removed by distillation and the residue was extracted six times with 20-ml. portions of ether. The last extract was optically inactive, indicating complete removal of the menthol. The alkaline solution was acidified and the abundant precipitate was extracted into ether. The extracts were dried and stripped of solvent to yield 1.80 g. (84.5%) of white solid, m.p. 153–161°. The crude acid was optically inactive. Recrystallization from dilute methanol raised the m.p. to 164–165.5°, unchanged by further crystallization.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.39, 73.44; H, 5.13, 5.23.

When an attempt was made to hydrolyze the above (−)-menthyl *p*-(α-hydroxybenzyl)benzoate in dilute acetic acid containing sulfuric acid, the crude acidic product was obtained in 43.5% yield and proved to be optically inactive in ethanol.

Acetylation and lithium aluminum hydride reduction of (−)-menthyl p-(α-hydroxybenzyl)benzoate. Crude (−)-menthyl *p*-(α-hydroxybenzyl)benzoate (2 g.) was dissolved in pyridine (20 ml.). Acetic anhydride (4 ml.) was added and the solution was heated under reflux for 8 min., then poured onto chopped ice. The oily product was extracted into ether, and the extract was washed thoroughly with 6*N* hydrochloric acid, water, and sodium carbonate solution. Drying and solvent removal yielded 1.87 g. (83.9%) of cream-colored sirup. The crude sirupy acetate was dissolved in anhydrous ether (30 ml.) and the solution was added dropwise with stirring to a slurry of lithium aluminum hydride (0.51 g.) in ether (30 ml.). After 2 hr. of reflux, the mixture was hydrolyzed and processed in the usual way, yielding 0.94 g. (95.9%) of *p*-(α-hydroxybenzyl)benzyl alcohol which crystallized spontaneously. The sample was optically inactive in chloroform (*c*, 6.37) and showed no mixed melting point depression with the *p*-(α-hydroxybenzyl)benzyl alcohol obtained by the above lithium aluminum hydride reduction of (−)-menthyl *p*-benzoylbenzoate.

The reaction of methylmagnesium iodide with (−)-menthyl p-benzoylbenzoate. Methylmagnesium iodide from magnesium turnings (0.83 g.) and methyl iodide (4.87 g.) in anhydrous ether (50 ml.) was added dropwise during 1 hr. to a stirred solution of (−)-menthyl *p*-benzoylbenzoate (10 g.) in anhydrous benzene (100 ml.), causing gentle refluxing. After addition the ether component was distilled and the remaining benzene solution was stirred under reflux for 5 hr., chilled in ice, and treated gradually with 6*N* hydrochloric acid (50 ml.). Customary processing yielded 10.6 g. (101%) of an amber sirup which solidified in a vacuum desiccator.

A sample of this crude (−)-menthyl *p*-(α-hydroxy-α-methylbenzyl)benzoate (5 g.) was dissolved in anhydrous ether and the solution was added dropwise to a slurry of lithium aluminum hydride (1.11 g.) in anhydrous ether over a 30-min. period. Glass beads were then introduced into the mixture, stirring under reflux was continued for an additional 5 hr. and the excess hydride was destroyed by cautious addition of water and 6*N* hydrochloric acid. Customary work-up, including steam distillation for menthol removal yielded 2.72 g. (90.7%) calculated as *p*-(α-hydroxy-α-methylbenzyl)benzyl alcohol) of yellow sirup which proved to be optically inactive in ethanol solution.

The above crude (−)-menthyl *p*-(α-hydroxy-α-methylbenzyl)benzoate (4.95 g.) was dissolved in ethanol (40 ml.) containing 2.5*N* aqueous potassium hydroxide (20 ml.). The mixture was refluxed for 4 hr., the ethanol was distilled and the residue was cooled and extracted thoroughly with ether until the extracts were optically inactive, indicating menthol removal. The alkaline layer was acidified, at which point a heavy amber oil separated. This was extracted into ether and the dried extracts were evaporated *in vacuo*, yielding 2.59 g. (82.2%) of cream-colored solid which proved optically inactive in ethanol. The latter was recrystallized four times from benzene to yield pure *p*-(α-hydroxy-α-methylbenzyl)benzoic acid, m.p. 135–139°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.22, 74.16; H, 5.71, 5.60.

STANFORD, CALIF.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Conformational Studies. I. The Relative Stabilities of the *cis*-2-Decalols[1]

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Equilibration of the isomeric *cis*-2-decalols in refluxing decalin in the presence of approximately 5 mole per cent of sodium showed that their free energies are about equal. A reinvestigation of the equilibration in the presence of excess sodium showed that the *cis-cis* isomer is present in 66 ± 2% in an equilibrated mixture rather than the previously reported 80%. The equilibria were approached from both sides and the isomer ratios determined by infrared intensity measurements and by the binary melting point diagram method. The results are briefly discussed in the light of conformational analysis concepts.

The flexibility of the *cis*-decalin system permits the existence of two interconvertible chair-chair conformations, so that in passing from one to the other an axial substituent becomes equatorial and *vice versa*. Thus, the situation is similar to that existing with cyclohexane derivatives except that the *cis*-decalins would be expected to have additional non-bonded interactions imposed by the second ring. Present conformational concepts as applied to *cis*-decalins seem to hold quite well and have aided greatly in stereochemical studies.[3]

It is possible for the *cis*-2-decalols to exist in four conformations having the most stable double-chair ring system. These are shown in Fig. 1 where Ia and Ib represent the two possible conformations of *cis-cis*-2-decalol, and IIa and IIb those for the *cis-trans*-isomer.[4]

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(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society in Richmond, Va., November, 1959.

(2) Taken in part from a dissertation submitted by L. C. Ellis in partial fulfillment of the requirements of the degree of Doctor of Philosophy, University of Virginia, 1961.

(3) For example, see (a) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954); (*b*) J. A. Mills, *J. Chem. Soc.*, 260 (1953).

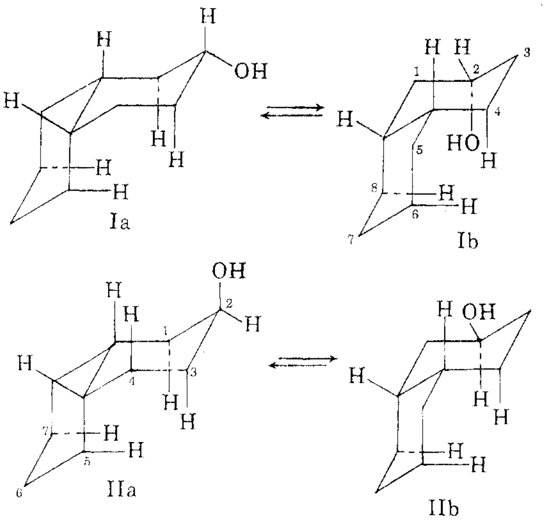

Figure 1

Dauben and Pitzer[5] have advanced the argument that of these four conformations, Ia and IIb should have comparable free energies since the interactions are similar. However, in the two conformations where the hydroxyl groups are axial, Ib can be expected to have a higher free energy than IIa because the hydroxyl group in the former is in a position similar to a skew butane conformation and should thus give rise to a steric interaction of larger magnitude than the normal $H_{(3)}$–$H_{(5)}$ interference found in IIa. The validity of this reasoning is supported by rate studies on esters of the two *cis*-2-decalols[6] and by equilibration studies on the isomeric *cis*-5-hydrindanols.[7]

Furthermore, at equilibrium there should be a larger number of molecules in form IIa than Ib while the populations of forms Ia and IIb should be about equal. The overall effect should give a higher concentration of *cis-trans*-2-decalol (II) over the *cis-cis*-isomer (I) in an equilibrated mixture.[5]

Hückel and Naab[8] carried out the equilibration of the *cis*-2-decalols in refluxing decalin in the presence of excess sodium and reported obtaining 80% of the *cis-cis*-2-decalol and 20% of the *cis-trans*-isomer when equilibrium was approached from either side. These results are in direct contrast to those expected from the conformational principles outlined above. Since these authors determined the percentages of isomers formed by direct isolation of the products and reported no overall yields, a reexamination of this equilibration seemed desirable.

In order to lessen the sources of error, direct isolation of the products was avoided in preference for an analytical method which would enable a direct determination of the isomer ratios in mixtures.[9] Direct infrared analysis was found to give acceptable results (well within ±1%) in the range of the equilibrated mixtures (Table I).[10]

TABLE I

PERCENT *cis-cis*-2-DECALOL IN KNOWN MIXTURES FROM INFRARED INTENSITY MEASUREMENTS AT 10.52 AND 11.03 μ

Mixture	Actual, %	Found, %	Deviation, %
1	45.8	47.0	+1.2
2	47.3	47.3	0.0
3	52.5	53.1	+0.6
4[a]	54.4	54.3	−0.1
5[a]	57.1	57.4	+0.3
6[a]	60.5	60.0	−0.5
7	70.2	69.7	−0.5
8	80.7	79.1	−1.6

[a] Cavity cells used.

In the preparation of the *cis*-decalols from 2-naphthol it was found that hydrogenation using a ruthenium oxide catalyst gave better yields than previously reported catalytic reduction methods.[11,22a] The equilibrations were carried out using the same conditions reported by the previous workers,[8] starting with both the *cis-cis*- and the *cis-trans*-isomers to insure that equilibrium had been reached. As these conditions employ an excess of sodium, the equilibrated alcohols are undoubtedly completely in the forms of their sodium salts, and under the experimental conditions employed, these salts were completely miscible in the reaction solvent. Actually, it is of just as great interest here to know the free energy difference between the isomeric free alcohols; therefore, the equilibration was also studied using only a few mole percent of sodium. It is interesting that the amount of sodium affects the position of equilibrium quite markedly (Table II). When excess sodium was used the

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[4] The nomenclature for the decalols described in this paper follows that proposed by W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954). Conformational assignments are made relative to the positions of the hydrogen atoms at C_9, C_{10} and C_9, C_2. For the establishment of the configurations of these epimeric decalols, see W. G. Dauben and E. Hoerger, *J. Am. Chem. Soc.*, **73**, 1504 (1951).

[5] W. G. Dauben and K. S. Pitzer, *Steric Effects in Organic Chemistry*, M. S. Newman, ed., Wiley, New York, 1956, pp. 27–30.

[6] Ref. 3a and b and references cited therein; W. Hückel, *Ber.*, **67 A**, 129 (1934).

[7] Ref. 5, p. 38, and references cited therein.

[8] W. Hückel and H. Naab, *Ber.*, **64**, 2137 (1931).

[9] An obvious method of choice here is vapor phase chromatography. Attempts to separate quantitatively the two isomers on Apiezon L, Dow Corning Silicone Grease, Carbowax 20 M and Silicone GE SE-30 using columns up to six and a half feet were unsuccessful. A major problem was the decomposition of the *cis-trans*-isomer at the temperatures (140–200°) required for practical retention times. At higher temperatures the *cis-cis* was also found to decompose. The feasibility of employing this analytical method in the present and similar cases is being explored further.

[10] Outside of this range (already evident in mixtures 1 and 8) the accuracy of the method diminishes rapidly. This is because the peaks become too weak in intensity for accurate calculations or begin to overlap seriously.

[11] D. M. Musser and H. Adkins, *J. Am. Chem. Soc.*, **60**, 664 (1938). S. G. Kulikov, *Uchenye Zapieki Moskov. Gosudarst. Univ. im. M.V. Lomonosova* No. **131**, 101–64 (1950) [*Chem. Abstr.*, **47**, 1171a (1953)].

TABLE II

EQUILIBRATION OF *cis*-2-DECALOLS IN REFLUXING DECALIN

Run	Starting Material Isomer	Grams	Moles	Solvent, Ml.	Sodium Grams	Moles	Reflux Time, Hr.	% *cis-cis* Isomer at Equilibrium
1	*cis-cis*	10.0	0.065	160	2.4	0.104	7	64.5
2	*cis-trans*	0.45	0.0029	30	0.25	0.0108	8	65.5
3	*cis-trans*	5.3	0.034	100	2.0	0.087	8	66.1
4	*cis-cis*	5.0	0.032	100	0.04	0.0017	7	53.5
5	*cis-cis*	5.0	0.032	100	0.04	0.0017	24	54.2 (52.5[a])
6	*cis-trans*	2.0	0.013	50	0.016	0.0007	8	52.0

[a] Not steam distilled (see Experimental).

TABLE III

ANALYSIS OF *cis*-2-DECALOL MIXTURES BY CONVERSION TO THEIR *p*-NITROBENZOATES

Mixture	Source	Reflux Time[a]	*p*-Nitrobenzoate % Yield	M.P.[b]	M.P. Diagram % *cis-cis*	% deviation	Infrared % *cis-cis*	% deviation
1	Known: 80.3[c]		93	61.5–92.0	78.5	−1.8	82.2	+1.9
2	Known: 81.3[c]		87	61.5–92.5	79.5	−1.8	83.5	+2.2
3	Known: 63.3[c]		82	60.5–85.5	64.5	+1.2		
4	Known: 70.0[d]						70.0	0.0
5	Equil.: *cis-cis*[e]	7	85	61.5–86.5	67.0		69.2	
6	Equil.: *cis-cis*[e]	7	90	60.0–86.0	66.0		68.8	
7	Equil.: *cis-trans*[e]	8	84	52.5–84.5	63.0		68.6	

[a] During equilibration. [b] Determined to the nearest 0.5°. [c] Amount of *cis-cis*-isomer. [d] A mixture of the pure esters containing 70.0% of *cis-cis*-2-decalyl *p*-nitrobenzoate. [e] Starting isomer.

equilibrated mixtures contained about 66% of the *cis-cis*-isomer, while the concentrations of the two isomers were about equal with the lesser amounts of sodium.[12,13] The recovery of alcohols was 90–95%.

The use of binary melting point diagrams for the analysis of isomer mixtures is frequently found in the literature and the present work provided an opportunity to compare this technique with the infrared method. Accordingly, we prepared the *p*-nitrobenzoates and 3,5-dinitrobenzoates of the two *cis*-2-decalols and plotted the melting point diagrams for these derivatives. The curves are shown in Fig. 2, and the data used in Table V. Mixtures 1–3 of Table III and 1–2 of Table IV, prepared using known amounts of the pure isomers, give an indication of the accuracy of the method. In the present case, the agreement is good between the isomer ratio values for the equilibrated mixtures as determined by the melting point diagram method and infrared analysis of the free alcohols.

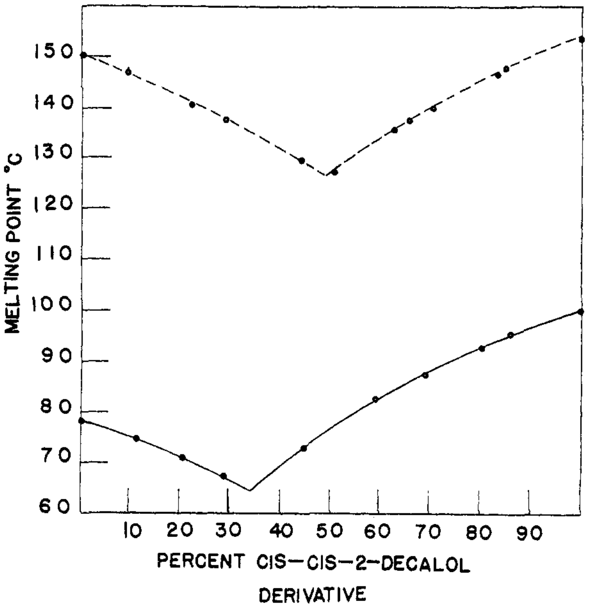

Fig. 2. Binary melting point diagrams of *cis*-2-decalol derivatives: (———) *p*-nitrobenzoates; (- - - - -) 3,5-dinitrobenzoates

It is interesting that although the yield of derivative differed somewhat for the various runs (column 4 in Tables III and IV), this seemed to have little effect on the results. Several bands in the infrared spectra of the *p*-nitrobenzoates were found suitable to allow quantitative isomer ratio determinations in the *p*-nitrobenzoate mixtures. However, the best bands were not as well defined as

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(12) Controls consisting of mixtures of known amounts of the two isomers when carried through the work-up procedure used in the equilibration runs, gave percentage values for the *cis-cis*-isomer which were consistently 2–4% higher than the true values. This error arises because the *cis-trans*-isomer has a relatively high vapor pressure and therefore a small amount is unavoidably lost during removal of the decalin solvent. Thus, the values given for Runs 4–6 in column 9 of Table II are several percent too high and actually represent a maximum value rather than the true value. This is not the case in Runs 1–3 where the alcohols are in the forms of their sodium salts during the decalin removal (see Experimental).

(13) Equilibration with aluminum isopropoxide in acetone–isopropyl alcohol appears to give still a different equilibrium constant. [W. Hückel, M. Maier, E. Jordan, and W. Seeger, *Ann.*, **616**, 81 (1958); personal observation].

TABLE IV

ANALYSIS OF *cis*-2-DECALOL MIXTURES BY CONVERSION TO THEIR 3,5-DINITROBENZOATES

Mixture	Source	Reflux Time[a]	3,5-Dinitrobenzoate		M.P. Diagram	
			Yield, %	M.P.[b]	*cis-cis*, %	Deviation, %
1	Known: 83.3[c]		59	126.0–147.0	84.0	+0.7
2	Known: 63.3[c]		91	124.5–136.0	62.7	−0.5
3	Equil.: *cis-cis*[d]	7	71	127.5–138.0	66.5	
4	Equil.: *cis-cis*[d]	7	81	126.5–139.5	68.0	
5	Equil.: *cis-cis*[d]	7	60	128.0–139.0	67.5	
6	Equil.: *cis-trans*[d]	8	81	121.5–137.5	66.0	

[a] During equilibration. [b] Determined to nearest 0.5°. [c] Amount of *cis-cis*-isomer. [d] Starting isomer.

TABLE V

THE MELTING POINTS OF MIXTURES OF *cis-cis*- AND *cis-trans*-2-DECALYL *p*-NITROBENZOATES AND 3,5-DINITROBENZOATES

p-Nitrobenzoates		3,5-Dinitrobenzoates	
% *cis-cis*-	M.P.	% *cis-cis*-	*M.P.*
0.00	77.5– 78.0	0.00	149.5–150.0
11.24	62.5– 74.5	8.99	127.0–147.0
20.40	61.5– 71.0	28.82	125.5–137.5
28.60	61.5– 67.5	22.20	126.5–140.5
44.44	61.5– 73.0	43.68	126.5–129.5
58.79	61.5– 82.5	62.46	126.5–135.5
68.99	61.5– 87.5	65.48	126.5–137.5
80.19	61.5– 93.0	70.64	126.5–139.5
85.95	63.0– 95.5	83.26	126.5–146.5
100.00	98.0–100.0	85.09	126.5–147.0
		100.00	153.0–153.5

those used with the free alcohols and so the percentages found are slightly less accurate (Table III, columns 8 and 9). The spectra of the *cis*-2-decalyl 3,5-dinitrobenzoates were found unsuitable for infrared analysis.

DISCUSSION

The data given in Tables II–IV clearly show that when the *cis*-2-decalols are equilibrated in decalin in the presence of excess sodium, the mixture contains a decided predominance of the *cis-cis*-isomer (I); whereas when only a few mole percent of sodium are used, the two isomers are present in approximately equal amount. In the latter case, the isomeric alcohols exist almost entirely in the free state, and, thus would appear to have approximately equal free energies under the present conditions of equilibration. These results are in much better agreement with present conformational views[5] than those reported previously.[3]

The question as to why the isomeric *cis*-2-decalols should have approximately equal free energies is an intriguing one which cannot be fully answered at present. Two possible explanations immediately present themselves; namely, that the two forms Ib and IIa are either present in too small amount to have any effect on the equilibrium or that their free energies are comparable. On the basis of findings concerning free energy differences between axial and equatorial hydroxyl groups in substituted cyclohexanols,[14] the contributions of these forms would not be expected to be insignificant. However, the two cases are not strictly comparable because of additional interring interactions which appear in the decalins and which probably cannot be neglected.[5]

Likewise, Ib and IIa would not be expected to have comparable free energies, as the O_2—H_8 interatomic distance in Ib of 1.7 Å (center to center) should give rise to considerable steric interference.[15] However, by a slight spreading of the valence angles of the hydroxyl containing ring, this interference can be largely alleviated with apparently little additional strain on the system.[16,17] A similar flattening of one of the rings apparently occurs in *cis*-decalin-$2\alpha,3\alpha$,-diol.[16]

With an excess of sodium, the data in Tables II–IV indicate an equilibrium ratio consisting of 66 ± 2% of the *cis-cis*-isomer. To explain the higher stability of the *cis-cis*-isomer it is tempting to consider bonding of the type shown in III as playing perhaps a minor, but important, role. To our knowledge such bonding has never been conclusively demonstrated, but a similar type of interaction has been suggested as an explanation for the greater stability of *cis*-1-hydrindanone over the *trans*-isomer.[18]

Because the free energy difference between the isomeric *cis*-2-decalols is small (approximately 0.6 kcal. in the case of the sodium salts and much smaller for the free alcohols, as calculated from the equilibrium constants) intermolecular interac-

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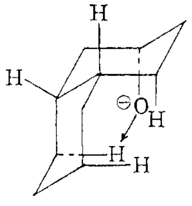
[14] For a lead reference, see R. A. Pickering and C. C. Price, *J. Am. Chem. Soc.*, **80**, 4931 (1958).

[15] The energy difference between the diaxial and diequatorial conformations of *cis*-3-methylcyclohexanol has been determined as 3.3 kcal./mole from esterification rates in pyridine at 25°. [E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957)]. If one assumes that the energy difference between Ia and Ib is of a comparable order of magnitude, the concentration of Ib would be reduced practically to zero.

[16] M. E. Ali and L. N. Owen, *J. Chem. Soc.*, 2119 (1958).

[17] Little information is available for the variation of energy with bond angle in alicyclic systems; however, it is probably quite small for moderate angle increases; see R. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 51 (1960).

[18] L. F. Fieser and M. Fieser, *Organic Chemistry*, 3rd ed., D. C. Heath and Co., Boston, 1956, p. 309; however, see also N. L. Allinger, *J. Org. Chem.*, **21**, 915 (1956).



III

tions and solvent effects cannot be assumed to be negligible. The evaluation of the importance of such factors must await additional and preferably more accurate equilibration data. Work along these lines is in progress and will be presented in a subsequent publication.

EXPERIMENTAL[19]

cis-cis-2-Decalol (I) *and cis-trans-2-decalol* (II). A mixture of 100 g. (0.69 mole) of 2-naphthol,1. 5 g. of ruthenium oxide,[20] and enough absolute ethanol to make a total volume of 400 ml. was hydrogenated at 1160–995 p.s.i. while slowly increasing the temperature to 91°. After 4 hr. the hydrogen uptake had ceased. The mixture was cooled, filtered, and the catalyst washed well with ethanol. As much of the ethanol as possible was removed from the filtrate by distillation *in vacuo* at 27–30°, and the residue dissolved in ether and washed with dilute aqueous sodium hydroxide. Removal of the ether left 98.0 g. of semisolid material which after several recrystallizations from petroleum ether (b.p. 90–110°) yielded 52.9 g. (0.34 mole) of *cis-cis*-2-decalol, m.p. 104–104.5° (lit.,[21] m.p. 105°).

The mother liquors were combined and the solvent removed *in vacuo*, leaving 44.8 g. of a sirupy mixture of *cis-cis*- and *cis-trans*-2-decalols. These were converted to the hydrogen phthalates[22] by refluxing for 17 hr. in 150 ml. of dry toluene with 70.0 g. (0.47 mole) of phthalic anhydride. The toluene was removed under reduced pressure, 200 ml. of water added and the mixture heated at 80–85° for 4 hr. After cooling, the solid was separated by filtration, dried, and dissolved in chloroform. The solution was refiltered, and the solvent removed. Repeated fractional crystallization of the residue from benzene-petroleum ether yielded 32.0 g. of pure *cis-trans*-2-decalyl hydrogen phthlate, m.p. 151–152° (lit.,[22a] m.p. 153°), and 30.0 g. of a mixture of *cis-trans*- and *cis-cis*-2-decalyl hydrogen phthalate.

The 30.0 g. of hydrogen phthalate mixture was hydrolyzed by refluxing with 100 ml. of 25% aqueous sodium hydroxide for 3 hr. After the solution had cooled, the decalols were extracted with ether and dried over sodium sulfate. Removal of the solvent under reduced pressure and crystallization of the residue from petroleum ether (b.p. 90–110°) gave an additional 5.6 g. of *cis-cis*-decalol, m.p. 103.5–104.5°, making the total yield of this isomer 58.5 g. (55%).

The solvent was removed from the mother liquors and the residue refluxed for 4 hr. with 16.0 g. (0.11 mole) of phthalic anhydride in 35 ml. of dry toluene. When worked up as previously described, this reaction yielded an additional 4.4 g. of *cis-trans*-2-decalyl hydrogen phthalate, m.p. 151–152°.

The 36.4 g. of *cis-trans*-2-decalyl hydrogen phthalate was hydrolyzed by refluxing overnight with 15.0 g. of sodium hydroxide in 150 ml. of water. After cooling, the product was extracted with ether and dried over sodium sulfate. Removal of the ether under reduced pressure left a sirupy residue which was distilled at 130–132° (16–17 mm.) giving 18.0 g. (17%) of *cis-trans*-2-decalol.[22]

Equilibration of the cis-2-decalols with sodium. The following procedure is typical of that followed in carrying out the equilibrations. In all runs, the sodium salts of the decalols were completely soluble in the decalin solvent under the conditions of equilibration.

A mixture of 5.3 g. (0.034 mole) of *cis-trans*-2-decalol and 2.0 g. (0.087 mole) of sodium was refluxed in 100 ml. of dry decalin for 8 hr. by immersion of the reaction flask in a Woods metal bath at 232–234°.[8] Upon cooling, the excess sodium was removed, and the decalin was removed by distillation at 90–93° (33–35 mm.) using a capillary attached to a nitrogen source. A 50% aqueous ethanol solution was added to the honey-colored residue and the mixture steam distilled. The distillate was extracted with ether, the combined ether extracts dried over sodium sulfate, and aliquots evaporated to dryness for the infrared analyses and the preparation of derivatives.

The solution remaining in the steam distillation flask was extracted with ether, and the ether then removed, leaving a small amount of oily residue which showed no bands characteristic of either of the decalols in its infrared spectrum. The total recovery of the *cis*-2-decalols was 4.95 g. (93%).

The cis-2-decalyl p-nitrobenzoates and 3,5-dinitrobenzoates were prepared by the standard procedure,[23] using a 1 to 3-hr. heating period. In recrystallization of the crude derivatives from ethanol, the mother liquors were tested by infrared analysis to insure that all of the desired products had been recovered.

The cis-2-decalyl p-nitrobenzoate and cis-2-decalyl 3,5-dinitrobenzoate binary melting point diagrams shown in Fig. 2 were prepared from the melting points of mixtures containing known percentages of the isomeric *cis*-2-decalyl derivatives. The mixtures were prepared by mixing known amounts of pure esters with an agate mortar and pestle. The melting points were determined to the nearest 0.5° in a Hershberg melting point apparatus, using Arthur H. Thomas total immersion thermometers. The temperature at which the last trace of material melted was then plotted against the percent of *cis-cis*-2-decalyl ester. Data used constructing the diagrams are shown in Table V.

Mixtures 1–3 of Table III and 1–2 of Table IV were prepared using known amounts of pure decalols. These were then converted to the *p*-nitrobenzoates or 3,5-dinitrobenzoates and their compositions analyzed from the melting point diagrams (and infrared spectra in the case of the *p*-nitrobenzoates).

Infrared analyses. The infrared analyses were made on a Perkin-Elmer model 21 spectrophotometer, using either 0.05-mm. sodium chloride, fixed-thickness, mounted cells or 0.1 mm. Type C sodium chloride cavity cells.[24] The settings on the instrument were as follows: pen speed 10.5, resolution 9.27, intensity 0.3 amps., autosuppression 5, response 1, gain 5, speed approximately 4 min. per μ. Chloroform was used as a solvent in all cases with a concentration of 202 mg. of sample per ml. of solvent for the free alcohols and 190 mg. per ml. for the *p*-nitrobenzoates.

The percentage compositions of the mixtures were calculated using the base line method of Wright[25] and the equation

$$\frac{C_{mc}}{C_{mt}} = \frac{A_t \log (I^\circ/I)_{mc}}{A_c \log (I^\circ/I)_{mt}}$$

which is easily derived from the Lambert-Beer Law.

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[19] All melting points are uncorrected except those concerned with the binary melting point diagrams.

[20] American Platinum Works, Newark, N. J.

[21] W. Hückel, *Ann.*, **441**, I, 15, 28 (1925).

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C_{mc} and C_{mt} are the relative amounts of *cis-cis-* and *cis-trans*-isomer in the mixture, respectively. $(I^0/I)_{mc}$ and $(I°/I)_{mt}$ are the peak heights of the *cis-cis-* and the *cis-trans*-isomer, respectively, as measured from the infrared spectrum of the mixture.

$A_t = \frac{1}{C_t} \log (I°/I)_t$ and $A_c = \frac{1}{C_c} \log (I°/I)_c$ where C_t = concentration of pure *cis-trans*-isomer, C_c = concentration of pure *cis-cis*-isomer, $(I°/I)_t$ = the peak height of the *cis-trans*-isomer measured from the base line, and $(I°/I)_c$ = the peak height of the *cis-cis*-isomer. Thus A_t and A_c represent constants which are determined from the spectra of the pure isomers. The peaks found best suited[25,26] for the infrared analysis of mixtures were the following: *cis-cis-*, 10.52 μ; *cis-trans-*, 11.03 μ; *cis-cis-p*-nitrobenzoate, 10.74 μ; *cis-trans-p*-nitrobenzoate, 10.54 μ.

Preparation of the samples for infrared analysis. The *cis-trans*-isomer is relatively volatile at room temperature and noticeable amounts are lost if unstoppered samples are exposed to the air for several days. For this reason, considerable care had to be exercised in preparing samples of the free alcohols for analysis. Reproducible results could be consistently obtained by allowing an aliquot ether portion of the equilibrated mixtures to evaporate overnight from an open, tared test tube. The last traces of solvent were removed by applying vacuum (water pump) for several minutes, and enough chloroform was then added to make a solution of the desired concentration for infrared analysis.

Preparation of the *cis*-2-decalyl *p*-nitrobenzoate samples required no special precautions.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, TOKYO INSTITUTE OF TECHNOLOGY]

Studies on the Beckmann Rearrangement. I. Dehydrations of Aldoximes with Methylketene Diethylacetal

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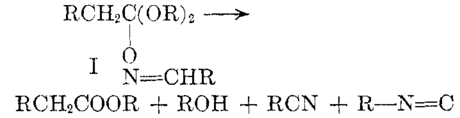
Dehydrations of aldoximes into isonitriles or nitriles by means of methylketene diethylacetal have been studied. Addition compounds of aromatic-*syn*-aldoximes and methylketene diethylacetal decompose, in the presence of a catalytic amount of boron trifluoride and mercuric oxide, into corresponding isonitriles in good yields. On the other hand, adducts of methylketene diethylacetal and aromatic-*anti*-aldoximes, as well as of methylketene diethylacetal and an aliphatic aldoxime, decompose to give corresponding nitriles under the same conditions.

The decomposition of an adduct of *p*-tolu-*syn*-aldoxime in the presence of Lewis acids other than boron trifluoride, of mercuric salts and of protonic acid has been investigated. Except in the case of one equivalent of zinc chloride, however, there cannot be found any other effective catalyst for the rearrangement. Further, an intermediate, presumably methylketene monoethyl monoaldiminoacetal, is obtained during the course of decomposing the adduct of *p*-tolu-*syn*-aldoxime. The mechanism of this reaction can be described in view of these results.

Dehydration reactions of primary nitroparaffins and aldoximes by means of organic reagents have been described in preceding papers.[1-4] It was shown there[2] that benzaldoxime is dehydrated with a ketene acetal in the presence of a catalytic amount of boron trifluoride and mercuric oxide to give benzonitrile and benzisonitrile, both of these dehydrated products being nearly equal in amount. The course of this reaction involves two stages, namely the initial formation of an addition compound (I) of an aldoxime and a ketene acetal, and the decomposition of the adduct which yields the dehydrated products along with an alcohol and a carboxylic ester.



$$R—CH{=}NOH + RCH{=}C(OR)_2 \longrightarrow \underset{\substack{|\\ O\\ N{=}CHR}}{RCH_2C(OR)_2}\ \text{I} \longrightarrow RCH_2COOR + ROH + RCN + R—N{=}C$$

It has been confirmed that the initial formation of the adduct (I) is carried out readily in the absence of catalysts and it is believed that such catalysts as a mixed catalyst of boron trifluoride and mercuric oxide used in the experiment are effective in the decomposition of the adduct.

Since the formation of an isonitrile by the reaction is considered to be the simplest model of the Beckman rearrangement, the dehydration of various aldoximes with methylketene diethylacetal has been studied in order to clarify the mechanism of this reaction.

The Beckman rearrangement has been demonstrated to occur by the process in which the migrating group approaches the migrating terminus, the nitrogen atom of oximes, from the side *trans* to the leaving group. Aldoximes exist in two forms, *syn* and *anti*, in which the hydroxyl group is respectively *cis* or *trans* to the aldehydic hydrogen. In order to know the stereochemical course of this reaction, the dehydration of *syn-* and *anti*-aldoximes with methylketene diethylacetal was tried first. Adducts were prepared from *syn-* and *anti*-al-

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