Tetrahedron, 1967, Vol. 23, pp. 2051 to 2059. Pergamon Press Ltd. Printed in Northern Ireland

CONFORMATIONAL ANALYSIS—LIII

THE REACTIONS OF THE CYCLOOCTENES WITH HALOGEN, AND THE DIPOLE MOMENTS OF THE *CIS*- AND *TRANS*-1,2-DICHLOROCYCLOOCTANES[1,2]

N. L. Allinger and L. A. Tushaus
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

(*Received in USA* 19 *August* 1966; *accepted for publication* 4 *October* 1966)

Abstract—The addition of chlorine to *cis*-cyclooctene yields the *trans*-dichloride, which has a dipole moment of 3·1D, that is slightly solvent dependent. The corresponding *cis*-dichloride was not obtained by the chlorination of the *trans*-olefin, but was synthesized indirectly, and found to have a dipole moment of 2·3D, which is also solvent dependent. The addition of halogen to *trans*-cyclooctene was shown to yield a complex mixture of products, the major one being 1,3-dihalo-2-methylcycloheptane.

INTRODUCTION

The dipole moments of the *cis* and *trans* isomers of 1,2-dichlorocyclohexane derivatives have been instructive in showing the conformations of the compounds, and how conformational equilibria shift with changing solvent.[3] It seemed likely that the same kind of information might be similarly informative regarding the cyclooctane ring. Prior to 1964 the available evidence appeared to indicate (although not conclusively) that the cyclooctane ring possessed some sort of a crown structure.[4] Since that time, work from a number of different research groups has thrown the question open again.[5–8]

The dipole moments of the *cis* and *trans* isomers of 1,2-dichlorocyclooctane cannot by themselves establish the conformation of the ring, but depending on the numerical values found, they could well exclude from consideration numerous potential conformations. Theoretical calculations[5] indicate that a number of cyclooctane conformations may be similar in energy. Since the one case in which the

---

[1] This research was supported by Grant GP 4290 from the National Science Foundation.

[2] Paper LII, N. L. Allinger and C. L. Neumann, *Tetrahedron* 23, 1279 (1966).

[3] W. Kwestroo, F. A. Meijer and E. Havinga, *Rec. Trav. Chim.* 73, 717 (1954). For a summary and Refs see: E. L. Eliel, N. L. Allinger, S J. Angyal and G. A. Morrison, *Conformational Analysis*, p. 159. Interscience Division of Wiley, New York (1965). The dipole moments of *cis*- and *trans*-dibromocyclooctane were reported in a paper which appeared after completion of this work (P. W. Henniger, E. Wapenaar and E. Havinga, *Rec. Trav. Chim.* 81, 1053 (1962)). The results therein for the *trans*-dibromide and dichloride agree reasonably well with those reported here for the dichloride. The marked difference between the dipole moment reported for the *cis*-dibromide, and that reported here for the dichloride may be due to any of a number of reasons, the reported instability of the dibromide being one.

[4] Ref. 3, p. 210.

[5] [a] J. B. Hendrickson, *J. Amer. Chem. Soc.* 86, 4854 (1964); [b] K. Wiberg, *Ibid.* 87, 1070 (1965).

[6] J. D. Dunitz and A. Mugnoli, *Chem. Commun.* 166 (1966).

[7] F. A. L. Anet and M. St. Jacques, *J. Am. Chem. Soc.* 88, 2585, 2586 (1966).

[8] J. Dale, I. Laszlo and W. Ruland, *Proc. Chem. Soc.* 190 (1964).

ring conformation has been definitely established[6] concerns the conformation in a crystal, and this may or may not pertain to the conformation of that compound, or of the ring in general, in solution. The dipole moments might thus furnish evidence at least allowing one to exclude certain conformations as major ones for these molecules in solution, and furthermore, a study of the variation of the dipole moments of these compounds with change in solvent would be expected to yield information as to the existence of conformational equilibria in these molecules.

RESULTS AND DISCUSSION

As far as the authors are aware, the 1,2-addition of chlorine or bromine to an olefinic linkage by an ionic reaction mechanism proceeds in an *anti*-fashion in all known cases. Thus one would predict, and it was found, that the addition of chlorine to *cis*-cyclooctene should proceed to yield a 1,2-dichloride, and since the reaction was smooth and clean it was inferred that the product was *trans*-1,2-dichlorocyclooctane. It was shown that the halogens were on adjacent carbons by the reaction of the compound with zinc dust to produce *cis*-cyclooctene.

trans-Cyclooctene might similarly be expected to react with chlorine to yield *cis*-1,2-dichlorocyclooctane. However, since the bromination of the cyclodecenes yields 1,6-dibromides,[9] and since *trans*-cyclooctene is very highly strained,[10] it might be anticipated that the outcome of the reaction would be less predictable in this case. It was in fact found that when *trans*-cyclooctene was treated with chlorine under the same conditions which led to the smooth *anti* addition in the case of the isomeric olefin, there was obtained a mixture of six major products, corresponding to mono and dichlorides. It was subsequently shown that none of the six major products corresponded to the anticipated *cis*-1,2-dichlorocyclooctane. The nature of these reaction products will be discussed below.

cis-1,2-Dichlorocyclooctane was prepared by several step sequence (flow sheet) beginning with *cis*-cyclooctene, which upon oxidation with peracetic acid yielded the known *cis*-cyclooctene oxide.[11] The latter, upon treatment with dry hydrogen chloride, opened to yield the *trans*-1,2-cyclooctene chlorohydrin. This material, upon treatment with base, reclosed to give back the *cis*-epoxide. When the chlorohydrin was treated with dry hydrogen chloride in trichloroacetonitrile, under reaction conditions which are known to strongly favor S_N2 substitution,[12] there was obtained a 1,2-dichloride. The same compound could also be obtained through the action of thionyl chloride and pyridine on the chlorohydrin. The vicinal nature of the halogens was shown by the reaction of the compound with sodium to yield cyclooctane and *cis*-cyclooctene. This dichloride was different from that obtained by the direct addition of halogen to *cis*-cyclooctene, and the geometric relationships of these two dichlorides is assigned on the basis of the outcome expected for the reactions used in the syntheses.

In the opinion of the authors, the bulk of the older evidence favors a distorted crown structure, either twisted or stretched,[3] for the cyclooctane ring, while recent evidence[5–7] tends to support a half-crown. In terms of the deformed crown, it will

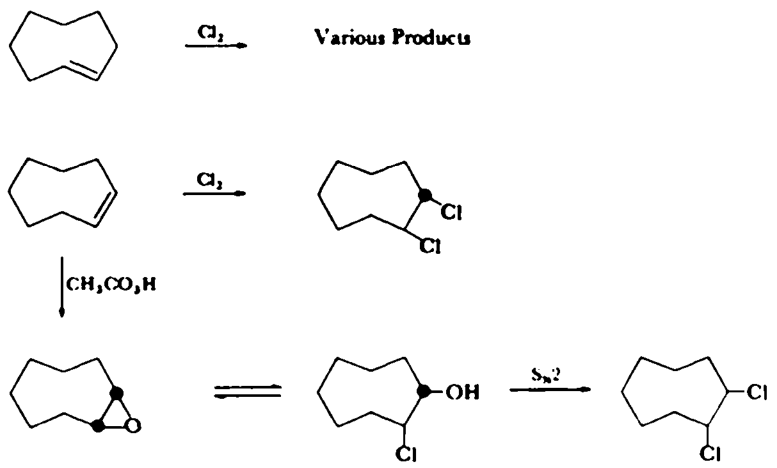
---

[9] J. Sicher, J. Zavada and M. Svoboda, *Coll. Czech. Chem. Commun.* 27, 1927 (1962).

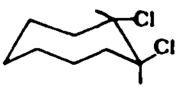
[10] R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.* 79, 4133 (1957).

[11] A. C. Cope, S. W. Fenton and C. F. Spencer, *J. Am. Chem. Soc.* 74, 5884 (1952).

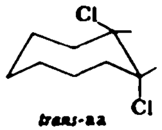
[12] F. Cramer and H. J. Baldauf, *Chem. Ber.* 92, 370 (1959).



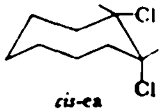
be clear from the figure that to the extent that the deformation of the ring from a regular geometry is averaged out, the *trans* isomer of a 1,2-disubstituted cyclooctane is a mixture of diaxial and diequatorial conformations, while the *cis* isomer is a single axial-equatorial conformation. The latter has a dihedral angle of roughly 90° between the dipoles, while of the former mixture of two conformations, one has a much smaller, and the other has a much larger, angle between the dipoles. The conformational equilibrium in the *trans* isomer should be susceptible to shifting by changing the solvent polarity analogous to what was found with the six-membered ring, hence the dipole of the *trans* isomer should increase markedly as the solvent becomes more polar. The *cis* isomer may show an increase in dipole moment with increasing solvent polarity also, simply from the deformation which gives the higher dipole moment being more firmly impressed on the molecule in the more polar solvent.



trans-ee



trans-aa



cis-ea

The dipole moment of each isomer of the 1,2-dichlorocyclooctanes was determined in heptane, benzene, and in dioxan. The *trans* isomer indeed showed the predicted behaviour with the dipole moment increasing from 2·98D to 3·20D with increasing solvent polarity. The *cis* isomer showed an equal change, from 2·17D to 2·37D. Hence, it is not possible to ascribe a fundamentally different conformational behaviour to the two different isomers with respect to changes in solvent polarity.

The contrast between the dipole moments of the isomeric 1,2-dichlorocyclooctanes compared to the corresponding cyclohexane derivatives is of interest. With the cyclohexane derivatives studied by earlier workers,[3] as expected, it was found that the *cis* isomer has a dipole moment which is invariant with solvent, since it can exist as only a single conformation, and it has the value 3·1D. The *trans* isomer, on the other hand, showed a dipole moment which was solvent dependent, and of a smaller magnitude, increasing from 2·3D in carbon tetrachloride to 2·7D in benzene. The results have been reasonably interpreted in terms of the *trans* isomer being a mixture of diaxial and diequatorial forms in similar amounts, with the latter increasing in proportion to the former as the polarity of the solvent increased.

Comparing these numbers with those obtained for the cyclooctyl derivatives, it may be noted that the *trans* isomer is the more polar in the eight-membered ring case, contrary to the six-membered ring case. From models, it would seem that the *cis* isomer must have a dihedral angle of around 100° between the dipole in the crown conformation, although as the molecule twists about, this angle may vary by 20° or so in either direction. If the molecule has the chair-boat or half-crown conformation, the *cis* dipoles can be located in a co-planar arrangement, or with a dihedral angle similar to that observed in the crown conformation. The dipole moment observed for the *cis* isomer, besides being variable with solvent, also is considerably smaller than that observed for the *cis* isomer in the cyclohexane ring. Only a qualitative interpretation of these numbers will be attempted, which is as follows. As the crown (or the chair-boat) conformation deforms by twisting, or stretching, the average dihedral angle between *cis* positions on the ring remains near 100°, with certain of these positions increasing and others decreasing the angle in question. In cyclohexylchloride, the observed moment is 2·24D, which is within experimental error of that observed for cyclooctyl chloride. The bond moment of the carbon chlorine bond in 1,2-dichlorocyclohexane was found to be 1·9D, and using the same value here, assuming an approximately tetrahedral geometry, the dihedral angles between the carbon-chlorine bonds were calculated to be 107° in heptane and 98° in dioxane. These numbers are certainly close to what would be expected, and are consistent with a deformed crown, (or chair-boat), in which the average deformation varies somewhat as a function of solvent, the more polar solvent tending to stabilize the smaller dihedral angle to a greater extent.

In contrast to the six-membered ring, in the eight-membered ring the *trans*-1,2-dichloride has a greater dipole moment than does the *cis*. The *trans* compound would be analogously considered to be a mixture of two conformations, diequatorial and diaxial, which have dihedral angles between the chlorines of about 40° and 160° respectively. The observed dipole moments correspond to similar amounts of the two conformations, with the diequatorial one increasing at the expense of the diaxial with increasing solvent polarity as would be anticipated.

The observed dipole moment results are thus quite consistent with the cyclooctane ring having a crown conformation or a chair-boat conformation in these derivatives. The relative magnitudes of the moments and their behaviour with changing solvent is as would be anticipated on the basis of conformational analysis.

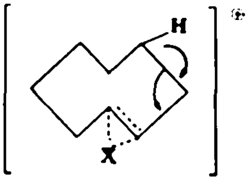
The rather unusual reaction of *trans*-cyclooctene with chlorine was investigated further. It was found that the same type of reaction occurred when *trans*-cyclooctene was treated with bromine, and the latter case was actually studied in more detail. The principle product (isolated in 36% yield) resulting from the treatment of *trans*-cyclooctene with bromine was a dibromide, B, which was shown to be 1,3-dibromo-2-methylcycloheptane.[13] The proof of structure is outlined on the flow sheet. Upon hydrogenolysis dibromide B yielded methylcycloheptane. Upon treatment of B with zinc dust, two compounds were obtained, C and D, both of which contain

---

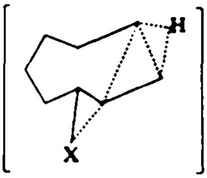
[13] This product was apparently first isolated (but not identified) by K. Ziegler and H. Wilms, *Liebigs Ann.* **567**, 1 (1950).

cyclopropane rings. One of these was independently synthesized from cyclohexene by the reaction scheme shown, and the other one must be the corresponding stereoisomer. The synthesis from cyclohexene was completely stereospecific in yielding just one stereoisomer. Because of the interference between the carboethoxyl group in the diazo compound and the cyclohexene ring during the course of the addition to the double bond, the isomer obtained is presumed to be C, with the methyl group having the stereochemistry shown, and the one not obtained must be D. Upon treatment with either tetraethylamonium acetate in acetone, or with silver acetate in acetic acid, the dibromide B was converted to an unsaturated acetate, which was in turn converted to 2-methylcycloheptanone as shown on the flow sheet.

Cope *et al.*[14] reported during the course of this work the identification of two of the minor solvolysis products of *trans*-cyclooctene oxide as 2-methyl-1,3-cycloheptanediol and 5-methyl-1,4-cycloheptanediol. The formation of dibromide B is visualized as occurring by a mechanism analogous to that suggested by Cope for the former compound. One of the unidentified dibromides obtained probably corresponds to Cope's second diol. The mechanism in either case involves the bromonium or corresponding ion as a starting point. While such an ion is geometrically more favorable than the *trans* olefin, it is nonetheless highly strained, and migration of the alkyl group as shown greatly relieves the strain. A hydride transfer must occur simultaneously or subsequently as indicated.

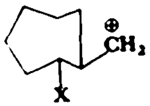


If it is a simultaneous process the intermediate (or transition state) ion (E) must be formed. If the process is a two-step one, the first formed ion (F) must undergo



B

a 1,3-hydride transfer. The latter step would seem an unlikely one for such an ion to undergo, hence the pathway involving a nonclassical ion appears more probable.

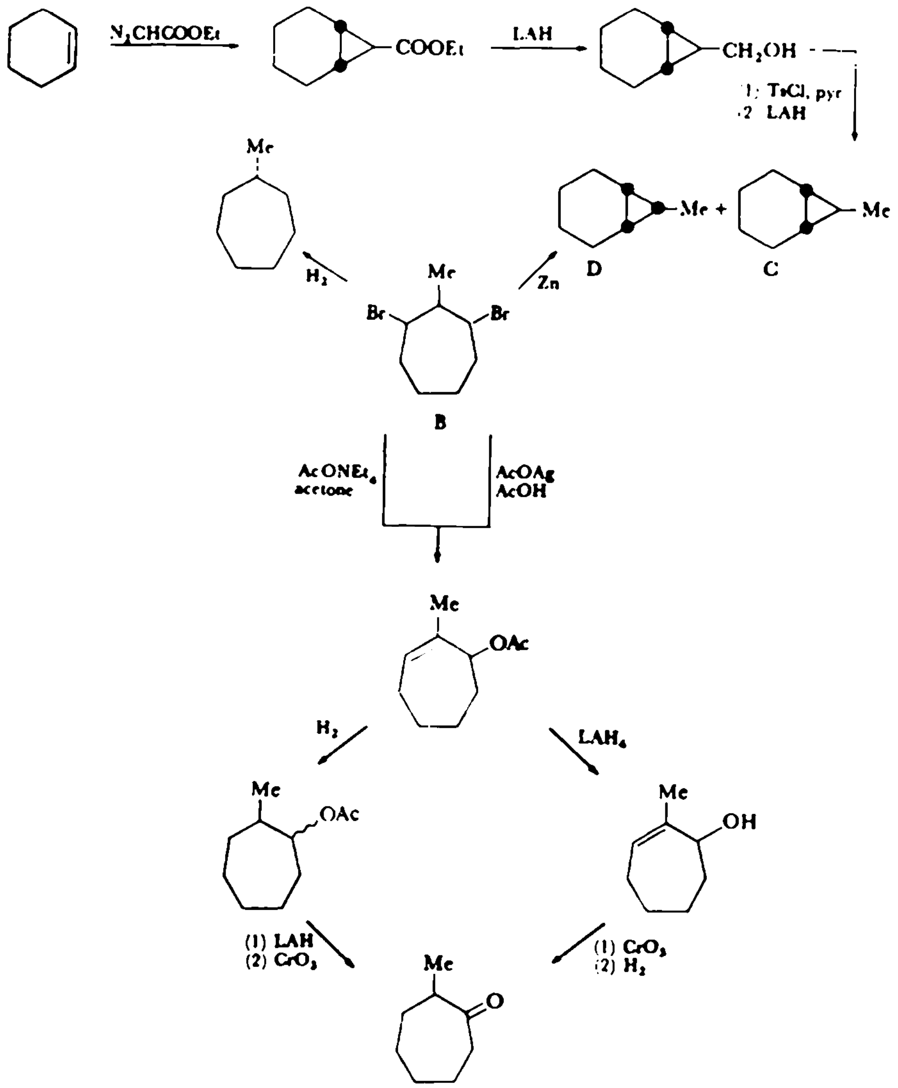


F

The stereochemistry of dibromide B was not established. Although the material appears to be a single compound from physical properties and VPC, different samples gave C and D in ratios varying from 0·3 to 5, and for a given sample, this ratio

---

[14] A. C. Cope, P. Scheiner and M. J. Youngquist, *J. Org. Chem.* 28, 518 (1963).



Reactions leading to the identification of dibromide B.

DIPOLE MOMENT DATA

Compound	*M*R	Solvent	α	ε_1	d_1	β	$P_{2\infty}$	μ(D)
Cyclooctyl chloride	41·81	Heptane	3·844	1·9138	0·6795	0·337	144·3	2·24 ± 0·02D
Cyclooctyl chloride		Dioxane	7·246	2·2231	1·0282	0·098	148·1	2·28 ± 0·02D
cis-1,2-Dichloro-cyclooctane	46·64	Heptane	3·712	1·9144	0·6795	0·531	142·5	2·17 ± 0·03D
cis-1,2-Dichloro-cyclooctane		Benzene	7·642	2·2717	0·8731	0·501	158·9	2·34 ± 0·03D
cis-1,2-Dichloro-cyclooctane		Dioxane	8·008	2·2235	1·0284	0·194	161·7	2·37 ± 0·03D
trans-1,2-Dichloro-cyclooctane	46·64	Heptane	6·640	1·9134	0·6795	0·521	227·6	2·98 ± 0·02D
trans-1,2-Dichloro-cyclooctane		Benzene	12·955	2·2714	0·8732	0·530	236·1	3·05 ± 0·02D
trans-1,2-Dichloro-cyclooctane		Dioxane	14·622	2·2355	1·0282	0·223	255·5	3·20 ± 0·03D

was independent of the exact reaction conditions (temperature, concentration, solvent), which would seem to indicate that the material is a mixture of stereoisomers, the proportions of which were different in different samples.

EXPERIMENTAL

trans-1,2-*Dichlorocyclooctane*. The dichloride was prepared in 73% yield by the addition of chlorine to *cis*-cyclooctene according to the procedure of Braude *et al.*[15] Dehalogenation with zinc yielded *cis*-cyclooctene as the major product, (about 70% by gas chromatography) showing the addition product to be a 1,2-dichloride; b.p. 74° (1 mm), n_D^{25} 1·5037 (reported[15] b.p. 74° (1 mm); n_D^{24} 1·5055). There was also obtained from the dehalogenation 15% cyclooctane and 15% *trans*-cyclooctene (identified by gas chromatography only).

cis-1,2-*Dichlorocyclooctane*. Similar to the preparation of the *trans*-dichloride, chlorine was added to *trans*-cyclooctene[16] in chloroform at −78°. Analysis of the reaction mixture on VPC (silicone gum rubber or Dow polyglycol E 20,000) after removal of the chf and excess Cl showed a complex mixture of at least six products, which from their retention times corresponded to mono- and dichlorides. The major dichloride product (A) estimated to be about 25–30% of the total products, was later shown to be neither *cis*- nor *trans*-1,2-dichlorocyclooctane and in fact was eluted faster on the VPC columns than either of these.

Authentic *cis*-1,2-dichlorocyclooctane was prepared by either of the following procedures, procedure B being preferred.

Cyclooctene chlorohydrin. cis-1,2-Cyclooctene oxide (49·5 g), b.p. 103–105° (53 mm), m.p. 57–58·5° prepared in 86% yield with peracetic acid,[11] was treated with anhyd HCl in chf according to the method described for the preparation of *trans*-2-chlorocyclohexanol.[17] *trans*-Chlorocyclooctanol was obtained in 88% yield, b.p. 96·5–97° (6·2 mm), m.p. 30–31·5°, n_D^{25} 1·4992. (Found: C, 59.11; H, 9·60; Cl, 21·60. Calc. for $C_8H_{15}ClO$: C, 59·07; H, 9·30; Cl, 21·80%.)

The chlorohydrin, when treated with potassium t-butoxide, reverted to the *cis*-cyclooctene oxide and was therefore the *trans*-chlorohydrin.

Procedure A. To 59·5 g $SOCl_2$ was added dropwise a soln of 39·5 g pyridine and 40·5 g (0·25 mole) *trans*-2-chlorocyclooctanol. The reaction temp was kept around 75° by use of an ice bath when necessary. The reaction was stirred at this temp for 6 hr, after which it was hydrolyzed by pouring it into ice water. The organic layer was extracted with CH_2Cl_2, washed several times with HClaq, and dried over Na_2SO_4. After the solvent had been evaporated, the mixture of *cis*- and *trans*-dichloride was distilled on a spinning-band column. The *trans* isomer, having the lower b.p., distilled first. Three middle fractions boiling at 94° (3·7 mm) were combined and redistilled on the spinning band column. The later fractions of the redistilled material were combined (2 g) and a sample was submitted for analysis; b.p. 89° (2·8 mm), n_D^{25} 1·5062. (Found: C, 52·88; H, 7·67; Cl, 39·39. Calc. for $C_8H_{14}Cl_2$: C, 53·05; H, 7·79; Cl, 39·16%.)

The dichloride reacted with excess Na in isopropyl alcohol to give a hydrocarbon mixture containing 90% cyclooctane and 10% *cis*-cyclooctene (by VPC only).

Procedure B. Anhyd HCl was bubbled into a cold (−5°) soln of 16·3 g (0·1 mole) *trans*-2-chlorocyclooctanol, 14·5 g (0·1 mole) trichloroacetonitrile, and 30 ml anhyd ether. After 7 hr the addition of HCl was stopped and the reaction mixture was kept at −15° overnight. Trichloroacetamide (14·7 g) was removed by filtration, the ether soln was washed several times with water, dried over $MgSO_4$ and distilled. The low boiling fractions were redistilled on a spinning band column to give a pure unsaturated monochloride, b.p. 72° (9·6 mm), n_D^{25} 1·4947, which has tentatively been identified as 3-chlorocyclooctene by comparison of its IR and NMR spectra and VPC chromatogram with those obtained from the product of *cis*-cyclooctene and t-butyl hypochlorite. The NMR spectrum showed a multiplet at 4·39 τ (vinyl protons) with twice the intensity of multiplet occuring at 5·93 τ (H—C—Cl). Three other multiplets occurred at 7·42, 7·96 and 8·45 τ, corresponding to the methylene protons. (Found: C, 66·33; H, 9·11; Cl, 24·64. Call. for $C_8H_{13}Cl$: C, 66·43; H, 9·06; Cl, 24·52%.)

---

[15] E. A. Braude, W. F. Forbes, B. F. Gofton, R. P. Houghton and E. S. Waight, *J. Chem. Soc.* 4711 (1957).

[16] A. C. Cope, R. A. Pike and C. F. Spencer, *J. Am. Chem. Soc.* **75**, 3212 (1953).

[17] R. A. Baxter and F. S. Spring, *J. Chem. Soc.* 613 (1943).

The higher boiling fractions were distilled twice on a spinning-band column to give *cis*-1,2-dichlorocyclooctane, b.p. 94·7 (4·0 mm), n_D^{25} 1·5063. Its IR spectrum and VPC chromatogram were superimposable on those of another sample prepared by procedure A.

Chlorocyclooctane. Anhyd HCl was bubbled into a mixture of 10 g cyclooctene, 30 ml benzene and 1 g anhyd $ZnCl_2$. After about 20 hr the product was washed with water and $NaHCO_3$aq, dried and distilled to give 9 g chlorocyclooctane, b.p. 78° (10 mm), n_D^{25} 1·4821 (reported[18] b.p. 87–90° at 19 mm).

Reaction of trans-*cyclooctene with bromine*. *trans*-Cyclooctene,[13] (16 g, in 75 ml of reagent grade chf was cooled to −78° by means of a Dry-Ice/MeOH bath. Stirring was maintained by a magnetic stirrer while approximately 20 g (theoretical amount is 23·2 g) Br in 50 ml chf was added dropwise until a slight yellow color persisted. The soln was again decolorized by the addition of 1 or 2 drops *trans*-cyclooctene. The chf was removed under reduced press on a steam bath. (The evolution of HBr gas could be noticed while the chf soln was warming to room temp. However, the product seemed to be a little effected whether or not the soln was first washed with $NaHCO_3$aq.) Most of the slightly yellow residual oil, which consisted of 35·2 g crude bromides, was then distilled on a spinning-band column. After removing the forerun which consisted of at least 2 major unsaturated monobromides (VPC analysis on a polyglycol column at 135° gave 2 major peaks with a shoulder on the first peak), 14·2 g (36%) of dibromide (B) was obtained, having b.p. 68–69° (0·2 mm), n_D^{25} 1·5432. This material appeared stable and on standing for a period of several months has remained colorless. (Found: Br, 59·43 and 59·11. Calc. for $C_8H_{14}Br_2$: Br, 59·19%; Found: 2·00. This is equiv to 0·36 C—CH_3. Calc. for C—CH_3: 5·50%.)

This material reacted quite rapidly (approx. 5 sec) with 2% $AgNO_3$ in EtOH. It did not react with KI in acetone. An IR spectrum of the material had a band of medium strength at 1380 cm^{-1} (C—Me).

Higher boiling fractions (8·5 g) were also obtained as a mixture of dibromides with a boiling range of 70–80° (0·2 mm), n_D^{25} 1·5565. Analysis of the highest boiling fraction showed no indication of the presence of any tribromides. This material gave an iodine color and also NaBr on treatment with NaI in acetone. (Found: Br, 59·08 and 59·11. Calc. for $C_8H_{14}Br_2$: Br, 59·19%.)

NMR spectrum of dibromide B. τ = 8·75 (d, J = 7 c/s), τ = 8·64 (d, J = 7 c/s), τ = 8·31 (m), τ = 7·86 (m), τ = 6·01 (m), τ = 5·63 (m).

Hydrogenation of dibromide B. A 0·5 g sample of dibromide B was added to 5 ml AcOH containing 0·3 g AcONa and 0·5 g 10% Pd-C. This material was hydrogenated for 20 hr at atm press and took up 85% of the theoretical amount of H. After this it was poured into 50 ml water and extracted with pentane. The pentane soln was washed with dil $NaHCO_3$aq and dried over $MgSO_4$. After the pentane was evaporated, the residue was analyzed on a VPC column (tris-1,2,3-β-cyanoethoxypropane) and was shown to contain essentially a single hydrocarbon plus a trace of cyclooctane. This hydrocarbon was found to be identical, by comparison of IR and NMR spectra and VPC chromatogram with methylcycloheptane which had been prepared from cycloheptanone and MeMgI, dehydration of the resulting tertiary alcohol and hydrogenation.

Hydrogenation of the reaction mixtures from the addition of chlorine and bromine to trans-*cyclooctene*. Samples (0·5 g) of the corresponding reaction mixtures after removal of solvent were subjected to atm hydrogenation as described above for dibromide B. VPC analysis showed the resulting hydrocarbons from the chloride mixture to consist of 70% cyclooctane and 30% methylcycloheptane, and those from the bromide mixture to consist of 57% cyclooctane and 43% methylcycloheptane.

The reaction of zinc with dibromide B. The dibromide (3·0 g) was refluxed at 100° for 2 hr with 2·2 g Zn dust and 10 ml water. The products were extracted with pentane, dried, and concentrated by evaporation of the pentane to give 1·2 g of a mixture of hydrocarbons (C and D). Pure samples were collected by VPC and used for subsequent tests and determinations. Hydrocarbon C, b.p. 130°, n_D^{25} 1·4478, reacted slowly with Br in CCl_4 but not at all with $KMnO_4$ in acetone. Its NMR spectrum was consistent with a cyclopropyl derivative (m at 9·25 τ). Hydrocarbon D, b.p. 145–145·5°, n_D^{25} 1·4637, exhibited the same properties as hydrocarbon C but its IR and NMR spectra were somewhat different although these likewise indicated a cyclopropyl derivative (m at 9·27 τ). Both NMR spectra showed the same pattern and no vinyl protons were observed.

---

[18] S. A. Miller and W. O. Jones, British Patent No. 738, 992 (to British Oxygen Co., Ltd.), Oct. 26, 1955. *Chem. Abstr.* 50, 10768f (1956).

Experiments carried out on the dibromide with Zn in refluxing MeOH or in water at 50° gave the 2 hydrocarbons in the same proportions. However, in varying samples of apparently similar purity, the 2 hydrocarbons were obtained in different proportions. This corresponded to a change in intensities of the Me peaks at 8·75 and 8·64 τ in the NMR spectra of different dibromide B samples. In 5 different experiments the hydrocarbon composition varied from 26% hydrocarbon C and 74% hydrocarbon D to 84%C and 16%D.

The pure compounds collected by VPC were also analyzed.

For Hydrocarbon C: (Found: C, 87·18; H, 12·88. Calc. for C_8H_{14}: C, 87·19; H, 12·81%.)

For Hydrocarbon D: (Found: C, 87·32; H, 12·91. Calc. for C_8H_{14}; C, 87·19; H, 12·81%.)

NMR spectra of hydrocarbons C and D. Hydrocarbon C: τ = 9·52 (m), τ = 9·0 (d, J = 5 c/s), τ = 8·82 (m), τ = 8·31 (m). Hydrocarbon D: τ = 9·27 (m), τ = 9·06 (d, J = 4·5 c/s), τ = 8·77 (m), τ = 8·49 (m).

trans-7-*Methylnorcarane.* This hydrocarbon was prepared according to the method described.[19] Ethyl diazoacetate was allowed to react with cyclohexene in the presence of a powdered Cu catalyst to give a 40% yield of *trans*-ethylnorcarane-7-carboxylate, which was converted in 15% yield to *trans*-7-methylnorcarane by LAH reduction to the alcohol (b.p. 104° at 20 mm), converted to the tosylate which was not isolated, and LAH reduction to the hydrocarbon (b.p. 131°). A pure sample of this material was collected by VPC and was found to be identical in all respects to hydrocarbon C as determined from IR spectra, VPC retention times and NMR spectra (described above).

Reaction of silver acetate with dibromide B. A mixture of 2·4 g of the dibromide, 6·0 g AcOAg and 35 ml glacial AcOH was stirred at 90° for 15 hr. The reaction mixture was filtered into 130 ml cold water. The organic layer was extracted 3 times with pentane, the pentane solns were washed with dil $NaHCO_3$aq and then with water, and were finally dried over $MgSO_4$. Evaporation of the pentane yielded a light yellow oil, 1·48 g, which gave one major peak on VPC (carbowax) but which seemed to partially decompose upon distillation or preparative scale VPC. Upon hydrogenation one molar equiv of H was absorbed. The original acetate acetate also gave a strongly positive test with Br in CCl_4. The material was apparently an unsaturated monoacetate (IR spectrum showed a shoulder at 3003 cm^{-1} and a strong absorption at 1745 cm^{-1}).

Reaction of tetraethylammonium acetate and dibromide B. A mixture of 6·8 g of the dibromide and 18·9 g tetraethylammonium acetate in 100 ml acetone was heated under reflux for 24 hr. Most of acetone was then distilled and the white crystals of tetraethylammonium bromide were removed by suction filtration. The filtrate was poured into water and the organic layer was extracted with pentane and dried. Evaporation of the pentane yielded 4·0 g of a yellow oil which by IR and VPC appeared to be essentially identical with the material obtained in the reaction with AcOAg.

The crude acetate was divided into 2 equal parts and each was subjected to a series of reactions. One part was reduced with LAH to a crude unsaturated alcohol which was oxidized with Jones reagent to an unsaturated ketone mixture. This was then hydrogenated over 2% Pd–C in ether at atm press to yield a single saturated ketone.

The second part was first hydrogenated over PtO_2 in AcOH to give a saturated mixture of isomeric acetates (as surmised from a doublet of equal intensities on VPC analysis). There were reduced with LAH to the corresponding alcohols which were then oxidized with Jones reagent to a single saturated ketone. The ketones obtained from both methods were identical and their IR and NMR spectra were superimposable on those of an authentic sample of 2-methylcycloheptanone.

Measurements of dipole moments. The dipole moments were measured at 25° on a series of 5 solns for each compound, with the mole fraction of halide always less than 0·1, and the data are given in the Table. The dipole moment apparatus has been described previously.[20] The moments were calculated by essentially the method of Halverstadt and Kumler,[21] utilizing an IBM 650 computer programmed as described earlier.[22] Atomic polarization was neglected.

Acknowledgement.—The authors are indebted to Dr. M. A. DaRooge for the dipole moments reported herein.

---

[19] V. Franzen, H. J. Schmidt and C. Mertz, *Chem. Ber.* **94**, 2942 (1961); *Chem. Abstr.* **56**, 7192e (1962).

[20] N. L. Allinger, H. Blatter, M. A. DaRooge and L. A. Freiberg, *J. Org. Chem.* **26**, 2550 (1961).

[21] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.* **64**, 2988 (1942).

[22] N. L. Allinger and J. Allinger, *J. Org. Chem.* **24**, 1613 (1959).