[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of Ketonization. IX. The 1,9-Enol of 1-Decalone[1,2]

BY HOWARD E. ZIMMERMAN AND AGO MAIS

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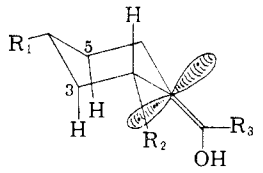
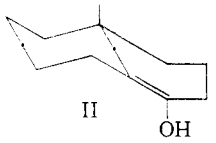
The stereochemistry of ketonization of the 1,9-enol of 1-decalone has been investigated. Depending on the proton donor, the stereoselectivity varies from a slightly favored formation of *trans*-1-decalone to a markedly preferential formation of *cis*-1-decalone. In the course of this study four, and possibly five, of the six theoretically possible mono-α-bromination products of 1-decalone have been isolated. These have been assigned structures and configurations on the basis of chemical and spectral evidence.

Previously,[3-10] evidence has been obtained that the stereochemistry of ketonization of enols is controlled in an essentially sp^2-hybridized transition state with prototopic attack proceeding from the less hindered approach to the enolic double bond.[11] It was proposed that in exocyclic cyclohexane enols such as I access of the proton donor to one lobe of the α-carbon p-orbital is blocked by the axial hydrogens at carbon atoms 3 and 5 of these molecules. In continuing these investigations we felt that the behavior of the 1,9-enol II of 1-decalone would be of special interest. Because of the structural simplicity of the system, including the absence of phenyl groups, its ketonization geometry promised to provide a critical test of the proposed stereochemical mechanism.



Ia, $R_1 = C_6H_5$, $R_2 = H$, $R_3 = OH$
Ib, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = OH$
Ic, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = CH_3$
Id, $R_1 = H$, $R_2 = C_6H_5$, $R_3 = C_6H_5$

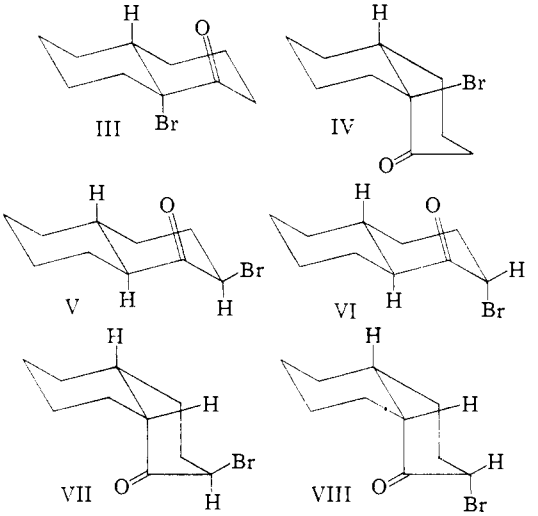


II

Since the debromination of α-bromoketones with dilute hydriodic acid or with zinc and a proton donor had proved to provide an excellent means of generating unstable enols,[3,4,6,10] a synthesis of one, or preferably both, of the stereoisomeric 9-bromo-1-decalones was sought. It was found that bromination of either *cis*- or *trans*-1-decalone in acetic acid led to a mixture of bromoketones from which by silica gel chromatography there could be isolated one dibromodecalone, melting at 63–64° and designated A, as well as three monobromodecalones; B, m.p. 38–39°; C, m.p. 37–38°; and D, m.p. 95.5–96.0°. By bromination in the presence of either a sodium acetate or a sodium sulfate buffer there was obtained, in addition to B, C and D, a fourth monobromodecalone, E, m.p. 34–35°. In later runs it was found that by crystallization of certain impure chromatographic fractions from unbuffered runs a second dibromodecalone, melting at 92.0–93.0° and labeled G, could be isolated. This appears to correspond to a dibromodecalone reported by Galinovsky.[12] That each of these compounds is a chemical entity, uncontaminated by the other bromoketones, was evidenced by the absence in the infrared spectrum of each of these compounds of at least one intense absorption band characteristic of each of the others (note Table III in the Experimental section).

Two additional syntheses of bromoketone C were found in the free radical N-bromosuccinimide bromination of the 1-decalones and in the bromination of the enol benzoate of 1-decalone. In the latter reaction there was isolated a small amount of a fifth monobromodecalone, F; but insufficient quantities were available to effectively purify and completely characterize this compound.

Thus four and possibly five of the six theoretically possible α-bromodecalones, represented by



III IV V VI VII VIII

(1) Presented at the Organic Division, A.C.S. Meeting, San Francisco, Calif., April, 1958; abstracts, p. 10-N.

(2) Abstracted in part from the Ph.D. thesis of Ago Mais.

(3) For paper I of the series and an introduction to the subject, see H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

(4) H. E. Zimmerman, THIS JOURNAL, **78**, 1168 (1956).

(5) H. E. Zimmerman and H. J. Giallombardo, *ibid.*, **78**, 6259 (1956).

(6) H. E. Zimmerman, *ibid.*, **79**, 6554 (1957).

(7) H. E. Zimmerman and T. E. Nevins, *ibid.*, **79**, 6559 (1957).

(8) H. E. Zimmerman and T. W. Cutshall, *ibid.*, **80**, 2893 (1958).

(9) H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **80**, 3060 (1958).

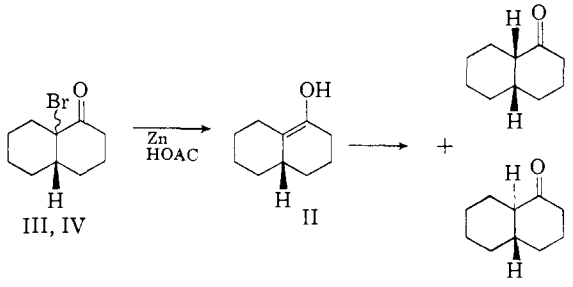
(10) H. E. Zimmerman and W. Chang, *ibid.*, **81**, 3634 (1959).

(11) In the case of endocyclic cyclohexane enols a second driving force is superimposed on the purely steric one, this being the requirement for continued overlap of orbitals; as has been noted by E. J. Corey and R. A. Sneen, THIS JOURNAL, **78**, 6272 (1956), this need is satisfied by axial protonation. For other enols, the overlap requirement will in general be satisfied by either approach.

(12) F. Galinovsky, *Ber.*, **76**, 230 (1943).

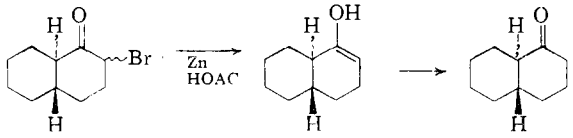
structures III through VIII, had been isolated. An assignment of the proper structure to each of these bromoketones seemed of interest as well as a necessary preliminary to the ketonization study, since only a 9-bromo-1-decalone (III or IV) could serve as precursor to the enol II. The evidence finally obtained bearing on this structural and configurational problem was fourfold: debrominative, spectral, thermodynamic and eliminative. This is considered in this order.

Each of the monobromodecalones B, C, D and E was debrominated with zinc and acetic acid. While B and C each gave mixtures of *cis*- and *trans*-1-decalone, D and E afforded pure *trans*-1-decalone. Furthermore, under the debromination conditions both *cis*- and *trans*-1-decalone were found to be stable. As a consequence it may be concluded that B and C are the stereoisomeric 9-bromo-1-decalones (III and IV, or IV and III), for only if the reaction proceeds *via* the 1,9-enol can both *cis*- and *trans*-1-decalone result.



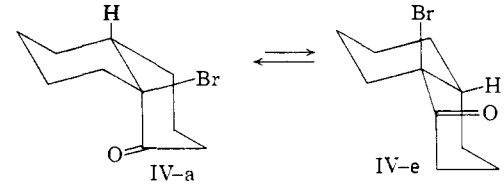
III, IV II

Conversely, it may be reasoned that since only a single stereoisomer results from the debromination of D and E, the 1,9-enol II cannot be a reaction intermediate; rather the reaction must be formulated as proceeding by way of the 1,2-enol IX and D and E are therefore 2-bromo-1-decalones. Also, the debrominative formation of *trans*-1-decalone in a reaction not disturbing the ring fusion requires that the ring fusion be originally *trans* and that D and E be the epimeric 2-bromo-*trans*-1-decalones (V, VI or VI, V).



IX

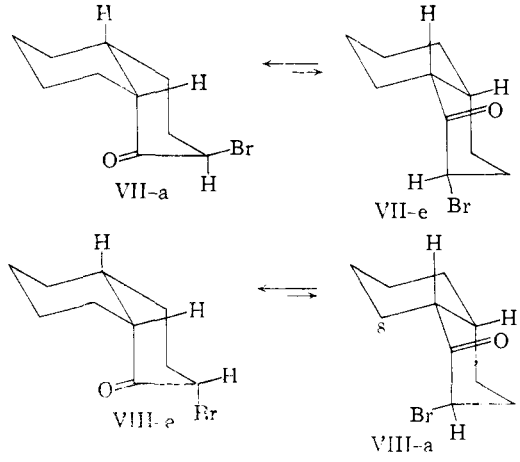
Additional evidence was available in the infrared spectra. Bromodecalones B, C and E exhibited carbonyl absorption bands at 5.85 mμ, characteristic[13,14] of axial bromoketones. In contrast, bromoketones D and F absorbed at 5.80 mμ and hence[13,14] are equatorial bromoketones. While the spectral evidence is of no value in deciding which of structures III and IV correctly represents bromodecalone B and which corresponds to C, for both ketones exhibit the same maximum, nevertheless it is reassuring that the axial absorption observed for B and C would indeed be expected for compounds having structures III and IV. Although in the case of IV two conformations are possible, one (IV-a) in which the bromine is axial in the carbonyl containing ring and one (IV-e) in which the bromine atom is equatorial in this ring, the axial conformation (IV-a) would be expected[14] to be favored by the avoidance of carbonyl and C–Br dipoles, since the carbonyl-C–Br angle is maximized in IV-a.



IV-a IV-e

Since D and E are known from the debrominative evidence (*vide supra*) to be the stereoisomeric 2-bromo-*trans*-1-decalones (V and VI, or VI and V), the finding that D is an equatorial bromoketone while E is axial allows an assignment of structure V to D and structure VI to E.

This leaves only structures VII and VIII, one of which must correspond to the remaining and equatorial bromodecalone F. Now although each of VII and VIII have available both axial-bromine and equatorial-bromine conformations, the assignment of structures is simplified by the expectation that in the case of VII the axial-bromine conformation VII-a would predominate as a result of



VII-a VII-e VIII-e VIII-a

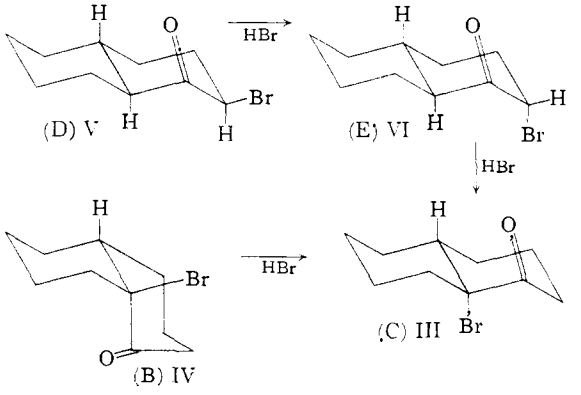
minimization of C=O–C–Br dipole interaction, while contrariwise, for VIII it is the equatorial-bromine conformation VIII-e which should be preferred. The reason for the differing situation of VIII lies in the presence in VIII-a of energetically serious van der Waals repulsions between the C-8 methylene group and the C-2 bromine atom, which are 1:3-axially related in the carbonyl containing ring; the literature indicates[14] that this steric interaction would raise the energy of VIII-a more than the dipolar interaction incurred in VIII-e due to the nearly coplanar carbonyl group and C–Br. Thus only structure VIII could account for the observed equatorial carbonyl absorption of bromodecalone F.

Thus far structures have been assigned to bromoketones D, E and F; in addition, it has been shown

(13) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952); R. N. Jones, *ibid.*, **75**, 4839 (1953).

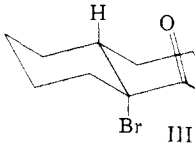
(14) E. J. Corey, *ibid.*, **75**, 2301 (1953).

that one of B and C has structure III and the other has structure IV. In an effort to resolve this final question, thermodynamic evidence was sought. Each of the bromodecalones B, C, D (V) and E (VI) was treated with hydrogen bromide in chloroform. Compounds B, D (V) and E (VI) on extended treatment with hydrogen bromide in chloroform were converted to bromodecalone C, while this compound was unaffected by similar treatment. With shorter reaction times it was observed that bromodecalone D (V) was converted partially to E (VI). Thus it is clear that bromodecalone C is thermodynamically more stable than its isomers, including B. This is interpreted to mean that B is 9-bromo-*cis*-1-decalone (IV) and that C is 9-bromo-*trans*-1-decalone (III). These conversions are formulated in Chart II.

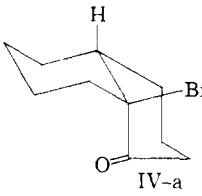


That it is the *trans*-isomer of 9-bromo-1-decalone which is more stable is by no means obvious. In fact, since evidence is available that at 250° *cis*-9-methyl-1-decalone is actually slightly more stable than the *trans* isomer[15] and in view of the similar van der Waals radii of bromine and methyl (1.95 and 2.0 Å.),[16] one might be inclined to conclude the reverse. Also, the calculations of Klyne[17] predict 9-methyl-*cis*-1-decalone to be more stable than the *trans* isomer, but only by 0.1 kcal./mole.

A calculation of the same type is now made for the *cis*- and *trans*-9-bromo-1-decalones (IV and III, resp.). These calculations predict 9-bromo-*trans*-1-decalone (III) to be 0.8 kcal./mole lower in energy than the lower energy conformation IV-a of 9-bromo-*cis*-1-decalone, hence justifying the configurational assignment (*vide supra*). The reversed situation in the 9-bromo-1-decalone system as compared with the 9-methyl-1-decalone case has its basis in a smaller skew $Br:CH_2$ energy of interaction (0.35 kcal./mole) than for skew $CH_2:CH_2$ (0.8 kcal./mole).[18] The calculations receive support from Fisher–Hirschfelder models which indicate a less encumbered bromine atom in the bromodecalones than in the corresponding methyldecalones and less total steric interactions in 9-bromo-*trans*-1-decalone than in the *cis*-isomer.



4 skew $Br:CH_2$ interactions $\times$ 0.35[14]	= 1.4
1 2-equat. alkyl: C=O interaction	= 1.0[17]
	2.4 kcal./mole



2 skew $Br:CH_2$ interactions	= 0.7
3 skew $CH_2:CH_2$ interactions $\times$ 0.8[17]	= 2.4
1 2-equat. alkyl: C=O interaction[17]	= 1.0
1 3-axial alkyl: C=O correction[17] of the 2.4 kcal./mole	= −0.9
	3.2 kcal./mole

Additional evidence bearing on the correctness of the assignments was found in experiments designed to test the relative ease of dehydrobromination of B and C with collidine. The finding that C was considerably more readily dehydrobrominated when *B* (*cf.* Table V) is reasonably interpreted on the basis of the assigned structures III and IV, respectively. Unlike III (C), bromoketone IV (B), in its preferred conformation IV-a, has no hydrogen atoms in a *trans* and coplanar relation to the 9-bromine atom, and thus it is not surprising[19]

TABLE I

SUMMARY OF EVIDENCE ALLOWING ASSIGNMENT OF STRUCTURES AND CONFIGURATIONS TO THE BROMODECALONES

Evidence	Conclusion
Debromination of B and C to *cis*- plus *trans*-1-decalone	B and C must be the stereoisomeric 9-bromo-1-decalones (III and IV or IV and III)
Debromination of D and E to pure *trans*-1-decalone	D and E must be the epimeric 2-bromo-*trans*-1-decalones (V and VI or VI and V)
I.r. spectra of B and C characteristic of axial bromoketones	Consistent with 9-bromo-1-decalone structures
I.r. spectrum of D characteristic of an equatorial bromoketone	D must be V rather than VI
I.r. spectrum of E characteristic of an axial bromoketone	E must be VI rather than V
I.r. spectrum of F characteristic of an equatorial bromoketone	Of the remaining two structures, VII and VIII, only VIII is acceptable
Equilibration of B to C	B must be IV and C must be III
More facile dehydrobromination of C than B	Confirms assignment of III to C and IV to B

(15) A. S. Dreiding, *J. Org. Chem.*, **20**, 905 (1955).

(16) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 30.

(17) W. Klyne, *Experientia*, **12**, 119 (1956).

(18) The reason for the misleading impression given by the similar van der Waals radii of methyl and bromine seems to be twofold. Firstly, the single bond radius of carbon is small (0.77 Å.) compared to that of bromine (1.14 Å.) with the result that the methyl group is held more closely to the molecule with increased steric interaction. Secondly, the van der Waals radius of the methyl groups of 2.0 Å. is based on packing in solid hexamethylbenzene; the approach in such a situation will be atypically close, since each of the methyl groups may rotate freely and present a hydrogen-free side to the hydrogen-bearing side of its neighbor. This is not possible for the 9-methyl-1-decalone molecule.

(19) The lower rate of reaction of B could be attributed solely to a low concentration of the reacting species IV-e. However, in addition it seems likely that the rate of reaction of conformation IV-e itself is lower than that of III which can *trans* eliminate to form the thermodynamically stable 9,10-double bond. Supporting this view

that a facile elimination is not observed.

The evidence leading to establishment of the structures and configurations of the five monobromodecalones is summarized in Table I.

With both stereoisomeric 9-bromo-1-decalones available for generation of enol II, the ketonization study was initiated. A method of analysis of mixtures of the *cis*- and *trans*-1-decalones was available in the infrared technique utilized in earlier studies[4-9]; the details are described in the Experimental section together with the results of analysis of known mixtures, which indicate a probable accuracy of ±2.5% units of *cis* isomer (note Table IV).

While it had been reported by W. Hückel[20] that *cis*-1-decalone isomerizes at least to the extent of 95% to *trans*-1-decalone, it seemed desirable to check this point in order to obtain a better idea of the equilibrium constant. An equilibrium mixture containing 7.5 ± 2.5% *cis*-1-decalone and 97.5 ± 2.5% of *trans*-1-decalone was approached from either direction, thus confirming the report of Hückel.

Of the two previously employed methods for generating unstable enols from α-bromoketones, debromination with dilute hydriodic acid in acetone[3,4,6,10] and reaction with zinc and a proton donor,[6,10] only the latter proved successful, since *cis*-1-decalone was found to be appreciably isomerized to the *trans* isomer under hydriodic acid debromination conditions.

In contrast, both 9-bromo-*cis*-1-decalone (IV) and 9-bromo-*trans*-1-decalone (III) were smoothly debrominated by zinc and miscellaneous proton donors, and under the reaction conditions *cis*-1-decalone was found to survive. The results of the debromination experiments are listed in Table II.

TABLE II

ZINC DEBROMINATION OF BROMODECALONES B AND C

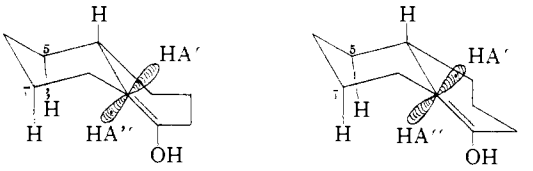
Run	Bromodecalone	Solvent	Reaction time, hr.	*cis*-1-Decalone, %
1	B	HOAc	4.5	37.2
2	C	HOAc	5.5	39.2
3[a]	B	Collidine	6.5	78.0
4[a]	B	Collidine	23.0	77.1
5[a]	C	Collidine	19.0	72.3
6[a]	C	Collidine	39.0	73.5
7[a]	C	Acetonitrile	8.0	51.7
8[a]	C	Methanol	19.0	58.5

[a] Run with collidine hydrochloride.

The formation of the same stereoisomer distribution, within experimental error, from the zinc–acetic acid debromination of either of the stereoisomeric 9-bromo-1-decalones represents confirmatory evidence for enol II as a debromination intermediate. The somewhat greater than experimental error difference in product distribution obtained on debromination with zinc and collidine hydrochloride in collidine could possibly be due to intervention of a small amount of reduction by an electrophilic process with retention of configuration. In these runs it was found that low values were obtained unless the reaction was complete; thus only the maximum percentages, obtained by lengthening the debromination time, are significant and are recorded.

Also of interest is the marked dependence of ketonization stereoselectivity on the nature of the proton donor. As the bulk of the proton donor increases, the formation of *cis*-1-decalone is enhanced until, with collidinium ion as the donor, over 70% *cis* product results; this finding has precedent in our earlier studies. More striking is the preferential formation of *trans*-1-decalone with the relatively small acetic acid donor; in previous cases, as the donor size decreased and the substrate susceptibility to its bulk diminished, the stereoselectivity approached one to one with both approaches to the enolic double bond becoming equivalent.

The present behavior may be understood if one considers the four possible ketonization transition states derived from the two conformers (X and XI) of enol II.



X (before attack of HA)
X′ (attack of HA′)
X″ (attack of HA″)

XI (before attack of HA)
XI′ (attack of HA′)
XI″ (attack of HA″)

Of these, transition states X′ and XI′ lead to *cis*-1-decalone while X″ and XI″ afford *trans*-1-decalone. In the case of the enol itself conformer X would be expected to be of lower energy than XI, since the latter has one (*i.e.*, C-5) methylene group pseudo axial with respect to the enolic ring while conformer X has none. The same considerations are true of the transition states derived from these conformers, so that, other things being equal, transition states X′ and X″ would be preferred over XI′ and XI″. However, two additional factors influence the energy of these transition states, these being first, the tendency for avoidance of van der Waals repulsions between the attacking proton donor and the enol substrate as noted in our earlier studies and, secondly, the need for continued p-orbital overlap as discussed by Corey.[14] Also, of the four possible transition states only two (X″ and XI′) collapse to known conformations of *cis*- and *trans*-1-decalone. Transition states X′ and XI″ lead[21] to boat conformations and must reflect, to some extent, the non-bonded interactions of these products. Of the acceptable transition states, X″ and XI′, both satisfy the overlap criterion with protonation axial in the oxygen bearing ring. Thus in the present situation overlap considerations are insufficient for prediction of the reaction geometry.

is the development of 9,10-octalone infrared bands as the dehydrobromination of C proceeds.

That the difference in ease of dehydrobromination is attributable to a higher energy transition state for B is certain, for this not being so, the less stable B would react at a greater rate.

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

(21) This statement assumes that during ketonization there is no change in the conformation of the single bond system of the carbonyl containing ring. Allowal of such conformational change to afford a low energy product conformation from X′ or XI″ is tantamount to direct consideration of transition states XI′ and X″ themselves.

However, of these transition states, X′ involves the least hindered approach to the enolic double bond with consequently minimum van der Waals repulsions. Hence, with a large proton donor, accentuating these repulsions, the formation of *cis* product is understandable. On the other hand, with a small proton donor this factor diminishes in importance with the result that transition state X″, derived from the more stable enol conformer, is now of lower energy with preferential formation of *trans* product.

Experimental[22]

Hydrogenation of α-Naphthol.—A solution of 65.0 g. (0.45 mole) of α-naphthol in 190 ml. of acetic acid was hydrogenated in a Parr apparatus using 2.63 g. of platinum dioxide catalyst. At the end of 62 hr. no further uptake of hydrogen was evident and 1.1 times the theoretical amount had been absorbed (*i.e.*, 4.9 moles). The solution was filtered and concentrated *in vacuo*. The residue was taken up in ether and washed with diluted sodium hydroxide to remove phenolic contaminants; the ether solution was then washed with water, dried over sodium sulfate and concentrated *in vacuo* to leave 59.0 g. of white solid, m.p. 65–85°. Crystallization from hexane–benzene afforded 21.2 g. of product, m.p. 88–89°. A second crop of 5.32 g., m.p. 88–89°, was obtained as well as a third crop weighing 3.81 g. and of m.p. 83–85° (reported[23] 93°).

***cis*-1-Decalone.**—To a solution of 15.0 g. (0.0974 mole) of *cis,cis*-1-decalol, m.p. 88–89°, in 50 ml. of acetic acid in a 250-ml. three-neck flask equipped with Hershberg stirrer and dropping funnel was added dropwise over 10 minutes with stirring and cooling in ice a solution of 7.15 g. of chromic acid (0.0715 mole) in 10 ml. of water. Stirring then was continued at room temperature for 5 hours at the end of which time the mixture was poured into 1500 ml. of water. The reaction mixture now was extracted with 1:1 ether–hexane; the extracts were washed successively with water, dilute sodium carbonate solution and finally with water until neutral. After drying over sodium sulfate, the extracts were concentrated under vacuum leaving 13.00 g. of essentially pure *cis*-1-decalone free of the *trans* isomer. The infrared spectrum differed markedly from that of the *trans* compound. For example, at 10.55 μ, where *trans*-1-decalone possessed a minimum, *cis*-1-decalone exhibited a maximum. Conversely, at 11.03 μ *cis*-1-decalone prepared in the above manner had a minimum while *trans*-1-decalone showed a maximum.

Equilibration of *cis*- and *trans*-1-Decalones.—A mixture of *cis*- and *trans*-1-decalone containing 69.4% of the former, as indicated by infrared analysis, was refluxed for 6.5 hours by heating in a metal-bath heated to 240–250°. The product was chromatographed on silica gel using ether–hexane; infrared analysis of the decalone fraction indicated 11.3% *cis* isomer. This material was refluxed for an additional 7 hours and again chromatographed. The product then analyzed for 10.0% *cis*-1-decalone.

Similar refluxing of a mixture of decalones containing 4.1% *cis*-1-decalone for 24 hours and chromatography of the product led to a mixture shown by quantitative infrared analysis to contain 5.2% *cis* isomer.

Bromination of *cis*-1-Decalone.—To a three-neck 500-ml. flask equipped with glass paddle stirrer and dropping funnel and cooled with an ice–salt-bath was added a solution of 8.24 g. (0.054 mole) *cis*-1-decalone in 250 ml. of acetic acid containing 2.50 ml. of 48% hydrobromic acid. To this was added dropwise with stirring over 5 minutes 8.65 g. (0.054 mole) of bromine. The color of bromine disappeared after an additional 15 minutes of stirring. At the end of this time the mixture was poured into 1600 ml. of water containing a few grams of sodium thiosulfate and extracted with 1:1 ether–hexane. The extracts were dried over sodium sulfate and concentrated *in vacuo* leaving 11.80 g. of an oil. Of this 6.00 g. was chromatographed on a 4.0 × 75.0 cm. column of silica gel (Davidson 40–200 mesh) packed with 10% ether in hexane and washed with hexane. Thirty-eight fractions were collected as follows: 1 through 13 obtained with a total of 1750 ml. of hexane contained no material. Elution with 5% ether in hexane was then begun. Fractions 14 through 17 obtained with a total of 500 ml. contained no material. Fractions 18 through 20 obtained by elution with a total of 235 ml. of 5% ether in hexane contained a total of 0.52 g. of solid, m.p. 63–66°; vacuum sublimation yielded a pure sample of m.p. 63–64° of dibromodecalone A. Fractions 21 and 22 were obtained by elution with a total of 200 ml. and contained 1.44 g. of a mixture of bromodecalone B and dibromodecalone G as an oily solid. Crystallization of this fraction from hexane afforded only dibromodecalone G, m.p. 92–93°. Bromoketone B was better prepared by the buffered bromination described below. Fraction 23 was obtained with 100 ml. of 5% ether in hexane and contained 0.60 g. of oil seen by infrared analysis to be bromodecalone C contaminated with traces of bromoketone B. Fractions 24 and 25 were eluted with a total of 210 ml. of solvent and contained 1.06 g. of oil which slowly crystallized. Crystallization from hexane brought the melting point to 37–38°; this represented pure bromodecalone C. Fractions 26 through 29 (220 ml. total of solvent) contained no material. Fractions 30 through 34 (total 600 ml. of solvent) were found to contain 0.36 g. of white solid, m.p. 92–94°. Sublimation *in vacuo* yielded pure bromodecalone D, m.p. 95.5–96.0°. Fractions 35 and 36 (375 ml. of solvent) contained no material. Elution with 10% ether in hexane then was begun. Fractions 37 and 38 (1000 ml. of solvent) contained 0.48 g. of oil shown by infrared analysis to be *trans*-1-decalone free of the *cis* isomer.

Anal. Calcd. for $C_{10}H_{14}OBr_2$ (dibromodecalone A): C, 38.73; H, 4.64. Found: C, 38.91; H, 4.31. Calcd. for $C_{10}H_{15}OBr$ (bromodecalone C): C, 51.96; H, 6.54. Found: C, 51.92; H, 6.49. Calcd. for $C_{10}H_{15}OBr$ (bromodecalone D): C, 51.96; H, 6.54. Found: C, 51.59; H, 6.18. Calcd. for $C_{10}H_{14}OBr_2$ (dibromodecalone G): C, 38.73; H, 4.64. Found: C, 40.03; H, 4.70.

Bromination of *trans*-1-Decalone.—The same procedure described above was used in brominating 5.00 g. of *trans*-1-decalone. From this, 6.17 g. of crude product was obtained; this was chromatographed as before to yield the same products in the following yields: dibromodecalone A, 0.50 g.; mixture of A and bromodecalone B, 0.34 g.; bromodecalone B, 0.98 g.; mixture of B and bromodecalone C, 0.50 g.; bromodecalone C, 0.95 g.; bromodecalone D, 0.64 g.; *trans*-1-decalone, 0.35 g.

Bromination of *cis*-1-Decalone in the Presence of Sodium Acetate.—To a solution of 4.00 g. of *cis*-1-decalone (0.026 mole) and 2.16 g. (0.026 mole) of sodium acetate in 80 ml. of acetic acid was added a solution of 4.20 g. (0.026 mole) of bromine in 50 ml. of acetic acid. To the stirred solution was added 48% hydrobromic acid periodically until at the end of 24 hours 1.25 ml. had been added and the color of bromine had disappeared. At the end of an additional 12 hours the mixture was poured into 800 ml. of water and worked up as before to yield 5.84 g. of crude product. This was chromatographed on a 4.0 × 75.0 cm. silica gel column packed by 10% ether in hexane and then rinsed with hexane. In addition to bromoketones C, B, D and A which were isolated previously, a new bromodecalone was obtained (bromodecalone E). The amounts of pure products isolated in order of their elution were: bromodecalone B, 0.25 g.; bromodecalone E, 0.16 g.; bromodecalone C, 0.76 g.; bromodecalone D, 0.35 g. The unreacted decalone fraction proved to be pure *trans* uncontaminated by the *cis* isomer.

Anal. Calcd. for $C_{10}H_{15}OBr$ (bromodecalone E): C, 51.96; H, 6.54. Found: C, 52.25; H, 6.48.

Another run was conducted as follows: To a 50-ml. acetic acid solution saturated with sodium acetate and sodium bromide was added 1.52 g. (0.00952 mole) of bromine. To the stirred solution was added a solution of 1.45 g. (0.00952 mole) of *cis*-1-decalone in 10 ml. of acetic acid. The mixture was heated to 55° for a half-hour without perceptible change in color. This was followed by stirring at room temperature for 67 hr. The mixture then was poured into 600 ml. of water containing sodium arsenite and extracted with 1:1 ether–hexane and washed with water, followed by dilute sodium carbonate and finally by water until neutral. The extracts were dried over sodium sulfate and concentrated *in vacuo*. Remaining was 1.68 g. of a yellow oil, which was chromatographed on silica gel as above. The yields of pure products were bromodecalone B, 91 mg.;

(22) Melting points were taken on a Fisher–Johns block.

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

bromodecalone E, 112 mg.; bromodecalone C, 110 mg.; bromodecalone D, 107 mg.

Bromination Employing a Potassium Sulfate Buffer.—To a solution of 7.00 g. (0.0459 mole) of 1-decalone, analyzing as 50% *cis* and 50% *trans* isomer, and 16.0 g. of potassium sulfate (0.0915 mole) in 400 ml. of acetic acid and 140 ml. of water in a liter three-neck flask equipped with heating mantle, dropping funnel, Hershberg stirrer and reflux condenser was added 6.30 g. (0.0395 mole) of bromine in 25 ml. of acetic acid. The temperature of the mixture was then gradually raised until after 90 minutes the temperature had reached 95° and the bromine color had been dissipated. The reaction mixture then was poured into 1500 ml. of water and was ether extracted. The extracts were washed successively with water, dilute sodium carbonate and finally with water. The extracts now were dried over sodium sulfate and concentrated *in vacuo* to leave 8.60 g. of oil. This was chromatographed on a 3.5 × 75.0 cm. silica gel column which was cooled with a water jacket. As usual, the column was packed with 10% ether in hexane and rinsed with hexane before use. Twenty-six fractions were collected as follows: 1 was obtained with 1750 ml. of hexane and contained no material. Elution with 5% ether in hexane was then begun. Fractions 2 through 5 totaled 1000 ml. and were devoid of material. Fraction 6 was obtained with 100 ml. of solvent and contained 65 mg. of dibromodecalone A, m.p. 60–61°. Fraction 7, eluted with 60 ml. of solvent, contained 0.21 g. of a mixture of A and bromodecalone B. Fractions 8 through 10 totaled 150 ml. and yielded 0.77 g. of bromodecalone B; 11 (70 ml.) contained 0.37 g. of a mixture of B and bromoketone E; 12 through 14 (total 210 ml.) afforded 0.86 g. of bromoketone E; 15 (70 ml.) gave 0.24 g. of a mixture of E and C; 16 through 17 (140 ml.) gave 0.34 g. of bromoketone C; 18 (70 ml.) contained 0.14 g. of a mixture of C and bromoketone D. Fractions 19 through 26 (totaling 920 ml.) afforded 1.50 g. of bromodecalone D.

In another run to a solution of 8.00 g. of *cis*-1-decalone in 420 ml. of acetic acid and 100 ml. of water containing 18.20 g. of potassium sulfate was added with stirring 7.20 g. of bromine in 20 ml. of acetic acid. The temperature was raised to 103° over 35 min. at the end of which time the bromine had decolorized. The crude bromoketone mixture was worked up as in the previous preparation and the 10.45 g. of yellow oil subjected to chromatography on a 3.5 × 75 cm. water-cooled silica gel column. Elution with 2 liters of hexane afforded no material, nor did the following 1250 ml. of 5% ether in hexane give material. The next fraction (6) eluted with 200 ml. of 5% ether in hexane contained traces of oil. Fraction 7, eluted with 70 ml. of the same solvent gave 0.19 g. of an oil shown by infrared to be a mixture of bromoketones A, B and G. Fractions 8 through 10, totaling 210 ml., afforded 2.24 g. of bromoketone B; this was recrystallized to a constant melting point of 38.0–39.0°. Fraction 11 (70 ml.) contained 0.58 g. of a mixture of bromoketones B and E; 12 (70 ml.) contained 0.58 g. of a mixture of B, E and C. Fractions 13–14 (140 ml.) gave 0.88 g. of a mixture of C and E. Fractions 15–18 (475 ml.) yielded 1.10 g. of C; 19 (125 ml.) contained 0.19 g. of an oily solid found to be a mixture of C and D. Fraction 20 (200 ml.) afforded 0.33 g. of nearly pure D, m.p. 80–86°. Fraction 21 (250 ml.) gave 0.29 g. of D, m.p. 85–87°. Fraction 22 (250 ml.) contained traces of oily solid, while fraction 23 (500 ml.) gave 1.23 g. of unreacted decalone.

Anal. Calcd. for $C_{10}H_{15}OBr$ (bromodecalone B): C, 51.96; H, 6.54. Found: C, 52.36; H, 6.41.

In a third run, to a solution of 9.00 g. (0.0591 mole) of *trans*-1-decalone and 20.50 g. (0.118 mole) of potassium sulfate in 495 ml. of acetic acid and 180 ml. of water was added 8.10 g. (0.0507 mole) of bromine. The temperature was raised to 105° over a period of 30 min. At the end of an additional 15 min. the bromine had decolorized. The mixture then was poured into 1500 ml. of ice-water containing a small quantity of sodium arsenite and the product was ether extracted. The extract was washed with water, sodium carbonate, then water and dried over sodium sulfate. Concentration afforded 11.90 g. of yellow oil which was chromatographed on a 3.5 × 75 cm. silica gel column, which was water jacketed. The following fractions were collected: 1, 2250 ml. of hexane, no material; 2–3, 1250 ml. of hexane, no material; 4, 100 ml. of hexane, traces of oil; 5, 125 ml. of hexane affording 1.31 g. of oil; 6, 125 ml. of hexane, containing 1.28 g. of oil found to be a mixture of bromoketones G, B and E with E predominating; recrystallization from hexane afforded 0.32 g. of pure E melting at 34.0–35.0°; 7, 125 ml. of hexane, containing 0.71 g. of bromoketone E only slightly contaminated with C; 8, 125 ml. of hexane affording 0.31 g. of C contaminated with some E; 9, 125 ml. of hexane, containing 0.24 g. of a mixture of C and D; 10, 125 ml. of hexane containing 0.57 g. of D, m.p. 82–86°; 11, 125 ml. of hexane containing 0.55 g. of D, m.p. 85–87°; 12–13, 250 ml. of hexane, containing 0.90 g. of D, m.p. 90–91°; 14, 125 ml. of hexane, containing 0.26 g. of oily solid found to be a mixture of D and *trans*-1-decalone; 15, 500 ml. of hexane, affording 1.32 g. of *trans*-1-decalone.

Enol Benzoylation of *cis*-1-Decalone.—A mixture of 9.76 g. (0.0641 mole) of *cis*-1-decalone and 113.4 g. (0.808 mole) of benzoyl chloride was heated to gentle reflux in a 500-ml. flask equipped with reflux condenser and calcium chloride tube. At the end of five hours the mixture was concentrated *in vacuo* at steam-bath temperature to leave 19.18 g. of a dark brown oil. This residue was subjected to distillation in a semi-micro modified Claisen apparatus. There was obtained 15.24 g. of 1-decalone enol benzoate, b.p. 141–142° at 0.75 mm.

TABLE III

CHARACTERISTIC ABSORPTION BANDS OF THE MONOBROMODECALONES

Wave length, μ	Bromodecalone B	C	D	E
8.01	Min.	Min.	...	Max.
8.20	Max.	...	Max.	Min.
8.33	Min.	...	...	Max.
9.59			Max.	
9.61	Min.			...
9.63		Max.		
9.70	Min.	...	Min.	Max.
10.00	Max.	Min.		Min.
10.03			Max.	
10.24	Max.	Min.	Min.	Min.
10.40	Min.	Max.	Min.	...
10.53	Max.	...	...	...
10.97	Min.	Max.	...	Min.
11.08			Max.	
11.18	Max.	Min.		Max.
13.17		Max.	Min.	Min.
13.25	Max.			
13.76	Min.	Min.	Max.	Min.
14.59	...	...	Min.	Max.
14.80	Max.	...	Min.	...

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.16; H, 7.67.

Reaction of Enol Benzoate with N-Bromosuccinimide in Aqueous Solution.—To a solution of 5.52 g. of N-bromosuccinimide (0.0310 mole) in 6.57 g. of anhydrous sodium acetate in 200 ml. of water containing 10.0 ml. of acetic acid was added a solution of 7.22 g. of enol benzoate (0.0282 mole) in 400 ml. of acetone. The reaction mixture was allowed to stand at room temperature for 5 hours. The acetone then was distilled off *in vacuo* at room temperature during one additional hour and the residue was poured into 1500 ml. of water. The mixture next was extracted with carbon tetrachloride. The extracts were washed with dilute sodium carbonate followed by water and were dried over sodium sulfate. Concentration *in vacuo* left 6.32 g. of a yellow oil. The infrared spectrum of this material showed it to be largely bromodecalone C; however, some additional absorption bands were noted. Chromatography on silica gel allowed isolation of 3.17 g. of bromodecalone C; this was eluted by 670 ml. of 4% ether in hexane after elution with 2000 ml. of hexane followed by 1190 ml. of 4% ether in hexane. Negligible material was obtained in the 125-ml. fraction subsequent to elution of bromodecalone C. However, the succeeding 715 ml. contained 0.37 g. of material whose infrared spectrum was markedly different from any of the previously described bromodecalones, except

that the presence of some bromodecalone D was apparent. Although not quite pure, this compound, bromodecalone F, was analyzed.

Anal. Calcd. for $C_{10}H_{15}OBr$: C, 51.96; H, 6.54. Found: C, 53.71; H, 6.17.

Preparation of the 2,4-Dinitrophenylhydrazone of Bromodecalone D.—To a solution of 0.30 g. (0.00130 mole) of bromodecalone D in 10.0 ml. of 95% ethanol was added a solution of 0.254 g. of 2,4-dinitrophenylhydrazine (0.00130 mole) in 10.0 ml. of ethanol containing 1.0 ml. of concentrated sulfuric acid. After several minutes the product crystallized out. The orange solid was filtered and weighed 88 mg. A second crop of 0.26 g. was obtained. The melting points of the two crops were 232–238° and 170–180°, respectively. Crystallization of the lower melting fraction from hexane–chloroform yielded 80 mg. of orange crystals, m.p. 240–243° dec. This was combined with the 88-mg. fraction and recrystallized repeatedly; the melting point rose only to 245–247°.

Anal. Calcd. for $C_{16}H_{19}N_4O_4Br$: C, 46.72; H, 4.66; N, 13.62. Found: C, 47.22; H, 4.80; N, 12.57.

Reaction of Bromodecalone C with Dinitrophenylhydrazine.—To a solution of 0.360 g. of 2,4-dinitrophenylhydrazine (0.00182 mole) in 10.0 ml. of ethanol containing 1.00 ml. of concd. sulfuric acid was added 0.42 g. (0.00182 mole) of bromodecalone C in 25.0 ml. of ethanol. After several minutes a red precipitate separated. This was filtered and washed with cold ethanol; the crude product weighed 0.30 g. and melted at 260–267° dec. One crystallization from hexane containing a minimum of chloroform afforded 0.10 g. of red crystals, m.p. 268–271° dec. A second crop of 0.14 g., m.p. 255–263 dec., was obtained. Crystallization of this from hexane–chloroform yielded 0.12 g. of red crystals, m.p. 269–272° dec., which was combined with the original first crop. Three additional crystallizations of this material from hexane–chloroform brought the melting point to 280–281° dec.; this was not altered by further crystallization. The final weight of this material was 81 mg.

Anal. Calcd. for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 58.29; H, 5.10; N, 17.12.

Reaction of Bromodecalone E with Dinitrophenylhydrazine.—To a solution of 0.18 g. (0.0091 mole) of 2,4-dinitrophenylhydrazine in 7.0 ml. of 95% ethanol containing 1.0 ml. of concd. sulfuric acid was added 0.21 g. (0.0091 mole) of bromodecalone E in 8.0 ml. of ethanol. After several minutes an orange solid separated which was filtered and washed with cold ethanol. The yield was 0.27 g. of material melting at 237–240° dec. One crystallization from chloroform–hexane raised the melting point to 238–240° dec. The melting point was not raised by further crystallization.

Anal. Calcd. for $C_{16}H_{19}N_4O_4Br$: C, 46.72; H, 4.66; N, 13.62. Found: C, 46.66; H, 4.65; N, 12.69.

Preparation of the Enol Acetate of 1-Decalone.—A solution of 10.0 g. (0.0657 mole) of *cis*-1-decalone and 2.00 g. of *p*-toluenesulfonic acid (0.0105 mole) in 250 ml. of acetic anhydride in a 500-ml. flask equipped with a 30-cm. Vigreux column was heated by Glascol so that gentle refluxing of the acetic anhydride and slow distillation of acetic acid resulted. At the end of 7 hours 1.72 g. of anhydrous sodium acetate was added (0.0210 mole). The acetic anhydride then was removed under reduced pressure. The dark residue was taken up in 500 ml. of benzene; this extract was washed first with water, then with dilute sodium bicarbonate and finally with water. The extract was dried over sodium sulfate and concentrated *in vacuo* leaving 12.40 g. of dark brown oil. Vacuum distillation in a semi-micro modified Claisen apparatus gave 9.13 g. of enol acetate, b.p. 63–66° at 0.75 mm.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 74.19; H, 9.34. Found: C, 73.59; H, 9.27.

Hydrogen Bromide Treatment of Bromodecalone D.—To 10.0 ml. of a 0.3472 *N* solution of hydrogen bromide in chloroform was added 87 mg. of bromodecalone D. After two hours at room temperature the mixture was diluted with 150 ml. of chloroform, washed with water, then by dilute sodium carbonate and finally by water. Concentration *in vacuo* left 75 mg. of oil. Infrared analysis indicated that in addition to starting material there was present bromoketone E. There also appeared to be present slight traces of bromoketone C. When the reaction product was treated for an additional three hours with HBr in chloroform of the same concentration, the infrared spectrum showed increased amounts of bromoketone E and some bromoketone C. Treatment of HBr in chloroform for a total of 16 hours resulted in a product consisting largely of bromoketone C with small amounts of bromoketones D and E still being present.

Hydrogen Bromide Treatment of Bromodecalone B.—To 50 ml. of 0.176 *N* hydrogen bromide in chloroform was added 0.15 g. (0.65 mmole) of bromodecalone B, m.p. 38.0–39.0°. This was allowed to stand at room temperature for 105 min. and then was diluted with 500 ml. of 1:1 ether–hexane. This was washed successively with water, dilute sodium bicarbonate solution and then water until neutral. The solution was dried over sodium sulfate concentrated *in vacuo* leaving 0.13 g. of oil whose infrared spectrum showed it still to be mainly bromoketone B. After an additional treatment as before, however, for two additional hours, only partial equilibration had occurred. Further reaction for 23 hr. afforded product consisting of bromoketone C only slightly contaminated with bromoketones D and E.

Hydrogen Bromide Equilibration of Bromodecalone E.—A 25-hr. treatment of 0.20 g. (0.886 mmole) of bromodecalone E with 50 ml. of 0.176 *N* hydrogen bromide in chloroform afforded bromodecalone C, identified by its infrared spectrum.

Hydrogen Bromide Treatment of Bromoketone E.—To 10.0 ml. of 0.3472 *N* hydrogen bromide in chloroform was added 0.41 g. (0.00178 mole) of bromodecalone E. At the end of two hours the mixture was diluted with 150 ml. chloroform and washed with water, followed by dilute sodium carbonate and finally water until the washings were neutral. The chloroform layer then was concentrated *in vacuo* to leave 0.36 g. of oil. The infrared spectrum indicated that little if any had reacted.

Hydrogen Bromide Treatment of Bromoketone C.—To a solution of 0.12 g. (0.00052 mole) of bromodecalone C in 10.0 ml. of chloroform was added 0.50 ml. of 0.292 *N* hydrogen bromide in chloroform. After 10 minutes there was added 10 ml. of chloroform and the solution was washed with water, dilute sodium bicarbonate and finally by water. Concentration *in vacuo* left 0.10 g. of residue which was shown by infrared analysis to be unchanged bromodecalone C.

When 0.11 g. of bromodecalone C was treated with 10.0 ml. of 0.262 *N* hydrogen bromide in chloroform for 20 minutes there was no reaction. Reaction times up to 18 hr. produced no change.

Zinc–Acetic Acid Debromination of Bromodecalone C.—To a solution of 0.45 g. of bromodecalone C (0.00195 mole) in 18.0 ml. of acetic acid in a 25-ml. flask equipped with magnetic stirrer was added 4.0 g. of zinc dust over a period of one hour with stirring. Stirring was then continued for an additional 4.5 hours. The mixture then was poured into 500 ml. of water and the zinc was filtered. The filtrate was ether extracted and the extract now treated with an equal volume of hexane. The extract then was washed with water, dilute sodium carbonate and finally again with water until neutral and dried over sodium sulfate. Concentration *in vacuo* at room temperature left 0.19 g. of oil. This was subjected to quantitative infrared analysis which indicated this to be a mixture of *cis*- and *trans*-1-decalone containing 39.2% of the former. The crude sample was then chromatographed on a 2.5 × 50.0 cm. silica gel column eluting with 5% ether in hexane. Six fractions were collected of which fractions 5 and 6 contained decalones. The combined fractions 5 and 6 then were analyzed by the infrared procedure and shown to contain 38.0% *cis*-1-decalone. Thus analysis of the crude reaction product is seen to be reliable.

Zinc–Acetic Acid Debromination of Bromodecalone B.—A solution of 0.45 g. of bromodecalone B in 20.0 ml. of acetic acid was treated with a total of 4.0 g. of zinc dust in portions over one hour with magnetic stirring. Stirring was continued for an additional 3.5 hours and the reaction mixture was worked up as in the previous run. The crude product was chromatographed on a 2.0 × 50.0 cm. silica gel column and the decalone product analyzed by quantitative infrared analysis which indicated this to consist of 37.2% *cis*-1-decalone.

Zinc–Acetic Acid Debromination of Bromodecalone D.—A solution of 0.46 g. of bromodecalone D in 20.0 ml. of

acetic acid was stirred magnetically and to this was added in portions over one hour 4.0 g. of zinc dust. The reaction mixture then was stirred at room temperature for an additional 3 hours. The crude reaction product was isolated as above by filtration, extraction and concentration of the extracts. The product was chromatographed on a 2.0 × 50.0 cm. silica gel column using first 800 ml. of 5% ether in hexane, which eluted no material. Then 200 ml. of 10% ether in hexane followed, the eluent containing no material. The succeeding 280 ml. contained the decalone product. Infrared analysis of this 0.19 g. indicated it to be pure *trans*-1-decalone containing no *cis* isomer.

Zinc–Acetic Acid Debromination of Bromodecalone E.—To a solution of 0.21 g. (0.00091 mole) of bromodecalone E in 10.0 ml. of acetic acid, was added 3.0 g. of zinc dust in portions over a period of 0.5 hour with magnetic stirring. The reaction mixture then was stirred for an additional 3 hours, poured into 500 ml. of water and filtered, the filtrate being extracted with 1:1 ether-hexane. The extract was washed with water, dilute sodium carbonate and finally with water and dried over sodium sulfate. Concentration *in vacuo* left 0.14 g. of residue which was shown by infrared analysis to be pure *trans*-1-decalone devoid of the *cis* isomer.

Zinc–Collidine Hydrochloride–Collidine Debromination of Bromodecalone C.—To a 25-ml. flask equipped with magnetic stirring bar was added 0.90 g. of zinc dust and 0.75 g. (0.00545 mole) of collidine hydrochloride. The flask was not quite filled with freshly distilled collidine and nitrogen gas was bubbled through the solution for 5 minutes to remove any dissolved oxygen. Then 0.15 g. (0.00065 mole) of bromodecalone C was added dissolved in several ml. of deoxygenated collidine of just sufficient volume to fill the flask. A solid plug then was placed in the standard taper opening in such a manner to exclude all air. The reaction mixture now was stirred magnetically for three hours at room temperature. The mixture then was filtered free of solid, taken up in 500 ml. of ether, washed with two portions of dilute citric acid solution followed by water and dried over sodium sulfate. Concentration *in vacuo* left 93 mg. of oil which was analyzed by quantitative infrared and found to contain 65.5% of *cis*-1-decalone.

General Procedure for Zinc Debrominations.—A number of zinc debrominations were run using zinc and collidine hydrochloride as in the preceding experiment but employing differing times of reaction and in some cases solvents other than collidine; these were methanol, acetonitrile and *t*-butyl alcohol. The procedure was otherwise exactly as described in the preceding experiment with 0.90 g. of zinc dust and 0.75 g. of collidine hydrochloride being used. The results are summarized in Table II.

Stability of *cis*-1-Decalone under Debromination Conditions.—Exactly the same procedure was followed as in the debromination experiments except that in place of the bromodecalone there were used known mixtures of *cis*- and *trans*-1-decalones. One stability run thus was made with *t*-butyl alcohol as the solvent and a 68.3% *cis*-decalone sample. The reaction was allowed to proceed for 24.5 hr. The product was isolated as in the debromination runs and analyzed as 71.5% *cis*-1-decalone.

Another run was made using a collidine solvent. At the end of 6 hours the percentage of *cis*-1-decalone had similarly remained unchanged within experimental error.

Quantitative Infrared Analysis of *cis*- and *trans*-1-Decalone Mixtures.—The method described previously[4-9] was used. Here $R = Q.F$ where R is the ratio of *cis*- to *trans*-decalone and

$$Q = \frac{D_t'D_m'' - D_t''D_m'}{D_c''D_m' - D_c'D_m''}$$

and F is determined empirically, the calibration data in Table II being used. D_t, D_c and D_m are optical densities of pure *trans* isomer, pure *cis* isomer and a given mixture, respectively. The superscripts refer to the analytical wave lengths 10.55 μ (D') and 11.03 μ (D''). All spectra were run at a total of 12.0 mg./0.50 ml. of CS_2 in 0.10-mm. cells. The average value of F = 1.02 was used in calculating the results in the last two columns of Table IV and the composition of unknown mixtures.

TABLE IV

Actual % *cis* isomer	D'	D''	Q	Actual R	Calcd. F	Calcd. R	Calcd. % *cis* isomer
0.0	0.0540	0.492	...	...	...	...	..
25.8	.137	.456	0.305	0.348	1.14	0.310	23.5
50.5	.175	.276	1.01	1.02	1.01	1.03	50.6
76.7	.262	.159	3.62	3.26	0.901	3.67	78.5
100.0	.284	.0450	...	...	...	...	..

The Dehydrobromination of Bromodecalones B and C with Collidine.—In each case 0.17 g. of the bromodecalone was dissolved in 20 ml. of freshly distilled collidine and the solution kept at the given reaction temperature for the indicated time. The mixture then was taken up in 500 ml. of ether and washed successively with water, citric acid solution, and finally with water until neutral. The ether phase was dried over sodium sulfate and concentrated *in vacuo*. The residual oil was then analyzed by infrared. The results of these runs are given in Table V.

TABLE V

DEHYDROBROMINATION OF THE 9-BROMO-1-DECALONES

Compound and conditions	D'	D''	Conversion, %
Bromodecalone B	1.260	0.610	...
Bromodecalone C	1.244	0.660	...
9,10-Octalone	0.0410	1.155	...
Bromodecalone B after 19 hr. in collidine at r.t.	1.366	0.114	2.62
Bromodecalone C after 19 hr. in collidine at r.t.	1.114	0.165	9.56
Bromodecalone B after 10 hr. in collidine at 80°	1.041	0.204	13.8
Bromodecalone C after 10 hr. in collidine at 80°	0.500	1.187	73.2

The ratio of octalone to bromodecalone reactant was obtained from the equation

$$R = \frac{1.252D'' - 0.0635D'}{1.155D' - 0.0410D''}$$

where D' and D'' are the optical densities at 5.84 and 6.01 μ, respectively.

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EVANSTON, ILL.