Butyl sulfide was added as a standard solution of the sulfide in acetic acid. Benzyl sulfide was weighed out and added directly. Trial experiments showed that the sulfides did not interfere with the titration of sulfinic acid by the nitrite method.

Products of the Benzyl Sulfide–Sulfinic Acid Reaction.—Benzyl sulfide (20.0 mmoles) and *p*-toluenesulfinic acid (5.00 mmoles) were dissolved and made up to 100 ml. in a solution of acetic acid–0.56 M H_2O containing 0.5 M sulfuric acid. The solution was deaerated and then heated under nitrogen at 70° for 1 hour, using the same procedure employed for the kinetic runs. At the end of this time titration of an aliquot showed 80% of the sulfinic acid (4.00 mmoles) had reacted. The reaction was stopped at this point by pouring the solution into 1 liter of distilled water. The resultant cloudy mixture was exhaustively extracted with ether. The ether extracts were washed several times with sodium bicarbonate solution. The ether solution was then dried and most of the ether removed by distillation through a 30-cm. helices-packed column. The remainder of the ether was then removed by distillation through a 35-cm. micro-Widmer column. The residue was taken up in a small amount of methylene chloride and placed on a 2 × 80 cm. column of acid-washed alumina. The column was eluted with the following solvents: 400 ml. of pentane; pentane–ether, 200 ml. 19:1; 200 ml. of 9:1; 200 ml. of 7:1; 100 ml. of 4:1; and 100 ml. of 3:1; 500 ml. of ether. Fractions of 20 ml. were collected. The solvents were removed by distillation through the micro-Widmer column to minimize product loss. The products obtained were the following: Unreacted benzyl sulfide (3.92 g., 18.5 mmoles) was identified by infrared and m.p. comparison with a known sample. *p*-Tolyl *p*-toluenethiolsulfonate (0.386 g., 1.40 mmoles) was identified by similar comparison with a known sample.[4] Benzyl *p*-toluenethiolsulfonate (0.153 g., 0.55 mmole) as obtained from the reaction was found to be identical with the prepared sample both by infrared and mixed m.p. For quantitative estimation the fractions containing benzaldehyde were treated with 2,4-dinitrophenylhydrazine in the usual way. The amount of 2,4-dinitrophenylhydrazone formed, m.p. 236°, indicated 0.39 mmole of benzaldehyde had been present. The infrared spectra of the fractions before treatment with 2,4-dinitrophenylhydrazine were equivalent to that of a known sample of benzaldehyde.

Products of the Butyl Sulfide–Sulfinic Acid Reaction.—The sulfide (20.0 mmoles) and *p*-toluenesulfinic acid (10.0 mmoles) were dissolved in the same acetic acid–water–sulfuric acid mixture used for the benzyl sulfide reaction, and the solution was deaerated. It was then heated at 70° for 1 hour. In one run the exit tube from the reaction vessel was connected to a trap containing a 2,4-dinitrophenylhydrazine solution, and nitrogen was passed through the solution throughout the decomposition. A precipitate, m.p. 121°, shown to be identical with a known sample of *n*-butyraldehyde 2,4-dinitrophenylhydrazone, formed in the trap. Tests on known mixtures of butyraldehyde in acetic acid showed, however, that the aldehyde could not be determined quantitatively by this procedure, and for this reason the following v.p.c. method was employed for that purpose. In this a sample of the reaction mixture was injected into a Perkin–Elmer model 154 vapor phase chromatograph equipped with Golay column and flame ionization detector, the column temperature being 96°. This procedure gave satisfactory separation of butyraldehyde from all other components of the mixture. However, quantitative estimation of the aldehyde was not very precise. From the average of a number of samples the aldehyde concentration in the final reaction mixture appears to be 0.04 ± 0.005 M.

The other products were investigated in a subsequent run. In this the solution at the end of the decomposition was poured into distilled water, extracted with ether, etc., in the same way as in the benzyl sulfide study. The residue after removal of the ether by distillation was chromatographed using much the same procedure as with the other sulfide. On removal of the solvent from the chromatographic fractions only two compounds were found. These were *p*-tolyl *p*-toluenethiolsulfonate (1.37 g., 4.96 mmoles) and unreacted butyl sulfide (2.1 g., 14.5 mmoles).

In another run the nitrogen exit gases were passed through a cadmium nitrate solution. No precipitate formed. In another they were passed through sodium hydroxide solution. This was subsequently heated with hydrogen peroxide to oxidize any sulfide to sulfate. On addition of barium chloride no precipitate formed. These results show clearly that hydrogen sulfide is not evolved from the reaction mixture.

In all of the butyl sulfide runs an insoluble scum formed on the surface of the solution during the course of a run. Although small in amount and not identified, this could have been elemental sulfur.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

Conformational Analysis. XXVI. Some Stereochemical Studies of the Cycloöctane Ring[1,2]

BY NORMAN L. ALLINGER AND SEYMOUR GREENBERG

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The *cis* and *trans* isomers of 5-*t*-butylcycloöctanol have been prepared and many of their reactions have been studied by quantitative methods. The results have been interpreted in conformational terms.

Introduction

While the conformational properties of the cyclohexane ring have been studied in considerable detail,[3] comparatively little is known about the corresponding properties of the cycloöctane ring.[4] This work was undertaken in an effort to learn more about the conformational effects involved in the 8-membered ring, and it was specifically intended to show, among other things, whether or not 1,5-transannular hydride migration did occur in this ring system. It was shown quite some time ago that either 1,3- or 1,5-hydride transfer did occur,[5] the 1,5-transfer appearing more likely by analogy with what had been observed in the cyclodecane system.[6] Recently Cope and his students reported that in fact both 1,3- and 1,5-hydride transfer occurred, and they determined the ratio in a particular case.[7]

Winstein and Holness,[8] Eliel and Ro,[9] and subsequently many others have shown that by using

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(1) Paper XXV, N. L. Allinger and L. Freiberg, *J. Am. Chem. Soc.*, **83**, 5028 (1961).

(2) This research was supported by a grant from the National Science Foundation.

(3) For recent reviews see: (a) H. H. Lau, *Angew. Chem.*, **73**, 423 (1961); (b) E. L. Eliel, *J. Chem. Ed.*, **37**, 126 (1960).

(4) N. L. Allinger and S. Hu, *J. Am. Chem. Soc.*, **83**, 1664 (1961).

(5) A. C. Cope, S. W. Fenton and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

(6) H. J. Urech and V. Prelog, *Helv. Chim. Acta*, **40**, 477 (1957).

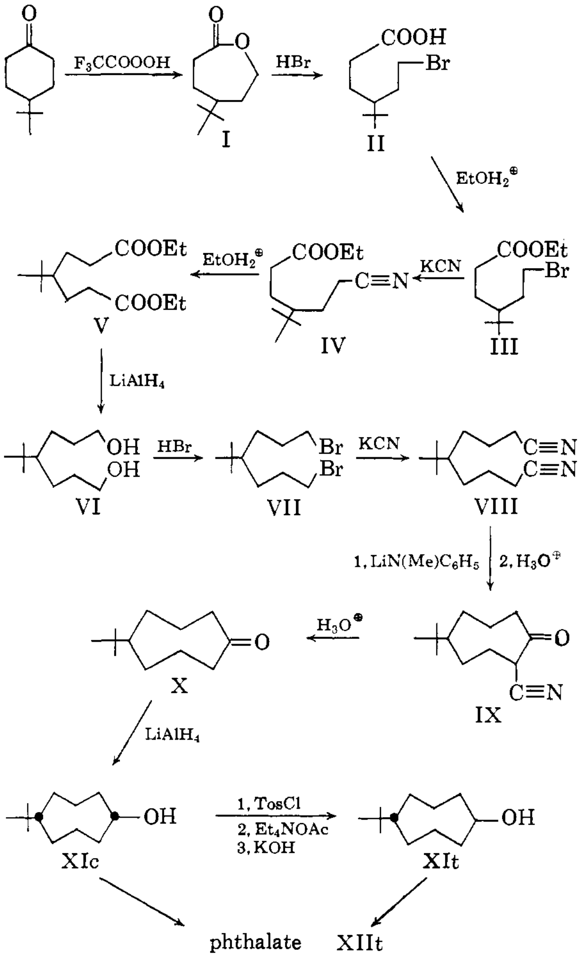
(7) A. C. Cope, G. A. Berchtold, P. E. Peterson and S. H. Sharmon *J. Am. Chem. Soc.*, **82**, 6366 (1960).

(8) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(9) E. L. Eliel and R. S. Ro, *Chemistry & Industry*, 251 (1956).

the *t*-butyl group to fix the conformation of a cyclohexane ring, small substituents at the other end of the ring are rigidly held in a fixed conformation uncomplicated by any large steric or polar effect of the *t*-butyl group. The application of this technique to the cycloöctane ring appeared to offer an opportunity for similar studies, and the *cis* and *trans* isomers of 5-*t*-butylcycloöctanol were therefore synthesized for study. The synthesis is fairly straight-forward and is outlined on the flowsheet.

A modified[10] Baeyer–Villiger reaction on 4-*t*-butylcyclohexanone gave a 58% yield of the crystalline lactone I. Upon treatment of the lactone with hydrobromic acid, bromoacid II was obtained. Esterification of this acid gave bromoester III. The latter was treated with potassium cyanide,[11] and gave cyanoester IV in 69% yield. The cyanoester was converted to diester V, and reduction of the latter with lithium aluminum hydride gave diol VI. The diol was converted to the dinitrile VIII *via* dibromide VII. The dinitrile was ring closed by a modification[12] of the Ziegler method and gave, after hydrolysis and decarboxylation, 5-*t*-butylcycloöctanone (X). The over-all yield of X from the dinitrile was 89%. This yield is noteworthy, since cyclization of azelaonitrile to cycloöctanone under similar conditions gave only a 30% yield. The effect of the *t*-butyl group on ring closure is an example of what has been referred to as the "*gem*-dimethyl effect,"[13] and the occurrence of the effect in the ring closure of medium rings was noted earlier.[4,14]



Ketone X was reduced to a mixture of alcohols (XI) with lithium aluminum hydride. This mixture of alcohols consisted, by infrared analysis, of 81% of an isomer which was assigned the *cis* configuration (see below), together with 19% of the *trans* isomer. The *cis* isomer, m.p. 60.5°, was isolated in 32% yield by recrystallizing the mixture from pentane at −20°.

When 5-*t*-butylcycloöctanone was reduced with hydrogen and platinum in acetic acid containing hydrogen chloride, a mixture of alcohols was obtained which, by infrared analysis, consisted of 42% *cis*- and 58% *trans*-XI. It did not prove possible to isolate the *trans* isomer from this mixture. The *trans* isomer, m.p. 59.5°, was however obtained by preparing the tosylate of the *cis* isomer, and converting it to the *trans*-acetate by reaction[15] with tetraethylammonium acetate, followed by hydrolysis of the acetate.

Results and Discussion

By X-ray diffraction studies on azacycloöctane hydrobromide, J. D. Dunitz has concluded the molecule has a mirror plane containing the nitrogen.[16] Extending this fact to cycloöctane, one can guess that the latter will have C_{2v}-symmetry. This particular type of deformed[17] crown structure was first advocated by Chiurdoglu, Doehaerd and Tursch[18] and seems to be in good agreement with all the evidence discussed earlier,[4] except possibly the infrared and Raman spectra.[19] Whether or not this structure is in fact in agreement with the spectra is not clear, since it seems not to have really been considered in detail. Since the spectra of various cycloöctane derivatives are nearly invariant with solvent, phase and temperature changes,[4] it seems clear that cycloöctane possesses a definite fixed conformation. The situation may in fact be very similar to that found with cyclohexanes,[20] except in this case there appear to be three different kinds of axial positions (a_1, a_2 and a_3) and three different kinds of equatorial positions (e_1, e_2 and e_3) (as indicated in A and B). This means a substance like cycloöctanol, instead of being a mixture of two con-

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(10) W. F. Sager and A. Duckworth, *J. Am. Chem. Soc.*, **77**, 188 (1955).

(11) J. R. Ruhoff, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 292.

(12) N. L. Allinger, M. Nakazaki and V. Zalkow, *J. Am. Chem. Soc.*, **81**, 5727 (1959).

(13) (a) T. C. Bruice and U. K. Pandit, *ibid.*, **82**, 5858 (1960); (b) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).

(14) A. T. Blomquist and G. A. Miller, *J. Am. Chem. Soc.*, **83**, 243 (1961).

(15) A. C. Cope and A. Fournier, Jr., *ibid.*, **79**, 3896 (1957).

(16) J. D. Dunitz, private communication.

(17) N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959).

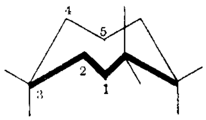
(18) G. Chiurdoglu, T. Doehaerd and B. Tursch, *Chemistry & Industry*, 1453 (1959).

(19) H. E. Bellis and E. J. Slowinski, Jr., *Spectrochim. Acta*, 1103 (1959).

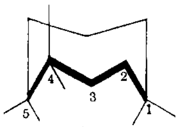
(20) The reasons are a little different, however. In cyclohexane the chair is rigid because it has unstrained bond angles as well as the absence of van der Waals and Pitzer strains. Cycloöctane has all of these strains, but they balance in such a way as to produce a conformation with a definite energy minimum, which appears to lead to a rigidity that would not be recognized from models of the Dreiding type.

formations as is cyclohexanol, is instead a mixture of six conformations (some possibly in negligible amounts).

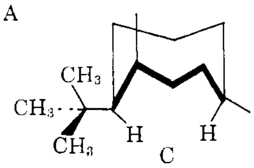
From scale models it is clear the *t*-butyl group in *t*-butylcyclooctane can best be accommodated in a specific position (as in C). This position is such



A



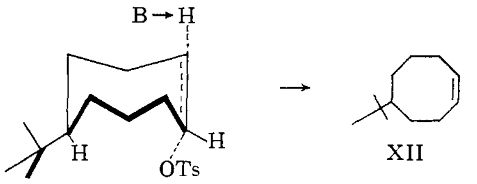
B



C

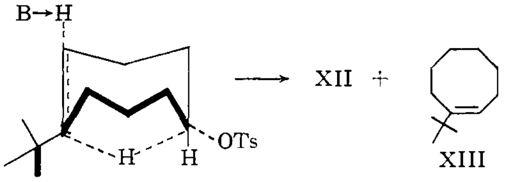
that generation of a carbonium ion at C-5 should for geometrical reasons yield a substantial amount of hydride transfer from C-1 to C-5, and none from C-3 to C-5. Such a transfer is also, of course, favored by the fact that a secondary carbonium ion is being converted to a tertiary one.

Solvolyses of the tosylates of the two isomers XIc and XIt would be predicted to yield somewhat different results. The geometry of the *trans* isomer is such that a preponderance of simple elimination to form XII might be expected.



XII

The *cis* isomer, on the other hand, has a geometry such that a hydride shift in the forming carbonium ion seems fairly likely, and the olefinic product would be predicted to be a mixture of XII and XIII. To the extent that a really free carbonium ion was formed of course, the same product would be expected from either isomer.



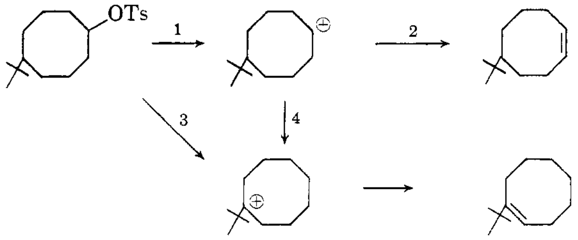
XIII

In order to facilitate discussion, assignments of the *cis* and *trans* structures to the isomers of XI are made at this point on the basis of their behavior on solvolysis. Additional evidence favoring this assignment comes from the n.m.r. spectrum and from chemical arguments given later.

When the tosylate of the *cis* isomer was solvolyzed in glacial acetic acid containing anhydrous sodium acetate, an olefinic fraction was obtained which showed two peaks on vapor phase chromatography in the ratio of 1:4. These peaks were assigned to XII and XIII, respectively, as discussed below. The *trans* isomer under similar conditions solvolyzed to give the same two materials, but this time the unrearranged material XII predominated 2:1. In both cases these two olefins were formed to the exclusion of the 3- and 4-*t*-butylcyclooctenes. The 1- and 5-*t*-butylcyclooctenes were shown to be stable under the reaction conditions. It is therefore clear that the rearranged isomer does not arise from the unrearranged one, and it does not arise by a series of 1,2-shifts,[21] but rather is obtained from the direct 1,5-hydride transfer of an intermediate (carbonium ion). Since the 1,5-hydride transfer occurs preferentially in one case, but not in the other, the *cis* structure can be assigned to the isomer in which hydrogen undergoes migration more readily, while the *trans* isomer, in which a *trans*-diaxial arrangement of leaving groups for a 1,2-elimination is more likely, must be the other one. These assignments are consistent with those arrived at from other considerations.

The lack of an isotope effect in the solvolysis reaction when the hydrogens in positions 5 and 6 are replaced by deuterium in the ten-membered ring can be interpreted as indicative of a shift subsequent to the rate-determining step[22]; in other words there is no neighboring group participation. In the present case, the geometry desirable for neighboring group participation is found in the *cis* isomer, but not in the *trans*. The hydride shift in the latter appears therefore to occur as a subsequent step. Since the amount of shift in the *cis* isomer is greater, this extra amount of shift occurs before the geometry of the starting material (including the surrounding solvent) is completely lost.

The simplest interpretation of these facts is that the reaction can initially proceed by either of two competing paths, step 1 or 3.



With the *trans* isomer, 3 cannot occur, but the carbonium ion from 1 partitions itself between reactions 2 and 4. These are essentially irreversible steps, and the ratio of products in the *trans* isomer is determined by the k_2/k_4 ratio.

The *cis* isomer can react by path 1 to yield the same carbonium ion as obtained from the *trans*, and this carbonium ion must react as previously. There is also another path open to the *cis* isomer, however, which is 3. The k_3/k_1 ratio for the *cis* isomer can be calculated from the data and is *ca.*2.3. Thus neighboring group participation by the migrating hydrogen appears to occur and anchimeric assistance appears to be important, though not overwhelmingly so. A more detailed study of the rates of these processes will be reported later.

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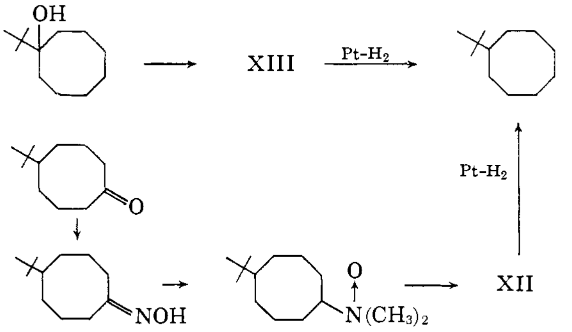
(21) The absence of a series of 1,2-shifts is inferred rather than proved by the experiments described here. An unequivocal proof that the shift is 1,5 was obtained by Dr. Irving Lillien in these laboratories and will be published in a later paper.

(22) S. Borcic, unpublished work quoted by V. Prelog, *Record Chem. Prog. (Kresge-Hooker Sci. Lib.)*, **18**, 247 (1957).

The structures were assigned to the two olefins obtained from the solvolysis as outlined on the flowsheet, and the arguments are briefly as follows. 1-*t*-Butylcycloöctanol was prepared by the addition of *t*-butyllithium to cycloöctanone, and was converted to 1-*t*-butylcycloöctene by heating with iodine. A sample of 5-*t*-butylcycloöctene was obtained beginning with *t*-butylcycloöctanone oxime, which was reduced to the amine. The latter was converted to the amine oxide and pyrolysis gave the olefin. This olefin was shown by vapor phase chromatography to consist of 3 compounds; the one present to the extent of 99% was assigned the *cis*-5-*t*-butylcycloöctene structure.[23] A trace of 1-*t*-butylcycloöctene was present, together with about 1% of a compound with higher retention time. This material was thought to be the *trans* isomer since the amine oxide pyrolysis yields the *trans*-olefin in the nine-membered ring.[24] While *trans*-olefin was not detected in the corresponding eight-membered ring product,[23] the infrared method available at that time would probably not have detected such a small amount.

The 1- and 5-olefins were each characterized by reduction to *t*-butylcycloöctane, which was also obtained from the Wolff–Kishner reduction of ketone X.



With the cyclohexane system there is only one kind of axial position and one kind of equatorial position. The *cis*- and *trans*-4-*t*-butylcyclohexanols therefore each have one or the other kind of hydroxyl, while cyclohexanol itself is a mixture of the two conformers. With the corresponding eight-membered ring compound no such simple arrangement can really be expected. The *t*-butyl compounds XI probably have their hydroxyl groups fixed in a single position by the necessity of accommodating the bulky *t*-butyl group (as in C), the *cis* isomer having an equatorial-like hydroxyl, the *trans* isomer having an axial-like hydroxyl. In the unsubstituted cycloöctanol, however, besides having a mixture of these two conformations, there are four other conformations. It can therefore be hoped that the axial-like and equatorial-like hydroxyls of XIt and XIc, respectively, will behave in the same relative way as they do in the cyclohexane case. There is no reason to expect that the behavior of cycloöctanol can be inferred from the behavior of the substituted derivatives, although one might hope that if the differences between equatorial and axial are large, the different equatorial types will be similar to one another and different from the axial types.

Two of the reactions studied by Winstein and Holness were investigated, the chromic acid oxidation of the alcohols and the saponification of their half-phthalate esters. With the cyclohexane system,[8] the half-phthalate ester of the equatorial alcohol hydrolyzes more rapidly than does its epimer, while the oxidation is more rapid with the axial epimer. Cyclohexanol itself is a conformational mixture in which the equatorial conformation predominates, and which shows rates which are intermediate between the pure conformations but nearer those of the equatorial.

The rates of saponification of the acid phthalates of XIc, XIt and cycloöctanol at 50.75° and 73.75° were measured, and are given in Table I along with the derived activation parameters. The most conspicuous result is that the unsubstituted cyclooctanol reacts more rapidly than does the *cis* isomer, which in turn reacts more rapidly than does the *trans* isomer. The *cis* is faster than the *trans*, as would be predicted, but only by a factor of two. The fact that the unsubstituted compound is faster than either of the 5-*t*-butylcycloöctanols is reasonably interpreted as outlined above. The outstanding point is the similarity of the rates, rather than the differences.

TABLE I

RATES OF SAPONIFICATION OF ACID PHTHALATES IN AQUEOUS SODIUM HYDROXIDE

Acid phthalate	Temp., °C.	Concn. × 10^2, M b	a	$k_2 \times 10^5$, l. mole^{-1} sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$ e.u.
Cycloöctyl	50.75	2.168	8.302	63.2 ± 1.0		
	50.75	2.252	8.218	63.4 ± 1.4		
	73.75	2.211	8.319	275.6 ± 2.1		
	73.72	2.170	8.360	280.7 ± 4.3	13.7	−31
cis-5-*t*-Butylcycloöctyl (XII)	50.75	1.932	8.538	40.6 ± 1.9		
	50.75	1.707	8.763	39.6 ± 3.2		
	73.75	1.531	8.999	224.3 ± 4.7		
	73.77	1.741	8.789	209.2 ± 11.5	15.7	−25.8
trans-5-*t*-Butylcyclooctyl (XIII)	50.75	1.828	8.702	22.6 ± 1.0		
	50.75	1.701	8.829	23.4 ± 1.1		
	73.78	1.549	8.981	150 ± 5.4		
	73.80	1.819	8.711	135 ± 6.9	17.0	−22.7

The rates of oxidation of XIc, XIt and cyclooctanol by chromic acid in acetic acid were also measured, and the data are summarized in Table II. Here the unsubstituted cycloöctanol reacts the slowest, the *trans* isomer is faster by a factor of 1.3, and the *cis* is faster by a factor of 1.7. Again the similarity of the rates is striking. Interpretation of these reactions is not really possible, since the transi-

TABLE II

RATES OF OXIDATION OF ALCOHOLS WITH CHROMIC ACID IN 75% ACETIC ACID

Alcohol	Temp., °C.	Concn. × 10^2, N b	a	$k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
Cycloöctanol	19.87	1.968	1.605	19.2 ± 0.5
	19.87	1.763	1.605	19.1 ± 0.6
cis-5-*t*-Butylcyclooctanol (XII)	19.87	2.148	1.605	32.2 ± 1.1
	19.87	1.787	1.605	34.2 ± 1.6
trans-5-*t*-Butylcyclooctanol (XIII)	19.87	1.964	1.605	24.0 ± 1.4
	19.87	1.771	1.605	24.9 ± 1.3

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

[24] A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955).

tion states and starting states are both important in determining the rates, and little is known about the former. In the chromic acid oxidation of *trans*-5-*t*-butylcycloöctanol, for example, the oxygen is compressed by the hydrogen at C-5, and relief of this compression should speed the reaction.[25] With the *cis* isomer a similar compression exists between the hydrogens at C-1 and C-5. Both of these compounds would be expected to react faster than the parent cycloöctanol in which the compression is probably less. The experimental data can of course be rationalized in these terms, but no confident predictions could possibly have been made in advance. Because of the similarity in rates between XIc and XIt it is clear that the hope of a group of axial-like positions being easily differentiable from a group of equatorial positions was not realized with these reactions.

It seems to be generally true that in the cyclohexane ring an axial hydrogen has its n.m.r. resonance absorption at higher field than does the corresponding equatorial hydrogen, and it seems likely that this situation arises from the ring current which is induced by the applied field, and which in turn induces a small field which reinforces the applied field at the location of the equatorial hydrogen.[26] The details of this effect have been well worked out for the benzene ring, where the ring current is quite large because of the high polarizability of the electrons. In cyclohexane the effect is smaller, but in the same direction. Since the magnetic transitions occur so slowly, in contrast to electronic transitions, the n.m.r. spectrum will correspond to an average conformation. The ring current should have a very similar effect here to that observed for cyclohexane.

The proton magnetic resonance spectra for the pertinent compounds were obtained and the locations of the peaks for the protons on the oxygen-carrying carbons are given in Table III. The hydrogen at C-1 in 4-*t*-butylcyclohexanol acid phthalate is seen at higher field for the *trans* than for the *cis* isomer. With the 5-*t*-butylcycloöctyl acid phthalates the corresponding hydrogen of the *cis* is at higher field than is the *trans*, and cycloöctyl acid phthalate itself shows absorption in between the *t*-butyl derivatives, but nearer the *cis* isomer. These data are interpreted in the following way.[27] The assumption made is that the axial positions will all be similar in the n.m.r. and the equatorial positions will all be similar to one another but different from the axial positions. Models indicate this may be a reasonably good assumption.

TABLE III

PROTON MAGNETIC RESONANCE DATA

Acid phthalate	τ
Cycloöctyl	4.80
cis-5-*t*-Butylcycloöctyl	4.92
trans-5-*t*-Butylcycloöctyl	4.60
cis-4-*t*-Butylcyclohexyl	4.85
trans-4-*t*-Butylcyclohexyl	5.09

In the cycloöctyl derivatives the C-1 hydrogen is more axial-like in the *cis* isomer than in the *trans* and in the parent compound the equatorial phthalate group predominates over the axial, on the average, in a ratio of 12/7. This gives an energy for the axial acid phthalate grouping relative to the equatorial of 0.3 kcal./mole (the corresponding difference in the cyclohexane ring is known only for the anion in water,[8] and is 1.2 kcal./mole), which is within experimental error of the energy difference measured between the two epimeric alcohols (XI) under Oppenauer conditions. The data thus bear out the validity in this case of the approximation of grouping the axial positions together on one hand, and the equatorial positions on the other. It seems likely that for conformational problems in the cycloöctane ring (and probably other medium rings), n.m.r. spectra may prove to be more definitive than will chemical methods.

There are for cyclohexanols many chemical facts which can be used to infer the axial or equatorial nature of the hydroxyl. Thus lithium aluminum hydride reduction of an unhindered ketone gives predominantly an equatorial alcohol, while catalytic reduction in acid solution tends to give the axial epimer. In the eight-membered ring, therefore, one would expect by analogy that similar results would obtain, and hence an independent basis for assignment of the structures of the alcohols was available, and led to conclusions consistent with the other evidence. As expected, equilibration of the epimers under Oppenauer conditions gave a mixture of the *cis* and *trans* isomers in the ratio of 1.78, which is in between the compositions of the two mixtures obtained by catalytic and lithium aluminum hydride reduction.

The cyclohexane ring presents an especially simple case, conformationally speaking. The five[28] and seven-membered[29] rings have a typical flexibility which makes them more difficult to understand. The eight-membered ring appears to be different from the latter two in that it is not really flexible. It is a mixture of a number of conformational isomers, however, and thus has much in common with the five- and seven-membered rings.

Experimental

γ-*t*-Butyl-ϵ-caprolactone (I).—To 25 g. of trifluoroacetic anhydride was added, with cooling and stirring, 2.63 ml. of 90% hydrogen peroxide. The temperature of the reaction mixture was maintained at 5–10° during the addition. After addition of the peroxide, 14.0 g. of 4-*t*-butylcyclohexanone was added with continued stirring and cooling, the temperature being maintained between 10–15°. A few minutes after the addition was complete, 250 ml. of chloroform was added and the solution was then neutralized with saturated sodium carbonate. Sufficient water was added to dissolve the precipitate which formed, the layers were separated and the water layer was extracted with chloroform. The combined chloroform extracts were dried over a mixture of anhydrous magnesium sulfate and sodium sulfite. The solution was filtered and after evaporation of the solvent the residue was distilled and gave 9.0 g. (58%) of material boiling 130–135° (2 mm.). The distillate solidified in the receiver and was recrystallized twice from heptane; m.p. 57.5–58.5°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.56; H, 10.66; sapon. equiv., 170. Found: C, 70.49; H, 10.95: sapon. equiv., 168.

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(25) J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **38**, 1529 (1955).

(26) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 387.

(27) E. L. Eliel, *Chemistry & Industry*, 558 (1959).

(28) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

(29) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).

4-*t*-Butyl-6-bromohexanoic Acid (II).[30]—A mixture of 10.0 g. of I, 17 ml. of 38% hydrobromic acid and 2 ml. of concentrated sulfuric acid was heated under reflux for 5 hours, cooled and poured onto ice. The resultant mixture was extracted with ether, the ether extracts were dried over magnesium sulfate, and the solution was filtered. Evaporation of the solvent and distillation of the residue gave 9.5 g. (64%) of bromo acid, b.p. 125–130° (0.2 mm.), $n^{25}\mathrm{D}$ 1.4842.

Anal. Calcd. for $C_{10}H_{19}O_2Br$: C, 47.81; H, 7.62; neut. equiv., 251. Found: C, 47.93; H, 7.46; neut. equiv., 259.

Ethyl 4-*t*-Butyl-6-bromohexanoate (III).—Beginning with 154 g. of 4-*t*-butylcyclohexanone, the ester was prepared *via* intermediates I and II without isolation or purification. The crude II obtained was dissolved in 5.50 ml. of absolute ethanol, 5 ml. of concentrated sulfuric acid was added and the mixture was heated under reflux for 5 hours. The cooled solution was poured into water. The organic layer was separated, diluted with ether and the resultant solution was washed with dilute sodium carbonate, then with water. The ether solution was dried, filtered and the solvent was evaporated. Distillation of the residue through a Vigreux column gave 206 g. (74% from II), b.p. 141–144° (8 mm.), $n^{25}\mathrm{D}$ 1.4674.

Anal. Calcd. for $C_{12}H_{23}O_2Br$: C, 51.61; H, 8.30. Found: C, 51.85; H, 8.27.

Ethyl 4-*t*-Butyl-6-cyanohexanoate (IV).[31]—A mixture of 20.0 g. of bromo ester III, 50 ml. of 95% ethanol and 5.6 g. of potassium cyanide was heated under reflux with stirring for 18 hours. An additional 5.6 g. of potassium cyanide was added and stirring and heating were continued for an additional 20 hours. The cooled solution was diluted with ether and filtered. The filtrate, after washing and drying, was concentrated, and the residue was distilled through a Podbielniak column and gave 10.9 g. (69%) of product, b.p. 161–164° (9 mm.), $n^{25}\mathrm{D}$ 1.4489.

Anal. Calcd. for $C_{13}H_{23}O_2N$: C, 69.29; H, 10.29. Found: C, 69.38; H, 10.07.

Diethyl 4-*t*-Butylheptan-1,7-dioate (V).[32]—A mixture of 10.0 g. of cyano ester IV, 13 ml. of 95% ethanol and 6.0 ml. of concentrated sulfuric acid was heated under reflux for 70 hours. The cooled mixture was diluted with water and extracted with ether. The ether extracts were washed with dilute sodium carbonate solution, then with water. The ether solution was dried and the solvent was evaporated. Distillation gave the product, 9.2 g. (75%), b.p. 134–136° (5 mm.), $n^{25}\mathrm{D}$ 1.4428.

Anal. Calcd. for $C_{15}H_{28}O_4$: C, 66.15; H, 10.36. Found: C, 66.03; H, 10.54.

4-*t*-Butyl-1,7-dihydroxyheptane (VI).[33]—A solution of 70.5 g. of diester V in 250 ml. of anhydrous ether was added dropwise to a stirred slurry of 15 g. of lithium aluminum hydride in 500 ml. of anhydrous ether. The excess lithium aluminum hydride was decomposed by the addition of water, and 10% hydrochloric acid was added until two clear phases were obtained. The ether solution was separated and the water layer was extracted with ether. The combined ether extracts were washed and dried and the ether was evaporated. Distillation furnished the diol, 49 g. (100%), b.p. 131° (0.7 mm.), $n^{25}\mathrm{D}$ 1.4657.

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 70.00; H, 12.62.

4-*t*-Butyl-1,7-dibromoheptane (VII).[34]—The crude glycol obtained from the reduction of 126 g. of V was heated in an oil-bath maintained at 125–130°. A rapid stream of anhydrous hydrogen bromide was passed into the glycol for approximately 30 minutes after which time considerable fuming occurred at the outlet of the flask. The addition was slowed down and continued for 5 hours. The resultant mixture was cooled, diluted with ether, and washed with water.

The ether solution was dried, the solvent was evaporated, and the residue was distilled and gave 133 g. (91% based on V), b.p. 130–132° (3 mm.), $n^{25}\mathrm{D}$ 1.4990.

Anal. Calcd. for $C_{11}H_{22}Br_2$: C, 42.06; H, 7.06. Found: C, 42.26; H, 7.22.

4-*t*-Butyl-1,7-dicyanoheptane (VIII).[31]—Dibromide VII, 62.3 g., was converted to the corresponding dinitrile with potassium cyanide in a manner similar to that described for IV; yield 30.7 g. (75%), b.p. 165–166° (2 mm.), $n^{25}\mathrm{D}$ 1.4579.

Anal. Calcd. for $C_{13}H_{22}N_2$: C, 75.67; H, 10.75. Found: C, 75.46; H, 10.52.

5-*t*-Butylcycloöctanone (X).—The cyclization experiments were all carried out in a modified[35] high dilution apparatus similar to that described by Zeigler and co-workers.[36] A solution of phenyllithium was prepared by the addition of 78 g. of bromobenzene to a stirred refluxing suspension of 30 g. of lithium metal in 1.5 l. of anhydrous ether, under a nitrogen atmosphere. The addition required about 2 hours. N-Methylaniline, 68 g., was then added rapidly and stirring and refluxing were continued for an additional hour. A solution of 20.6 g. of VIII in 900 ml. of anhydrous ether was then added during 48 hours. The cooled reaction mixture was decomposed with water, the organic layer was separated and evaporated to dryness under reduced pressure. The residues from three such cyclizations were combined and mixed with 300 ml. of 33% (by volume) sulfuric acid. The mixture was stirred under gentle reflux for 36 hours during which time the distillate was allowed to condense in a liquid–liquid extractor. The ketone which steam distilled was collected in the steam chamber while the aqueous phase was returned to the flask. The distillate was then diluted with ether and washed with water. The ether solution was dried, the ether was evaporated and the residue was distilled to give 42.2 g. (77%) of ketone, b.p. 113–115° (7 mm.), $n^{25}\mathrm{D}$ 1.4714. When the pot residue from the distillate was treated once again with 33% sulfuric acid, additional ketone was collected and the yield was raised to 89%.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.16; mol. wt., 182. Found: C, 79.07; H, 12.09; mol. wt. (Rast), 195.

The 2,4-dintrophenylhydrazone prepared in the usual way[37] had m.p. 172–173° (from ethanol).

Anal. Calcd. for $C_{18}H_{26}N_4O_4$: C, 59.65; H, 7.23. Found: C, 59.61; H, 7.33.

The semicarbazone had m.p. 188–189° (from ethanol).

Anal. Calcd. for $C_{13}H_{25}N_3O$: C, 65.23; H, 10.53. Found: C, 65.04; H, 10.49.

In some cases, when the crude product from the cyclization was incompletely hydrolyzed, the last portions of the steam distillate contained a white crystalline nitrogen-containing solid, m.p. 97.5–98.5° (from ether). This compound is believed to be 5-*t*-butyl-2-cyanocycloöctanone (IX).

Anal. Calcd. for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; mol. wt., 207. Found: C, 75.54; H, 10.41; mol. wt. (Rast), 206.

***cis*-5-*t*-Butylcycloöctanol (XIc).**—Ketone X, 20.3 g., was reduced with 2 g. of lithium aluminum hydride in ether as described for the preparation of VI. The residue, after removal of all of the ether, was crystallized twice from pentane at −20° and gave 6.5 g. (32%) of material, m.p. 55–57°. The analytical sample obtained by repeated recrystallization had m.p. 60–60.5°.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.03; H, 13.23.

The *p*-nitrobenzoate had m.p. 109.5–110°.

Anal. Calcd. for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.61; H, 8.32.

***trans*-5-*t*-Butylcycloöctanol (XIt).**—Six grams of XIc was dissolved in 35 ml. of dry pyridine. *p*-Toluenesulfonyl chloride, 6.22 g., was added and the solution was allowed to stand overnight at room temperature. The solution was cooled in ice, diluted with 250 ml. of cold 10% hydrochloric acid and the mixture was extracted with ether. The ether

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(30) O. Kamm and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 30.

(31) J. R. Ruhoff, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 292.

(32) R. Adams and C. S. Marvel, *J. Am. Chem. Soc.*, **42**, 310 (1920).

(33) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197, 2548 (1947).

(34) W. R. McEwen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 227.

(35) The apparatus is briefly described in ref. 12. For a detailed description see S. Greenberg, "Conformations of the Cycloöctane Ring," Ph.D. Thesis, Wayne State University, submitted 1959.

(36) K. Zeigler, H. Eberle and H. Ohlinger, *Ann.*, **504**, 94 (1933).

(37) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Fourth Edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 219.

extracts were washed with sodium bicarbonate solution and water, were dried and the solvent was evaporated. The residue was taken up in 125 ml. of dry acetone, 34 g. of tetraethylammonium acetate monohydrate[38] was added and the solution was heated under reflux for 16 hours. The bulk of the solvent was then removed by distillation and the residue was diluted with water. The mixture was extracted with ether. The ether solution was washed with water and the ether was evaporated. The residue was dissolved in 100 ml. of 95% ethanol containing 12 g. of potassium hydroxide and the solution was heated under reflux for 1.5 hours. The cooled solution was diluted with water and extracted with ether. The ether extracts were washed with water, the solution was dried and the ether was evaporated. The residue was dissolved in pentane and poured onto a column of 60 g. of alumina. The column was washed with pentane and gave an oil which is described below. The column was then washed with pentane–60% ether and gave 3.2 g. (53%) of XIt, m.p. about 45°. Repeated recrystallization from pentane at −20° raised the m.p. to 58.5–59.5°.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.24; H, 13.13.

The *p*-nitrobenzoate had m.p. 83.5–84.5°. The mixed melting point with the *p*-nitrobenzoate of XIc (m.p. 109.5–110°) was 74–79°.

Anal. Calcd. for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.15; H, 8.03.

Samples of XIc and XIt each weighing 100 mg. were oxidized with chromium trioxide in acetic acid and the ketone was isolated as the 2,4-dinitrophenylhydrazone. The purified compound in each case melted at 172–173° and gave no mixture melting point depression with the 2,4-dinitrophenylhydrazone of X.

***cis*-5-*t*-Butylcycloöctyl Acid Phthalate (XIIc).**—Compound XIc, 2.0 g., and 1.6 g. of phthalic anhydride were heated in 3 ml. of dry pyridine at 90° for 17 hours.[8] The cooled mixture was acidified with 10% hydrochloric acid, diluted with water and extracted with ether. The ether solution was washed with water, dried and the ether was evaporated. The residue was recrystallized from pentane and gave 3.06 g. (85%) of material, m.p. 86–87.5°. Three recrystallizations raised the m.p. to 88.5–89°.

Anal. Calcd. for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.66; H, 8.49.

***trans*-5-*t*-Butylcycloöctyl Acid Phthalate (XIIt).**—The alcohol was esterified as described for the preparation of XIIc; m.p. 121–122° (from ether–pentane).

Anal. Calcd. for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.11; H, 8.38.

Cycloöctyl Acid Phthalate (XIII).—The ester was prepared from cycloöctanol in a manner similar to that described for XIIc.[5] The ester was obtained as large dense crystals, m.p. 134–135°.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.69; H, 7.50.

Rates of Saponification.[8]—The temperature was constant to within ±0.03°. During each rate run approximately 2 meq. of ester was dissolved in 0.1 *N* sodium hydroxide solution at room temperature. The mixture was diluted to 100 ml. with the same solution of base, and aliquots were placed in Pyrex ampoules. The ampoules were sealed and placed in a constant temperature bath. After approximately 10 minutes, a sample was removed from the bath and cooled rapidly in Dry Ice. The time of removal from the bath was taken as zero and the concentration of base as determined by titration was taken as "*a*". The difference between "*a*" and the theoretical infinity titer was taken as "*b*." The quantity "*x*" was the difference between "*a*" and the concentration of base at time "*t*." Aliquots ordinarily were removed directly from the ampoules with a pipet; however, when the alcohol produced in the reaction solidified and obstructed the pipet it was found convenient to filter the mixture through a sintered glass funnel into a buret from which the aliquot was then removed. Excess base was titrated with 0.1 *N* potassium acid phthalate solution using cresol red indicator. Rate constants were calculated using the integrated form of the equation for a second-order reaction[39]

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

where t = elapsed time, a = initial concentration of base, b = initial concentration of ester and x = meq./ml. of ester saponified in time "t". The recovery of the pure alcohols from the saponification runs was 79%.

Rates of Chromic Acid Oxidation.[8]—The reaction mixture was prepared by dissolving approximately 1 meq. of alcohol in the chromic acid reagent and diluting the solution to 50 ml. with the same reagent at the reaction temperature. The chromic acid reagent was prepared by dissolving chromium trioxide in 75% acetic acid (three volumes of acetic acid to one volume of water) and standardizing against 0.01 *N* sodium thiosulfate solution. The rates of oxidation of the alcohols were followed by removing 5-ml. aliquots from the mixture, adding 0.5 ml. of 5% sulfuric acid and 1 ml. of 25% potassium iodide solution and titrating the liberated iodine with standard potassium thiosulfate using starch indicator. An excess of alcohol over chromic acid was employed to minimize oxidation of the ketone. Rate constants were calculated using the integrated form of the bimolecular rate equation in a manner similar to that described for saponification. Rate constants were evaluated employing oxidation–reduction normalities for alcohol and chromic acid concentrations. These rate constants were then multiplied[8] by the factor 3, and the adjusted values are listed in Table II. The units of k_2 in Table II are such as to represent the rate in moles of alcohol being oxidized per liter when concentrations of alcohol and chromium trioxide are each 1 *M*.

The alcohols used for the oxidation studies were obtained by saponification of the purified acid phthalate esters.

Oxidations were carried out in a manner similar to that employed in the rate runs and the ketones were isolated as the 2,4-dinitrophenylhydrazone in close to theoretical yield. After one recrystallization, the material had m.p. 165–168°, yield 65–72%. The mixture melting points with authentic 5-*t*-butylcycloöctanone 2,4-dinitrophenylhydrazone were undepressed.

Aluminum Isopropoxide Equilibration of XIc and XIt.—Alcohol XIc, 300 mg., was dissolved in 25 ml. of isopropyl alcohol (refluxed over and distilled from calcium oxide) containing 1 g. of redistilled aluminum isopropoxide and 3 drops of acetone. The solution was heated under reflux for 15 days. The cooled reaction mixture was diluted with 10% hydrochloric acid and extracted with pentane. The pentane extracts were washed with sodium bicarbonate solution and water and dried. Evaporation of the solvent gave a solid residue which was used directly for the infrared analysis. The analysis was carried out using the band at 11.15 μ for the *trans*, and the band at 11.70 μ for the *cis* isomer. Solutions of about 25% in carbon tetrachloride were used. The accuracy determined from known mixtures was ±3%.

The other isomer, XIt, was equilibrated exactly as described above. The identical equilibrium mixture was obtained from each isomer.

Description of Gas Phase Chromatography.—The column used for the separations described was about 7 feet in length and contained a packing made of 1,5-dicyano-3-methyl-3-nitropentane (22% by weight) adsorbed on 80–100 mesh base-washed firebrick. The column temperature was maintained at 101°.

Solvolysis of *cis*-5-*t*-Butylcycloöctyl *p*-Toluenesulfonate.—Alcohol XIc, 0.5 g., and 1.0 g. of *p*-toluenesulfonyl chloride were dissolved in 5 ml. of pyridine and the solution was allowed to stand overnight. The mixture was cooled in ice and diluted with cold water. The organic material was extracted with ether. The ether extracts were washed with 10% hydrochloric acid, sodium bicarbonate solution and water. The solution was dried, the ether was evaporated at room temperature under reduced pressure, the residue was taken up in 10 ml. of acetic acid containing 0.14 g. of anhydrous sodium acetate and the solution was heated under reflux overnight. The cooled reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with sodium bicarbonate solution and water. The ether solution was dried, concentrated to a volume of about 10 ml. and the resultant solution was heated under reflux for 3 hours with lithium aluminum hydride to reduce any acetates that may have formed. The cooled reaction mixture was decomposed with water followed by 10% hy-

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(38) J. Steigman and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 2536 (1937).

(39) S. Glasstone, "Textbook of Physical Chemistry," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1054.

drochloric acid, and the organic material was removed by extraction with pentane. The pentane solution was washed with sodium bicarbonate solution and water and was dried over a mixture of anhydrous potassium carbonate and anhydrous magnesium sulfate. The solution was filtered and poured onto a column containing 4 g. of alumina. The column was washed with *n*-pentane. The eluate was collected and the solvent was removed. The residual oil showed two sharp well resolved peaks upon vapor phase chromatography (see below) having retention times of 8 and 10 minutes. The addition of authentic 1-*t*-butylcycloöctene to the original oil augmented the 8-minute peak while the 10-minute peak was augmented when authentic 5-*t*-butylcycloöctene was so added. The ratio of the 8-minute peak to the 10-minute peak was 4:1 in the original oil.

The yield of olefin mixture is uncertain because of the difficulty of working with volatile material on a small scale. It is thought the yields of olefins were determined primarily by mechanical considerations, and the amount of acetates formed must have been very small.

Solvolysis of *trans*-5-*t*-Butylcycloöctyl *p*-Toluenesulfonate.—The solvolysis was carried out in a manner similar to that described for XIc. The oil isolated in this case showed the same two sharp well-defined peaks with retention times of 8 and 10 minutes, respectively. In this case, the ratio of 8-minute compound to 10-minute compound was 1:2.

Stability of the Olefins under Solvolysis Conditions.—5-*t*-Butylcycloöctene, 100 mg., was heated under reflux overnight in 5 ml. of acetic acid containing 100 mg. of anhydrous sodium acetate and 10 mg. of *p*-toluenesulfonic acid. The cooled reaction mixture was diluted with water, 5% hydrochloric acid was added and the solution was subjected to a work-up similar to that described above for solvolysis of the *p*-toluenesulfonate of XIc, except the lithium aluminum hydride treatment and the subsequent chromatography was omitted. Gas phase chromatography showed that the olefin survived the treatment unchanged.

The same control experiment was carried out with 1-*t*-butylcycloöctene and again the material was unchanged.

A mixture of 3-*t*-butylcycloöctene and 4-*t*-butylcycloöctene was prepared by pyrolysis of 3-*t*-butylcycloöctyl acetate.[40] It was shown that these two olefins were separable from the 1- and 5-*t*-butylcycloöctenes by vapor phase chromatography, and it was established that they were not present in significant amount in the solvolysis products of the 5-*t*-butylcycloöctyl tosylates.[40]

***t*-Butylcycloöctane *via* Wolff–Kishner Reduction[41] of 5-*t*-Butylcycloöctanone.**—5-*t*-Butylcycloöctanone, 0.05 g., was heated under reflux for 1.5 hours in 5 ml. of diethylene glycol containing 350 mg. of anhydrous hydrazine and 400 mg. of potassium hydroxide. A few drops of material was allowed to distil while the temperature of the heated bath was raised to 210° and the mixture was heated under reflux at this temperature for 6 hours. The cooled mixture was diluted with water and the hydrocarbon was steam distilled. The distillate was diluted with pentane and the pentane layer was washed with 10% hydrochloric acid, sodium bicarbonate solution and water. The solution was dried, the pentane was evaporated and the residue was distilled to yield 210 mg. of product at a bath temperature of 120° (21 mm.), $n^{25}\mathrm{D}$ 1.4647.

5-*t*-Butylcycloöctane from Hydrogenation of 1-*t*-Butylcycloöctene.—1-*t*-Butylcycloöctene, 0.5 g., was reduced with hydrogen in the presence of platinum oxide in acetic acid solution. The solution was filtered and diluted with water. The mixture was extracted with pentane and the pentane phase was washed with sodium bicarbonate solution then water. The pentane solution was dried, the solvent was evaporated and the residue was distilled at a bath temperature of 130° (25 mm.), $n^{25}\mathrm{D}$ 1.4620. The infrared spectrum was identical with that of the sample obtained from Wolff–Kishner reduction of X.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.62; H, 14.37. Found: C, 85.68; H, 14.11.

5-*t*-Butylcycloöctanone Oxime.—Hydroxylamine hydrochloride, 1.15 g., and anhydrous sodium acetate, 1.64 g., were mixed with 3.0 g. of ketone X in 25 ml. of 60% methanol. The mixture was warmed on a steam-bath for several minutes with occasional shaking. The mixture was allowed to cool and crystals slowly formed. When crystallization appeared to be complete 35 ml. of water was added and the mixture was stored at 0° overnight. The precipitate was collected; wt. 3.07 g. (94.5%), m.p. 82–86°. Several recrystallizations from pentane raised the melting point to 89–90°.

Anal. Calcd. for $C_{12}H_{23}NO$: C, 73.05; H, 11.75. Found: C, 73.13; H, 11.45.

5-*t*-Butylcycloöctylamine.—5-*t*-Butylcycloöctanone oxime, 3.70 g., in 50 ml. of anhydrous tetrahydrofuran containing 0.59 g. of lithium aluminum hydride was heated under reflux with stirring overnight. The cooled reaction mixture was decomposed by the addition in order of 1 ml. of water, 1 ml. of 15% sodium hydroxide solution and 3 ml. of water. The solution was filtered, the filtrate was diluted with water and the resultant mixture was extracted with ether. The ether extracts were dried and the solvent was evaporated. Distillation furnished 2.3 g. (81%) of amine, b.p. 115–119° (7 mm.), $n^{25}\mathrm{D}$ 1.4859. For analysis the oxalate salt was prepared by mixing ether solutions of the amine and anhydrous oxalic acid. The precipitate was collected and recrystallized twice from ethanol; m.p. 273–274° (dec., sealed tube).

Anal. Calcd. for $C_{26}H_{52}N_2O_4$: C, 68.40; H, 11.48. Found: C, 68.28; H, 11.53.

N,N-Dimethyl-5-*t*-butylcycloöctylamine.—5-*t*-Butylcycloöctylamine, 2.3 g., was added to 2.7 ml. of 88% formic acid. To this solution was added 3.8 ml. of 30% formaldehyde. The resulting mixture was heated at 100° for a few minutes until vigorous bubbling commenced. The flask was removed from the bath until the reaction subsided and was then reimmersed and heated at 90–100° overnight. Concentrated hydrochloric acid, 2 ml., was added to the resultant cooled solution and the volatile material was removed. Ten ml. of water was then added to the residue followed by a solution of 3 g. of potassium hydroxide in 10 ml. of water. The resultant mixture was extracted with ether. The ether layer was washed with water, dried and the solvent was evaporated. Distillation of the residue furnished 2.1 g. (79%) of product, b.p. 125–140° (7 mm.), $n^{25}\mathrm{D}$ 1.4800.

***cis*-5-*t*-Butylcycloöctene.**—To a solution of 2.1 g. of N,N-dimethyl-5-*t*-butylcycloöctylamine in 5 ml. of methanol cooled in an ice-bath was added 3.5 ml. of 30% hydrogen peroxide. The mixture was stirred for 20 hours and allowed to warm to room temperature. The excess hydrogen peroxide was then destroyed by the addition of a few mg. of platinum black. The filtered solution was concentrated under reduced pressure at 40°. The residual amine oxide was then decomposed at a pressure of 25 mm. Decomposition commenced at about 110°. The temperature of the bath was gradually raised to 200° and the pressure was then lowered to 7 mm. to ensure distillation of all volatile material. The distillate was diluted with pentane and the solution was washed with 10% hydrochloric acid followed by sodium carbonate solution, then water. The dried and filtered pentane solution was concentrated and the product was distilled; wt. 330 mg. (20%), b.p. 105–110° (20 mm.), $n^{25}\mathrm{D}$ 1.4735.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.75; H, 12.81.

Vapor phase chromatography of this olefin gave three peaks, the larger peak corresponding to 99% of the material, with smaller peaks, one before and one after the major peak. The minor peak of low retention time corresponded to 1-*t*-butylcycloöctene. The minor peak of higher retention time may correspond to *trans*-5-*t*-butylcycloöctene, since in a sample of olefin which had stood for 6 months this peak had essentially vanished.

1-*t*-Butylcycloöctanol.[42]—A suspension of 8.3 g. of lithium metal in 100 ml. of mineral oil was heated until the lithium melted and was powdered by vigorous stirring and cooling. Pentane, 200 ml., was added to the suspension and then 55.6 g. of *t*-butyl chloride in pentane was added with stirring during a 2-hour period. A solution of 14 g. of cycloöctanone in pentane was added to the mixture dropwise and the resulting mixture was heated under reflux with continued stirring overnight. The reaction mixture was treated with saturated ammonium chloride and the organic layer was separated and washed with water. The solvent was evaporated from the dried solution and the residue was distilled and gave 5 g. of recovered cycloöctanone, b.p. 75–80° (11 mm.), followed by

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[40] I. J. Lillien, unpublished work.

[41] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[42] A. C. Cope and H. O. VanOrden, *J. Am. Chem. Soc.*, **74**, 175 (1952).

8 g. (68% based on ketone not recovered) of the desired alcohol, b.p. 118–120° (11 mm.), $n^{25}D$ 1.4860. The alcohol solidified upon standing.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.16; H, 12.85.

1-*t*-Butylcycloöctene.[42]—A solution of 3.2 g. of 1-*t*-butylcycloöctanol and 60 mg. of iodine in 25 ml. of toluene was heated under reflux for 17 hours. The water formed was removed with a Dean–Stark trap. The toluene was distilled and the residue was diluted with pentane. The pentane solution was washed with sodium thiosulfate solution followed by water. After drying the solution, the pentane was evaporated and the product was distilled; wt. 1.9 g. (66%), b.p. 88–89° (11 mm.), $n^{25}D$ 1.4750.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.39; H, 13.48.

N.m.r. spectra were obtained at 60 mc. in deuteriochloroform solvent with internal tetramethylsilane reference.

[CONTRIBUTION NO. 1038 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY, BLOOMINGTON, IND.]

The Mechanisms of Substitution of Propargylic Halides. 3-Bromo-3-methyl-1-butyne[1]

BY V. J. SHINER, JR.,[2] AND JOSEPH W. WILSON[3]

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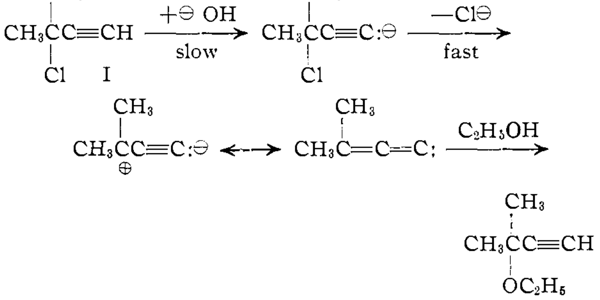
A study of the kinetics, salt effects, deuterium exchange with the solvent and product proportions shows that the base-promoted solvolysis of 3-bromo-3-methyl-1-butyne in 80% aqueous ethanol proceeds through at least three stages involving successively the conjugate base, the zwitterion-carbene, and the products, ethyl ether and carbinol. The initially neutral solvolysis involves the usual carbonium ion mechanism.

Introduction

A special mechanism involving an unusual zwitterion-carbene intermediate has been proposed by Hennion and Maloney[4,5] for the *second-order* reaction of a *tertiary* propargylic halide, 3-chloro-3-methyl-1-butyne (I) with sodium hydroxide in "80%" aqueous ethanol.



Two observations formed the original basis for this proposal: (1) a comparison of the kinetic behavior of this chloride with that of saturated analogs and (2) the nature of the products of the second-order reaction. The saturated analog, *t*-amyl chloride, was found to solvolyze in initially neutral "80%" aqueous ethanol at 25° *61 times faster* than the acetylenic chloride. Whereas the addition of sodium hydroxide at moderate concentration is known not to affect drastically the solvolysis rate of simple tertiary alkyl halides,[6] Hennion and Maloney noted that the propargylic halide I showed a fairly rapid second-order reaction with added base. The chief product of this process, isolated in 56.6% yield, was the ethyl ether of 2-methyl-3-butyne-2-ol.

Because the Hennion mechanism requires the presence of an unsubstituted ethynyl group (—C≡C—H), the report by Burawoy and Spinner[7] that the compound related to I by replacement of the acetylenic hydrogen with a methyl group (4-chloro-4-methyl-2-pentyne, II) showed "saturated behavior" (a fast first-order reaction that was unaffected by added base) in its replacement reaction was later cited by Hennion[5] as providing strong supporting evidence for his mechanism. Without commenting on Hennion's earlier proposal Burawoy and Spinner[7] had, however, suggested that "the alkaline hydrolysis of 3-chloro-3-methyl-1-butyne in 80% aqueous ethanol. . .occurs by a bimolecular (SN2) mechanism."

Indeed, although the arguments for the Hennion mechanism seemed most reasonable, they did not appear completely compelling and a case could be advanced for the belief that the SN2 mechanism obtained. First, the relationship between the nature of the products and the mechanism of their formation is ambiguous because of the equilibrium:

$$CH_3CH_2\text{-}O^- + H_2O \rightleftharpoons CH_3CH_2\text{-}OH + {}^-OH$$

It has been estimated that only about 60% of the stoichiometric base concentration in 80% ethanol is in the form of the hydroxide ion.[8,9] Since ethoxide may be a better nucleophile than hydroxide toward saturated carbon, as it is toward carbonyl carbon,[10] a direct displacement predominantly by ethoxide ion cannot be ruled out. Second, there is the possibility that the ethynyl group with its greater electronegativity and smaller size than an alkyl group could promote an SN2 attack. Several authors have argued that electron-withdrawing substituents

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(1) (a) Taken from the thesis submitted by Joseph W. Wilson to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Presented in part before the Division of Organic Chemistry at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 3, 1961. (c) Supported in part by Grant G 5062 from the National Science Foundation, Washington, D. C.

(2) Alfred P. Sloan Research Fellow.

(3) Dow Fellow, 1960–1961.

(4) G. F. Hennion and D. E. Maloney, *J. Am. Chem. Soc.*, **73**, 4735 (1951).

(5) G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

(6) C. A. Bunton and B. Nayak, *J. Chem. Soc.*, 3854 (1959).

(7) A. Burawoy and E. Spinner, *ibid.*, 3752 (1954).

(8) E. F. Caldin and G. Long, *ibid.*, 3737 (1954).

(9) R. G. Burns and B. D. England, *Tetrahedron Letters*, **24**, 1 (1960).

(10) M. L. Bender and W. A. Glasson, *J. Am. Chem. Soc.*, **81**, 1590 (1959).