Campbell and Harris,[25] was converted to Δ^9-octalin epoxide (XVI) with perbenzoic acid.[26] This epoxide was reduced with lithium aluminum hydride and the 9-decalol (XVII) isolated was identical with the isomer assigned a *trans* configuration by Hückel.[7] It is well established that the reaction of lithium aluminum hydride with

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[23] The stereochemistry using the definition in footnote[16] and called *trans*-10-methyl-2-*cis*-decalol by Hussey.

[24] A discussion of anomalous reaction of tertiary aliphatic acids is to be found in C. Schuerch and E. H. Huntress, THIS JOURNAL, **71**, 2233 (1949).

[25] W. P. Campbell and G. C. Harris, *ibid.*, **63**, 2721 (1941).

[26] W. Hückel, R. Danneel, A. Schwartz and A. Gerke, *Ann.*, **474**, 212 (1929).

epoxides proceeds by a bimolecular nucleophilic displacement to yield a *trans* product since it has been shown by Trevoy and Brown[27] that 1,2-dimethyl-1,2-epoxycyclohexane and 1,2-dimethyl-1,2-epoxycyclopentane yield the *trans* isomers of 1,2-dimethyl-1-cyclohexanol and 1,2-dimethyl-1-cyclopentanol, respectively. Plattner, Heusser and Feurer[28] also have reported the isolation of 3β,6β-dihydroxycholestane from the reduction of 3β-acetoxy-5β,6β-epoxycoprostane. Thus the configurations assigned by Hückel to the 9-decalols are correct.

In view of the establishment of the stereochemistry in this series, it is of interest to look back on the stereochemical course of the reactions of decalins with other oxidizing agents. It can now be stated that the reaction of decalin with ozone to yield a 9-decalol proceeds with full retention of configuration, *i.e.*, *trans*-decalin yields *trans*-9-decalol and *vice versa*. As for the reaction of these hydrocarbons with oxygen,[5] Criegee has reported that when *cis*-decalin is allowed to react with oxygen, *trans*-9-decalyl hydroperoxide (XVIII) is formed and this latter compound, in turn, can be hydrogenated to *trans*-9-decalol. Since the hydrogenation reaction must proceed by retention of configuration, the stereochemistry of the hydroperoxide is as originally assigned. To date, no product has been reported from this oxidation[5] reaction with *trans*-decalin and so one cannot make any statement about the stereospecificity of the reaction of oxygen.

Table I lists the properties of the amines and alcohols when arranged with their proper stereochemistry.

TABLE I

PROPERTIES OF 9-SUBSTITUTED DECALINS

	9-Decalols		9-Decalylamines		
	ol	chromate	amine	acet-amide	benz-amide
cis	65°	....	−13°	127°	147°
trans	54°	78–85°	−25°	183°	148°

The Reaction of Nitrous Acid with 9-Aminodecalins.—The reaction of nitrous acid with primary acylic amines has been widely investigated and recently Ingold[29] has reviewed the steric course followed in such deaminations. It was concluded by him that such a reaction was clearly of the SN1 type involving racemization and inversion. Such has not been found to be the case with primary amine in the alicyclic series.[7,30] The results obtained in a *cis-trans* isomeric pair differ widely, one isomer yielding an alcohol of the same configuration and the other epimer affording olefin and largely *inverted alcohol*. Such results have led various workers[21,22,31,32] to suggest certain generalizations which attempt to correlate the steric course of the deamination reaction in the alicyclic series with the conformation of the amino group. It normally is found that when the amino group is in an equatorial conformation the reaction product is an alcohol of the same configuration whereas if the amino group is in an axial conformation, both elimination and substitution occur and the alcohols formed are an epimeric mixture with the isomer of equatorial conformation in predominance.

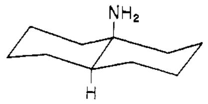
In view of the establishment of the stereochemistry of the 9-aminodecalins discussed earlier, it is of interest to examine the results obtained by Hückel[3] in a study of their reaction with nitrous acid. The results of the deaminations are summarized in Table II. It is seen that the *trans*-9-amine yields 20% of the epimeric 9-decalols and 80% of the isomeric octalins. The alcoholic fraction was not carefully investigated and only the *trans*-9-decalol, isolated as a solid chromate ester, was identified. The octalin mixture was separated *via* the solid nitrosyl chloride addition products and it was found to be composed of 88% of the Δ^9-isomer and 12% of the $\Delta^{1(9)}$-compound. The *cis*-9-amino isomer also yields an alcoholic and olefinic fraction but in this case the alcoholic material was found to be almost pure *cis*-9-decalol and the octalin fraction was found to consist of 78% of the $\Delta^{1(9)}$ and 22% of the Δ^9-isomer.

TABLE II

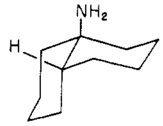
PRODUCTS OF THE REACTION OF 9-AMINODECALINS WITH NITROUS ACID

Configuration of amine	Composition of product, %			
	9-Decalols		Octalins	
	cis	*trans*	$\Delta^{1(9)}$	Δ^9
trans	(20)		10	70
cis	40	Trace	35	10

Before discussion of the results from a conformational viewpoint, the unique situation of a ring juncture substituent in a *cis*-decalin (XX) must be considered. In this case when a substituent is equatorial to one ring it is axial to the other. Nevertheless, since it does possess some equatorial character is should be more sterically favored than a pure axial substituent of a *trans*-decalin. In general, it is true that an epimer of equatorial character is thermodynamically more stable than an axial epimer but such need not always be the case (*i.e.*, *cis*-1- and 2-decalyl derivatives)[22] and in a 9-decalol there are non-bonding interactions not involving the hydroxyl group which are present in the *cis* but not in the *trans*. For example, in decalin itself, the *trans*-isomer possesses its ring juncture hydrogens in an axial conformation and yet is 2.4 kcal.[33] more stable than the *cis*-isomer in which one of the atoms at the ring juncture can be viewed as being equatorial. It seems reasonable to assume, therefore, that the *trans*-9-decalol is the more stable, thermo-



XIX



XX

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[27] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[28] P. A. Plattner, H. Heusser and M. Feurer, *Helv. Chim. Acta*, **32**, 587 (1949).

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dynamically, while in the immediate vicinity of the hydroxyl group the *cis* isomer is less hindered.

Examination of the steric results of the alcoholic fraction obtained from each isomeric amine in the deamination reaction shows that they are in accord with the generalized conformational postulates of this reaction. In the *trans*-amine XIX, the amino group is axial and only a small amount of a mixture of alcohols was obtained but in the *cis* compound XX where the amino group is both equatorial and axial, the reaction gave rise to a good yield of an alcohol of retained configuration. As has been shown previously, an amine possessing an equatorial–axial type of conformation[22] always gives both elimination and substitution but in this case where the amine is attached to a tertiary carbon atom, the degree of elimination is increased. The formation of a *cis* alcohol is of particular interest since it demonstrates that the reaction product is conditioned by the stereospecificity of the reaction as controlled by close range steric interactions and not by the over-all thermodynamic stability of the compound.

The composition of the olefins from these two isomeric amines also gives further insight into the steric course of the elimination reaction. It is seen that the *trans* isomer yields mainly Δ^9-octalin whereas the *cis*-amine yields $\Delta^{1(9)}$-octalin as the predominate isomer. Such results clearly show that an axial–axial transition state is preferred[34] and that if this steric feature is met by elimination toward either a methylene or a methine group, elimination toward the latter grouping is preferred. Thus, the elimination reaction resembles a bimolecular process (E_2) of the halide–tosylate type rather than the "onium" type. Furthermore, the above results strongly suggest that an E_1 process of the normal type is not involved[35] since if such were the case, the polar aspects of the reaction should predominate over the steric restrictions and mainly Δ^9-octalin should be obtained from each isomer. These conclusions are in agreement with the earlier postulates[21,22] with regard to the pathway of elimination in the nitrous acid deamination reaction.

Experimental[36]

2-Keto-10-carbethoxy-$\Delta^{1(9)}$-octahydronaphthalene (I).—The compound was prepared following the procedure of DeFeu, McQuillin and Robinson[13] and from 102 g. (0.6 mole) of 2-carbethoxycyclohexanone, 69 g. (73%) of the ketone was obtained, b.p. 154–156° (3.8 mm.), $n^{25}D$ 1.5043. The semicarbazone was prepared in the usual manner, m.p. 205–208° (lit.[13] 208°).

***trans*-10-Carbethoxy-2-decalone (II).**—The foregoing unsaturated keto ester (55.5 g., 0.25 mole) was dissolved in 150 ml. of absolute ethanol, 2.0 g. of palladous hydroxide on strontium carbonate[37] added and the mixture hydrogenated at low pressure. After 3 hours the reaction was complete, the catalyst was filtered and the product distilled through a column, b.p. 111–113° (0.5 mm.), 135–136° (3.5 mm.), $n^{25}D$ 1.4829, yield 48.5 g. (87%). Hussey, *et al.*,[12] report b.p. 146–148° (2 mm.), $n^{25}D$ 1.4790.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.43; H, 8.96.

The semicarbazone was prepared from 1.9 g. of ketone and recrystallized from dilute aqueous ethanol, m.p. 193.5–194.0°, yield 1.9 g. (96%).

Anal. Calcd. for $C_{14}H_{23}O_3N_3$: C, 59.78; H, 8.24. Found: C, 59.82; H, 8.27.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner and chromatographed on a silicic acid-Super-Cel column. The chromatogram was developed with 20:1 hexane–ether, the column extruded and the zone containing the derivative cut out and eluted with ether. The product was recrystallized from aqueous ethanol, m.p. 130.6–131.9° (lit.[12] 167°).

Anal. Calcd. for $C_{19}H_{24}O_6N_4$: C, 56.43; H, 5.98; N, 13.85. Found: C, 56.09; H, 5.93; N, 14.25.

***trans*-9-Decalincarboxylic Acid. (a) From *trans*-10-Carbethoxy-2-decalone.**—The ketone (5.0 g., 0.022 mole) was dissolved in 40 ml. of diethylene glycol containing 3 ml. of 85% hydrazine hydrate and 3.4 g. of potassium hydroxide. The solution was heated under reflux for 90 minutes, the condenser removed, the internal temperature allowed to rise to 210° and then the solution allowed to reflux for 16 hours. After cooling, the solution was poured into 150 ml. of water and the white solid filtered. The filtrate was extracted 3 times with ether, the solvent evaporated and the residue added to the precipitate. The total yield of crude *trans*-9-decalincarboxhydrazide was 1.4 g. (32%). The material was first recrystallized from aqueous ethanol, then from carbon tetrachloride and finally sublimed, m.p. 139–143°.

Anal. Calcd. for $C_{11}H_{20}ON_2$: C, 67.30; H, 10.28; N, 14.28. Found: C, 67.45; H, 10.17; N, 14.28.

The hydrazide was refluxed with base for 16 hours but only starting material was recovered. When 2.0 g. was heated with acetone, N′-isopropylidene-*trans*-9-decalincarboxhydrazide was obtained, yield 2.01 g, (83%), m.p. 170.7–171.9°.

Anal. Calcd. for $C_{14}H_{24}ON_2$: C, 71.14; H, 10.23; N, 11.86. Found: C, 71.28; H, 10.10; N, 12.03.

The alkaline solution was acidified and the precipitate filtered. The filtrate was extracted with ether and combined with the solid. After removal of the solvent, the acid was recrystallized three times from aqueous ethanol, yield 2.4 g. (55%), m.p. 133–134° (Hussey, *et al.*,[12] report 134.6–135.4°).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.65; H, 9.92.

The mother liquors from the recrystallization of the acid yielded solid which melts from 85–105° and analyzed correctly for pure acid.

The methyl ester of the pure acid was prepared with diazomethane and subjected to reaction with anhydrous hydrazine at 200°. After processing, only starting ester and acid could be isolated.

When the reaction was run using 40.4 g. (0.18 mole) of the ketone, 300 ml. of diethylene glycol, 55 ml. (0.94 mole) of 85% hydrazine hydrate and 28 g. (0.42 mole) of potassium hydroxide, 10.2 g. (30%) of the acid and 21 g. (59%) of the hydrazide were obtained.

(b) From *trans-trans*-2-Bromo-10-decalincarboxylic Acid (VII).—The bromide (2.49 g., 0.095 mole) was dissolved in 40 ml. of methanol and added to a solution of 1.00 g. of sodium in 60 ml. of methanol. Raney nickel (25 ml.) was added and the mixture hydrogenated at low pressure. After filtration of the catalyst, the filtrate was diluted with water and then concentrated. Acidification yielded a solid which upon recrystallization melts from 133–134°, yield 1.49 g. (86%).

***trans*-9-Decalincarboxamide (XII).**—*trans*-9-Decalincarboxylic acid (1.0 g.) was dissolved in 10 ml. of dry benzene containing 2 ml. of thionyl chloride and the solution allowed to stand for 24 hours. The benzene and thionyl chloride were removed under reduced pressure and the acid chloride dissolved in 15 ml. of dry ether. The ethereal solution was

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(34) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951).

(35) For an excellent example of this type of control in the menthylneomenthyl series, see S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, THIS JOURNAL, **74**, 1127 (1952).

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

(37) This catalyst was prepared in the following manner. Aqueous solutions of 90 g. of strontium chloride hexahydrate and 50 g. of sodium carbonate were mixed and the resulting solid centrifuged and washed with water. Palladous chloride (1 g.) was dissolved in 10 ml. of dilute hydrochloric acid and added to the aqueous suspension of the strontium carbonate. After stirring for 12 hours, the material was centrifuged, washed 4 times with water and dried for 48 hours at 110°.

added to a solution of 1.6 g. of lithium amide in liquid ammonia and the mixture stirred for 1 hour at −35°. After adding 3.5 g. of ammonium chloride, the ammonia was allowed to evaporate and the residue mixed with water and extracted with carbon tetrachloride. The crude amide (881 mg.) was recrystallized from chloroform–hexane, m.p. 125.1–125.7°.

Anal. Calcd. for $C_{11}H_{19}ON$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.91; H, 10.64; N, 7.47.

trans-**9-Decalincarbonyl Chloride.**—The pure material could be prepared in 88% yield as described above with thionyl chloride or in 70% yield from oxalyl chloride, b.p. 110–111° (8 mm.).

Anal. Calcd. for $C_{11}H_{17}OCl$: C, 65.82; H, 8.54; Cl, 17.67. Found: C, 65.65; H, 8.44; Cl, 17.60.

trans-**9-Decalylcarbinol (IX).**—Lithium aluminum hydride (10.0 g., 0.26 mole) was dissolved in 200 ml. of dry *n*-butyl ether at 100° and a solution of 9.1 g. (0.05 mole) of *trans*-9-decalincarboxylic acid in 100 ml. of dry *n*-butyl ether added dropwise. After stirring for 4 days at 100°, the suspension was cooled and water added to decompose the excess hydride. Hydrochloric acid then was added and the ether layer separated, washed with base, water and dried. After removing the solvent, the material was distilled, b.p. 96–100° (1.7 mm.), yield 8.05 g. (95%). The solid distillate was recrystallized from aqueous ethanol, m.p. 77–78° (Hussey, *et al.*,[12] report 84.2–84.6°).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.83; H, 12.16.

The 3,5-dinitrobenzoate was prepared and melts 131–133°.

Anal. Calcd. for $C_{18}H_{22}O_6N_2$: C, 59.66; H, 6.17; N, 7.72. Found: C, 59.77; H, 6.13; N, 7.75.

trans-**9-Decalyl Carbinyl Tosylate (X).**—*trans*-9-Decalylcarbinol (6.77 g., 40 mmoles) was dissolved in 50 ml. of dry benzene and to this was added a solution of 8.4 g. (0.04 mole) of *p*-toluenesulfonyl chloride in 30 ml. of dry benzene. The solution was allowed to stand for 9 hours at 0°, poured into water and the mixture made alkaline with ammonia. The precipitate was filtered, dried and recrystallized from benzene–hexane, yield 12.4 g. (96%), m.p. 139.7–141.7° (Hussey, *et al.*,[12] report 141.0–141.6°).

Anal. Calcd. for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13; S, 9.94. Found: C, 67.04; H, 7.98; S, 9.62.

trans-cis-**2-Hydroxy-10-decalincarboxylic Acid Lactone (VI).**—*trans*-10-Carbethoxy-2-decalone (10.6 g., 0.047 mole) was dissolved in 60 ml. of absolute ethanol and hydrogenated at low pressure in the presence of 0.2 g. of platinum oxide. The catalyst was filtered, the ethanol evaporated and the product distilled, b.p. 125–126° (1.7 mm.), n^{25}D 1.5000, yield 7.38 g. (87%), Hussey, *et al.*,[12] find b.p. 128–131° (2 mm.), n^{25}D 1.5010.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.98; H, 9.33.

trans-cis-**2-Hydroxy-10-decalincarboxylic Acid (Vb).**—When 10 g. of the decalone was hydrogenated as above and prior to distillation allowed to react at 100° for 4 hours with 20 ml. of acetic anhydride, the product upon distillation yielded 10.5 g. (88%) of *trans-cis*-10-carbethoxy-2-decalyl acetate, b.p. 172–175° (9.5 mm.), n^{20}D 1.4797.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.36; H, 9.04.

The acetate ester (9.45 g.) was refluxed for several hours with 6 *N* potassium hydroxide in methanol, diluted with water and extracted with chloroform. After removal of the solvent, the residue upon distillation yielded 0.85 g. of lactone, b.p. 147–157° (5 mm.), n^{25}D 1.4990.

The alkaline solution was partially concentrated to remove the methanol and the solution acidified. The white precipitate was filtered and the filtrate extracted with ether and the material combined with the precipitate. The product was recrystallized from ethanol–hexane, yield 4.23 g. (69% based upon recovered lactone), m.p. 152.4–152.9° (Hussey, *et al.*,[12] report 149.2–150.6°).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.45; H, 9.39.

The hydroxy acid was transformed to the lactone upon distillation.

trans-trans-**2-Bromo-10-decalincarboxylic Acid (VII).**—The *trans-cis*-lactone (5.02 g., 0.028 mole) was heated on a steam-bath for 23 hours with 50 ml. of acetic acid saturated with hydrogen bromide. The solution was diluted with water, cooled to 0° and filtered. The crude bromo acid was recrystallized from hexane, yield 4.64 g. (86.5% based upon recovered lactone), m.p. 157.9–158.3° dec. The melting point depends on the rate of heating since it is readily transformed to the lactone.

Anal. Calcd. for $C_{11}H_{17}O_2Br$: C, 50.59; H, 6.65; Br, 30.60. Found: C, 50.82; H, 6.86; Br, 30.44.

The aqueous filtrate from the reaction was extracted with chloroform, the solvent removed and the product upon distillation yielded 1.34 g. (27%) of lactone.

trans-**9-Aminodecalin (XIII).** (a) **From** *trans*-**9-Decalincarboxamide (XII).**—The amide (100 mg., 0.55 mmole), dissolved in 2 ml. of methanol, was added to a solution of 23 mg. (0.1 mmole) of sodium in 2 ml. of methanol. Bromine was added dropwise to the stirred solution until a yellow color persisted (about 80 mg. required). The solution then was heated on a steam-bath for 20 minutes, acidified with glacial acetic acid and heated to remove the methanol. The residual liquid was dissolved in a small amount of hexane and added to a mixture of 0.50 g. of calcium oxide and 0.25 g. of water in a test-tube. The tube was warmed to remove the hexane, then a cold finger type condenser inserted and the solid heated strongly to distil the amine. After cooling the apparatus, the cold finger was washed with ether. The condenser again was inserted and the process repeated several times. The combined ethereal solution was heated on a steam-bath with 5 ml. of acetic anhydride and the ether distilled. The residue was dissolved in hexane and washed with water and base. Upon evaporation of the hexane, a solid acetamide was obtained which was recrystallized from benzene–hexane, yield 31.1 mg. (29%), m.p. 181.3–182.1° (lit.[3] Hückel reports 183° for his arbitrarily assigned "*trans*" and 127° for his "*cis*").

(b) **From** *trans*-**9-Decalincarboxhydrazide (IV).**—The hydrazide (0.5 g., 2.55 mmoles) was dissolved in a mixture of 5 ml. of benzene and 5 ml. of acetic acid and cooled to −10°. Sodium nitrite (0.25 g.), dissolved in 1 ml. of water, was added and the mixture allowed to stand at −10° for 30 minutes. The reaction was diluted with 25 ml. of benzene and the mixture poured into 125 ml. of saturated aqueous sodium carbonate solution. The layers were separated, the aqueous layer extracted again with benzene and the combined benzene extracts concentrated to 10 ml. Concentrated hydrochloric acid then was added, the mixture refluxed for 9 hours, the benzene steam distilled and on cooling the aqueous acidic solution was made alkaline and extracted with benzene. Acetic anhydride (10 ml.) was added to the benzene extract and the mixture refluxed for 9 hours. The solution was washed with water, alkali and concentrated to a volume of 5 ml. Upon addition of hexane, the acetamide crystallized, yield 180 mg. (36%), m.p. 180.0–181.5°. A small portion was recrystallized from benzene, m.p. 183.0–183.4°.

Anal. Calcd. for $C_{12}H_{21}ON$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.98; H, 10.55; N, 6.94.

Another Curtius reaction was performed on 14.7 g. of the hydrazide as described above except after hydrolysis with hydrochloric acid, the basic solution was extracted with ether and 4 ml. of formic acid added. A total of 6.46 g. (43%) of the amine formate was obtained. After recrystallization from ethyl acetate, the material melts with decomposition over a range of less than 1° and the melting point can be obtained anywhere between 165 and 169° depending upon the rate of heating (lit.[3] Hückel reports 172° dec. and 165–166° dec. for the two isomers).

Reaction of *trans*-**9-Aminodecalin with Nitrous Acid.**—The formate salt of the amine (5.0 g., 0.025 mole) was dissolved in 10% acetic acid and a concentrated solution of 2.0 g. (0.029 mole) of sodium nitrite in water added. The solution was heated on the steam-bath for 3.5 hours and then extracted 3 times with ether. The ethereal solution was washed with acid and base, dried and the ether removed. Upon distillation of the residue, 1.8 g. (62% based upon recovered amine), b.p. 72–74° (11 mm.), n^{25}D 1.4957 of mixed octalins was obtained and 0.65 g. (19% based upon recovered amine), b.p. 83–85° (6 mm.), n^{25}D 1.4932, of mixed decalols was isolated.

The acid washings from the above were basified and extracted with ether. Formic acid was added to the ether and 0.49 g. (10%) of starting amine formate was obtained.

The olefin mixture was characterized by conversion to the nitrosyl chloride addition products. The olefins (0.8 g.) were mixed with 2 ml. of freshly prepared ethyl nitrite at −7° and 1.5 ml. of concentrated hydrochloric acid added dropwise with stirring. After 1 hour, the blue precipitate was filtered and washed with cold ethanol. The filtrate, upon standing, deposited a mixture of blue and white crystals.

The first crop of blue crystals was dissolved in acetone, filtered hot and on cooling yielded 0.33 g. of blue crystals, m.p. 89.9–90.4° (lit.[3] 91°). The remaining crude material was dissolved in the acetone filtrate and on concentration an additional 0.08 g. of blue crystals was obtained, m.p. 88.0–90.2°. The total yield of 9-nitroso-10-chlorodecalin was 0.41 g. (34%). From the mother liquor a small amount of white crystals was obtained, m.p. 112° dec. (lit.[3] value for $\Delta^{1(9)}$-octalin nitrosochloride is 127°).

Δ^9-Octalin Epoxide (XVI).—Δ^9-Octalin[26] (6.2 g., 0.045 mole) was dissolved in 20 ml. of chloroform and added to a solution of 6.90 g. (0.05 mole) of perbenzoic acid in 100 ml. of chloroform. The reaction mixture was allowed to stand in the dark for 3 days at room temperature and then the chloroform solution neutralized with dilute sodium hydroxide solution. A white solid appeared which partially dissolved after the mixture had been shaken. The chloroform layer was separated, washed with water, dried and then the solvent removed. The Δ^9-octalin epoxide was distilled through a 10-plate column, yield 4.9 g. (71%), b.p. 88° (16 mm.), n^{19}D 1.4851 (lit.[27] b.p. 82–83° (8–9 mm.), n^{20}D 1.4847).

***trans*-9-Hydroxydecalin (XVII).**—A solution of 1.0 g. (6.6 mmoles) of Δ^9-octalin epoxide in 5 ml. of dry ether was allowed to react with 20 ml. of a 1 *M* solution of lithium aluminum hydride at room temperature for 12 hours. Water and alkali were added, the ether layer separated and the aqueous layer extracted twice with ether. The combined ethereal extracts were washed with water, dried and the solvent removed. The crude product was distilled, b.p. 61–62° (1.4 mm.) and the distillate solidified on standing, m.p. 35–45°, yield 0.49 g. (48%). Durland and Adkins[6] report a b.p. 57–59° (1 mm.) and m.p. 52°.

A solution of 0.2 g. of the crude alcohol was dissolved in 10 ml. of petroleum ether and stirred with a solution of 0.30 g. of chromic acid in 10 ml. of water for 2 hours. The organic layer was separated, washed with 5% sodium bicarbonate and then dried. After removal of the solvent, the residue crystallized. The solid was recrystallized from petroleum ether by cooling to −65° to yield 0.23 g. (62%) of yellow ester, m.p. 78–86° (lit.[26] m.p. 77–85°).

The ester (0.23 g.) was heated under reflux for 1 hour with a mixture of 0.25 g. of zinc dust, 4 ml. of acetic acid and 6 ml. of water. The product was recovered by steam distillation and extracted from the distillate with ether. The crude material was sublimed and the crystalline alcohol melts from 50.0–51.5°.

1,2-Di-(*trans*-9-decalyl)-ethylene Glycol (XIV).—*trans*-9-Decalincarboxylic acid (1.0 g.) was converted to the acid chloride in the usual manner and the chloride, dissolved in dry ether, was added slowly to a dark blue solution of sodium in liquid ammonia. The excess sodium was decomposed with ammonium chloride and ethanol and the solution allowed to warm to room temperature. Water was added, the solution partially concentrated, and then extracted with chloroform. The chloroform solution was concentrated, pentane added and the crystals which formed melt from 163–165°. The material was recrystallized from aqueous ethanol, yield 0.31 g. (52% based upon recovered acid), m.p. 167.7–168.7°.

Anal. Calcd. for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45. Found: C, 79.00; H, 11.51.

The alkaline solution from the reaction upon acidification yielded 0.36 g. of starting acid.

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On Some Dehydrogenation Products of α-Carotene, β-Carotene and Cryptoxanthin

BY G. KARMAKAR[1] AND L. ZECHMEISTER

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By treatment of α-carotene, $C_{40}H_{56}$, β-carotene, $C_{40}H_{56}$, and cryptoxanthin, $C_{40}H_{55}OH$, with N-bromosuccinimide and (in part) with N-bromoacetamide, three new crystalline pigments, "dehydrocarotenes I–III," have been isolated, besides dehydro-β-carotene, bisdehydro-β-carotene and anhydro-eschscholtzxanthin. Dehydrocarotene I was obtained only from α-carotene, II from β-carotene and III from both carotenes. Their spectral curves are characterized by the lack of fine structure in the visible region. Upon treatment of dehydrocarotenes (or of desoxylutein I) with boron trifluoride etherate and subsequent chromatographic resolution, fine structure appears in the spectrum of the main product. Some structural, stereochemical and spectral features of these compounds are discussed.

It has been reported recently, in collaboration with Wallcave,[2] that carbon tetrachloride solutions of β-carotene, $C_{40}H_{56}$, (11 double bonds), when refluxed with N-bromosuccinimide, showed marked deepening of the color and yielded, after chromatography, three crystalline pigments, *viz.*, dehydro-β-carotene,[3] $C_{40}H_{54}$, bisdehydro-β-carotene, $C_{40}H_{52}$, and anhydro-eschscholtzxanthin,[4] $C_{40}H_{50}$. We find that N-bromoacetamide is also an effective dehydrogenating agent for β-carotene, although it did not produce any anhydro-eschscholtzxanthin under the conditions applied.

Upon refluxing α-carotene with N-bromosuccinimide, bisdehydro-β-carotene and anhydro-eschscholtzxanthin were isolated while dehydro-β-carotene was absent from the reaction mixture. A similar treatment with N-bromoacetamide has resulted in the isolation of bisdehydro-β-carotene only (Table I).

The correct chromatographic separation of the three intensely colored products just mentioned required a strong developer, such as hexane plus 8% acetone, on the lime–Celite column; the chromatographic filtrate was then orange-yellow. Its pigment content could likewise be resolved when the weak developer hexane was used. This resulted in the isolation of two new crystalline pigments termed dehydrocarotenes I and III.

Dehydrocarotene III also was obtained from β-carotene besides a third crystalline compound,

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[1] We wish to thank The Rockefeller Foundation for a Fellowship and a grant.

[2] L. Zechmeister and L. Wallcave, THIS JOURNAL, **75**, 4493 (1953).

[3] R. Kuhn and E. Lederer, *Ber.*, **65**, 637 (1932); P. Karrer and G. Schwab, *Helv. Chim. Acta*, **23**, 578 (1940).

[4] P. Karrer and E. Leumann, *ibid.*, **34**, 445 (1951).