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Conformational Analysis. LXVI. Some Studies Involving the 3-*t*-Butylcyclooctyl Ring System[1]

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3-*t*-Butylcyclooctyl tosylate (one stereoisomer) was prepared and solvolyzed in acetic acid and in 80% ethanol, and the solvolysis rates of this compound and related compounds were measured. Very little transannular hydride transfer was observed. Of the olefins obtained, 3-*t*-butylcyclooctene predominated strongly over the 4 isomer, and this predominance appears to result from a subtle steric effect. The other stereoisomer of 3-*t*-butylcyclooctanol could not be obtained in spite of many attempts. Reaction of the tosylate with tetramethylammonium acetate under conditions known to give mainly inversion of configuration with other compounds (including other cyclooctyl compounds) here appeared to give largely retention of configuration (plus much elimination) presumably *via* an SN mechanism.

The relatively unusual physical and chemical properties of the eight-membered ring have long been known, and are considered to be largely due to conformational effects.[3] Actual definitive evidence concerning the conformation of cyclooctane derivatives is scarce, however. From crystallographic studies, it is known that a boat–chair conformation is preferred in two particular cases.[4] The most detailed theoretical calculations carried out to date on the cyclooctane ring suggest that this conformation is either the one of lowest energy, or very close to it.[5] There are two other conformations which have calculated energies within 2 kcal of that of the boat–chair in the case of cyclooctane itself, and it seems likely that these conformations will be observed in due course in substituted molecules.

Cope and coworkers found many years ago[6] that cyclooctane rings undergo transannular reactions, in which hydride ions were observed to migrate 1,5 across the ring when an electron-deficient center was generated, and, in the case of acid-catalyzed ring openings of cyclooctane epoxides, both 1,5 and 1,3 hydride transfers were observed. Additional studies have shown that *cis*-5-*t*-butylcyclooctyl tosylate solvolyzes at a very much faster rate than does cyclooctyl tosylate itself, and, during the solvolysis, nearly 100% transfer of a hydride from C-5 to C-1 occurs.[7] Models show very clearly that it is quite easy for the hydrogen at C-5, which is *trans* to the leaving group, to move over and displace the leaving group in an inversion process. Models also show that it is quite difficult to obtain a reaction of this sort in a simply substituted cyclooctane ring from a hydride at C-3. Cope[8] determined the percentages of 1,5 *vs.* 1,3 hydride transfer in the ring opening of 5,6-d_2-*cis*-cyclooctene oxide, which were found to be 61 and 39%, respectively. However, the epoxides are highly deformed cyclooctanes, and their behavior is not necessarily that to be expected from simply substituted cyclooctanes.

That the hydride transfer observed with *cis*-5-*t*-butylcyclooctyl tosylate occurs from C-5 rather than from C-3 can be interpreted in terms of the stability of the carbonium ion formed after the hydride has migrated. If the migration occurs from C-5, the resulting carbonium ion is tertiary, whereas, if the hydride ion had migrated from C-3, the carbonium ion would have been secondary. That the hydride migrates exclusively from C-5, therefore, can be understood easily enough quite apart from the details of the conformational properties of the ring.

Since models suggest that a hydride transfer from C-3 is not sterically so feasible as it would be from C-5, one might ask what results would be expected from the solvolysis of 3-*t*-butylcyclooctyl tosylate. Carbonium ion stability indicates that hydride transfer from C-3 should occur, but the steric situation in the molecule suggests that this is not feasible, and, on that basis, participation would not be expected. The actual situation was investigated in the present work by means of a rate and product study.

Discussion

2-Cyclooctene-1-one[9] underwent conjugate addition of *t*-butylmagnesium chloride to furnish 3-*t*-butylcyclooctanone (I) in 74% yield. Lithium aluminum hydride reduced the ketone I to 3-*t*-butylcyclooctanol (II) in 84% yield. The latter, after distillation and recrystallization from pentane, showed a melting point of 43–44°.

When the *p*-nitrobenzoate of II was prepared, recrystallized, and then hydrolyzed to give back the

(1) This research was supported by Grant 2916 from the Petroleum Research Fund administered by the American Chemical Society. Part LXV: N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **91**, 337 (1969).

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(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1966, p 210.

(4) J. D. Dunitz and A. Mugnoli, *Chem. Commun.*, 166 (1966).

(5) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964); K. B. Wiberg, *ibid.*, **87**, 1070 (1965); N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968).

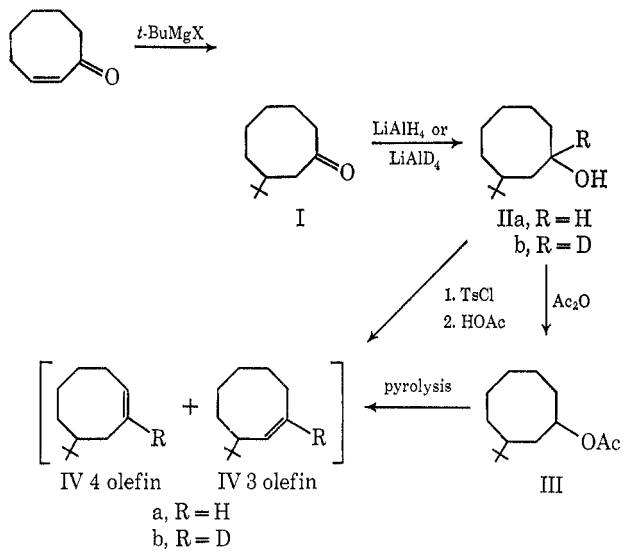
(6) For a review, see A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966).

(7) N. L. Allinger and S. Greenberg, *J. Amer. Chem. Soc.*, **84**, 2394 (1962); N. L. Allinger and W. Szkrybalo, *Tetrahedron*, **24**, 4699 (1968).

(8) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Amer. Chem. Soc.*, **82**, 6366 (1960).

(9) A. C. Cope, M. R. Kinter, and R. T. Keller, *ibid.*, **76**, 2757 (1954).

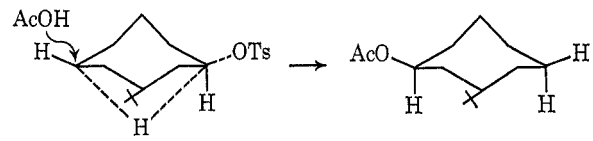
starting alcohol, material of the same melting point was obtained. The infrared spectrum of the alcohol recovered after purification through the nitrobenzoate was the same as prior to this treatment. The alcohol showed only one peak on vapor phase chromatography on a variety of columns under different conditions. It was therefore judged as most probable that the alcohol



obtained was a single stereoisomer. However, the possibility that the material is in reality an inseparable mixture of stereoisomers had to also be considered. With the 5-*t*-butylcyclooctanols, one isomer was easily obtained by methods similar to those above, and the other isomer was most easily obtained by converting the first isomer into the tosylate and then displacing the tosyl group with tetramethylammonium acetate, which gave an inverted configuration in good yield. When a similar reaction sequence was tried with the 3-*t*-butylcyclooctyl tosylate, the acetate obtained (in only 20% yield) was identical with that prepared by acetylation of the starting alcohol. Furthermore, saponification and esterification of the resulting alcohol with *p*-nitrobenzoyl chloride gave the *p*-nitrobenzoate of the starting alcohol (by melting point and mixture melting point). Thus it would seem that an SN1 reaction had occurred with essentially complete retention of configuration. This is quite an unusual circumstance, but it is known to happen in at least a few other cases.[10]

We were never able to isolate the other stereoisomer of 3-*t*-butylcyclooctanol, nor were we able to establish with certainty which stereoisomer we had in hand. We are reasonably certain that it was, however, a single pure (racemic) stereoisomer, on the basis of several experiments to be described below, and because persistent efforts to separate it into two compounds always resulted in failure.

In an attempt to convert the 3-*t*-butylcyclooctanol into its epimer, the compound was treated with aluminum isopropoxide under conditions which bring about the epimerization of 5-*t*-butylcyclooctanol. No change in the compound appeared to occur, judging by the fact that the infrared spectrum and the vapor phase chromatogram of the compound were not changed. Thus it appeared that the solvolysis had gone with *retention* of configuration. Since it is most unusual for an SN1 (or an SN2) reaction to go with *retention* of configuration, the following possibility was considered. If the attack by acetate were at the 5



position, and a simultaneous hydride transfer occurred as the tosylate ion departed (in analogy to the predominant reaction of the 5-*t*-butyl isomer), it would be conceivable that the apparent retention of configuration would be in fact due to a double inversion. This possibility was eliminated by preparing the 1-deutero-3-*t*-butylcyclooctyl tosylate and treating it under these circumstances. If a 1,5 hydride shift had occurred, the product would be the acetate of 3-*t*-butyl-5-deuterio-cyclooctanol. The infrared spectrum of the product was identical with that of 1-deuterio-3-*t*-butylcyclooctyl acetate, however.

By the usual criteria, the 3-*t*-butylcyclooctanol is a single pure diastereomer. However, it has been noted previously that the *cis–trans* isomers of cyclooctane derivatives differ very little in energy.[4,11] It is therefore unclear why we are not able to isolate a second diastereomer, and the possibility that the isolated compound is a mixture of diastereomers needs careful consideration. If it is, the mixture apparently contains close to equilibrium amounts of the two diastereomers, and is nicely crystalline both as the alcohols and as the *p*-nitrobenzoates.

Results

Our previous solvolysis work on related compounds, and also the preparative work, has been done in glacial acetic acid with acetate buffer. Rough values for rate constants were obtained in acetic acid, but it was found for instrumental reasons that the rates could be more easily determined in alcohol. The relative rates are qualitatively similar in either solvent. For quantitative rate constants, the solvolysis rates of a number of cyclooctyl tosylates were determined in 80% ethanol, and the results are summarized in Table I.

TABLE I

Compd	Rate constant, sec^{-1}	Relative rate
2-Pentyl tosylate	3.2×10^{-6}	1
cis-5-*t*-Butylcyclooctyl tosylate	9.97×10^{-4}	312
trans-5-*t*-Butylcyclooctyl tosylate	2.92×10^{-5}	9.1
Cyclooctyl tosylate	1.26×10^{-4}	39
3-*t*-Butylcyclooctyl tosylate	5.46×10^{-4}	171

A comparison of the numbers of Table I shows that, relative to a simple open-chain tosylate, cyclooctyl tosylate solvolyzes quite rapidly. This is one of the classical manifestations of I strain,[12] the unfavorable torsional situation being relieved to some extent as the cyclooctyl derivative is converted into a transition state

(10) D. J. Cram and F. L. Harris, Jr., *J. Amer. Chem. Soc.*, **89**, 4642 (1967); P. von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 4197 (1964); E. H. White and F. W. Bachelor, *Tetrahedron Lett.*, **77**, (1965), and references cited therein.

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

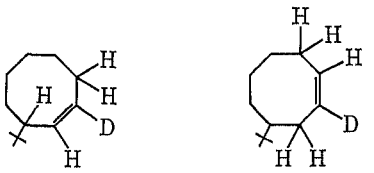
(12) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *ibid.*, **73**, 212 (1951); H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

with a carbonium ion type of geometry. *trans*-5-*t*-Butylcyclooctyl tosylate solvolyzes about one-fourth as rapidly as cyclooctyl tosylate itself, and this would seem to be due to a small unfavorable steric effect. It is known[7] that very little rearrangement accompanies this solvolysis. The *cis* isomer of 5-*t*-butylcyclooctyl tosylate, on the other hand, solvolyzes about eight times faster than cyclooctyl tosylate, and is almost completely rearranged by a 1,5 hydride transfer. It seems likely that neighboring-group participation is being observed in this case, although the rate difference is not sufficient to unequivocally rule out a steric effect.

In the present work, we found that 3-*t*-butylcyclooctyl tosylate solvolyzes about four times faster than cyclooctyl tosylate, or a little over one-half as fast as *cis*-5-*t*-butylcyclooctyl tosylate. However, the olefin mixture obtained from 3-*t*-butylcyclooctyl tosylate shows that only about 1% of a 1,3-hydride transfer has occurred. Thus the fast rate is best not attributed to neighboring-group participation, but must be a result of steric effects in the ring system.

There are two olefins that would be expected to be formed from a simple elimination reaction by 3-*t*-butylcyclooctyl derivatives: 3-*t*-butyl- and 4-*t*-butylcyclooctene. These compounds are not independently known, but a mixture of them was prepared by pyrolysis of 3-*t*-butylcyclooctyl acetate. From that reaction, two compounds were obtained which appeared to be *t*-butylcyclooctenes, and upon hydrogenation they gave material which appeared to be *t*-butylcyclooctane, from the retention time on vpc. The two *t*-butylcyclooctenes obtained from this pyrolysis were different from 1-*t*-butylcyclooctene and from 5-*t*-butylcyclooctene, both of which were known from previous work. They were characterized by their nmr spectra, and each showed a *t*-butyl group with nine equivalent protons and two vinyl hydrogens. The question as to which was 3-*t*-butyl- and which was 4-*t*-butylcyclooctene was more difficult, as indicated below.

When the solvolysis of 3-*t*-butylcyclooctyl tosylate was carried out in acetic acid, and the product then subjected to vpc, there was observed about 1% 1-*t*-butylcyclooctene, about 1% an unidentified compound, 66% the acetate of 3-*t*-butylcyclooctanol, 31% 4-*t*-butylcyclooctene, and 1% 3-*t*-butylcyclooctene. In different runs the ratio varied somewhat, but it was noteworthy that the 4-*t*-butylcyclooctene always *strongly* predominated over the 3 isomer. We were unable to deduce from a study of models which isomer would be preferentially formed, and, while this preference must be the result of a conformational effect, it does not appear to us to be any simple, obvious one. It was therefore felt desirable to establish experimentally which of the olefins was 3-*t*-butyl- and which was 4-*t*-butylcyclooctene. In order to do this, 1-deuterio-3-*t*-butylcyclooctanol was prepared by reduction of 3-*t*-butylcyclooctanone with lithium aluminum deuteride. This alcohol was converted into the tosylate and the latter was solvolyzed as previously. Two olefins [IV-3(b) and IV-4(b)] were isolated as before, and they were clearly of the structures indicated; the problem was to determine which was which. This was done by examining their nmr spectra, and particularly by considering the vinyl hydrogens. It can be seen that IV-3(b) has only one proton vicinal to the vinyl hydrogen, while IV-4(b)



IV-3 (b) IV-4 (b)

has two. The former should, therefore, to the first-order approximation, show a doublet in the vinyl region, while the latter should show a quartet (or a triplet if the coupling constants are accidentally the same), and the coupling constants should be in the range of 4–10 cps. Such an interpretation is not expected to be completely adequate, however, because allyl coupling of the type H_a—C—C=C—H_b generally has J_{ab} in the range of 0–3 cps.[13] Several other long-range couplings of the order of 0–1 cps are also to be expected.

The nmr spectra of these compounds showed them both to be *t*-butylcyclooctenes, since they each showed a sharp singlet at δ 0.88 (*A* 9), a broad complex methylene resonance at δ 1.06–2.44 (*A* 11), and a complex vinyl resonance at *ca.* δ 5.45 (*A* 1).

The nmr spectrum of the compound assigned structure IV-4(b) showed the vinyl proton as a multiplet, which appeared as a large central peak flanked on each side by two peaks, similar in height and half as high as the central peak. Additional fine structure was also present. The interpretation given is a triplet (J = 6.9 cps) further split into doublets (J = 3.0 cps). This interpretation is not completely convincing, but it appears to be the best available.

The compound assigned the IV-3(b) structure showed the vinyl proton as a doublet of triplets, with the spacing between the components of the doublet 10.0 cps, and the spacings between the components of the triplets 1.2 cps. In addition, five sharp peaks were scattered across the vinyl region, and accounted for about 10% of the total area. Since this compound was only obtained in very small yield, we suspect that these extra peaks are impurities. The nmr spectra are unfortunately rather complex, and we do not regard our structural assignments as completely unequivocal.

Even accepting that 4-*t*-butylcyclooctene predominated very largely over the 3 isomer in the solvolysis products of 5-*t*-butylcyclooctyl tosylate, a study of models still led to no conclusive results regarding the conformation of the ring and/or the substituents during the solvolysis reaction. It may well be that what we are observing here is a thermodynamic effect, rather than something characteristic of the reaction. 3,3-Dimethylcyclohexene is known to be more stable than the 4 isomer by about 1 kcal,[14] and a related sort of effect may be present with the olefins being studied here.

This work has raised some questions which we are unable to answer. It is disappointing to be unable to explain the apparent preponderance of one diastereomer

(13) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 145.

(14) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **90**, 5773 (1968).

of 3-*t*-butylcyclooctanol over the other, which seems to result from both thermodynamic and kinetic control. The conformations of the ring which are possible, their relative energies, and the conformational energies of attached substituents[15] are believed to be fairly well understood, but do not suffice to explain the observed facts. The strong predominance of 4-*t*-butylcyclooctene over the 3 isomer in the solvolysis reactions also remains poorly understood.

We are, however, able to draw some definite conclusions. Hydride migration from the 3 position of cyclooctyl tosylate does not occur to any appreciable extent during solvolysis,[16] and placing a *t*-butyl group at C-3 so that the carbonium ion generated by the hydride migration is tertiary, rather than secondary, does not substantially alter the situation. The rate of reaction here, where neighboring-group participation appears to be insignificant, is only a factor of two less than in *cis*-5-*t*-butylcyclooctyl tosylate solvolysis, which indicates that the fast rate of the latter does not have to result from participation, but may be a result of a simple steric effect of the *t*-butyl group.

Experimental Section

All infrared spectra were determined on liquid films, and nmr spectra in $CDCl_3$ solvent with TMS standard.

2-Cycloocten-1-one.[17]—This compound was prepared in 50–55% yield *via* Oppenauer oxidation of 2-cycloocten-1-ol. It was freed from residual traces of alcohol by chromatographing on Merck acid-washed alumina and eluting with pentane, bp 52–56° (0.5 mm), $n^{26}D$ 1.4960 (lit.[15] $n^{25}D$ 1.4953).

3-*t*-Butylcyclooctanone (I).—A 29-g sample of 2-cyclooctan-1-one in 50 ml of ether was added dropwise with good stirring to the Grignard reagent prepared from 55.2 g of *t*-butyl chloride and 16 g of magnesium in 500 ml of ether, maintained at −20 to −30°. Stirring was then continued overnight while the reaction mixture was allowed to come to room temperature. The mixture was hydrolyzed with a saturated ammonium chloride solution, and the ether layer was removed, washed, and dried. Evaporation of the ether left an oil, which after two passes through a column of Merck acid-washed alumina in pentane solution showed only a little OH absorption in the infrared. The oil was distilled through a small column. After a small forerun, the major fraction was collected at 62–63° (0.5 mm). The product was free of OH and conjugated ketone absorption in the infrared: yield 31.5 g (73.9%); $n^{22}D$ 1.4760; λ_{max} 5.87 (CO) and 7.30 μ (*t*-butyl).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.12; H, 12.09. Found: C, 79.25; H, 12.08.

The *p*-nitrophenylhydrazone of 3-*t*-butylcyclooctanone, recrystallized from ethyl acetate–petroleum ether, had a melting point of 165–166°.

Anal. Calcd for $C_{18}H_{27}N_3O_2$: C, 68.14; H, 8.52. Found: C, 68.10; H, 8.62.

3-*t*-Butylcyclooctanol (II).—To a stirred slurry of 1.52 g of lithium aluminum hydride in 200 ml of ether was added 4 g of 3-*t*-butylcyclooctanone in 100 ml of ether at a rate sufficient to maintain gentle reflux. The mixture was stirred for 1 hr, after which time the excess lithium aluminum hydride was decomposed by ethyl acetate followed by water, the solution was dried, and the solvent was evaporated, leaving a viscous oil which resisted attempts at crystallization. It was distilled at reduced pressure: yield 3.4 g (84%); bp 92–94° (1.5 mm); $n^{21}D$ 1.4834; ir 3.1 (OH), 7.32 (*t*-butyl), and 9.51 μ (CO). This material was purified through the *p*-nitrobenzoate (see below). It was later found that the distillate could be induced to solidify by seeding. The solid was contaminated with a small amount of oil at room temperature, and could be purified by crystallizing from pentane. Either way, the alcohol had a melting point of 45–46°.

Attempted Equilibration of the *cis* and *trans* Isomers of II.—A solution of 500 mg of crystalline II, 250 mg of aluminum isopropoxide, and 1 drop of acetone were dissolved in 25 ml of isopropyl alcohol, and the solution was heated under reflux for 45 hr. The solvent was evaporated, the residue was poured into 100 ml of water, and the solution was extracted with ether. The ether layer was separated, washed with water, and dried over sodium sulfate. After evaporation of the solvent, the residual oil crystallized, yield 470 mg, mp 45–46°. The infrared spectrum and the vpc showed the product to be indistinguishable from II. Under the same conditions *cis*-5-*t*-butylcyclooctanol was converted into a mixture of the *cis* and *trans* epimers.

Attempted Epimerization of 3-*t*-Butylcyclooctanol.—A solution of 0.9 g of the pure crystalline tosylate of II (see below) and 5 g of tetraethylammonium acetate monohydrate in 100 ml of dry acetone was stirred for 7 days at room temperature, and then the mixture was heated under reflux for 1 hr. The solution was reduced in volume, and the mixture was poured into water and extracted with ether. The ether extracts were separated, washed, and dried over sodium sulfate, and the ether was evaporated under reduced pressure, leaving 5 g of residual oil. Analysis of this oil was carried out on an 8-ft, 10% Carbowax column at 180°. There were three major peaks, two olefins and the acetate, with retention times of 1.5, 2.0, and 12.0 min. The peak areas of total olefin to acetate were in the ratio 5.3:1.

A solution of 0.5 g of potassium hydroxide in 8 ml of ethanol was added to the oil, and the solution was refluxed for 1 hr and allowed to stand overnight. A 100-ml portion of water was added to the solution, which was extracted with ether. The ether layer was separated, washed, and dried and the ether was evaporated, leaving 0.4 g of an oil. The oil was taken up in 2.5 ml of dry pyridine, and 0.4 g of *p*-nitrobenzoyl chloride was added. The solution was allowed to stand overnight and then diluted with 50 ml of water, and the precipitated oil was extracted with benzene. The benzene layer was washed with dilute hydrochloric acid and then with water, and the benzene was evaporated under reduced pressure. The residual oil was then crystallized from ethanol and recrystallized from ethyl acetate, yield 122 mg, mp 94–94.5°. The infrared spectrum was identical with that of an authentic sample of the *p*-nitrobenzoate of II, and they showed no mixture melting point depression.

Under the same reaction conditions, *cis*-5-*t*-butylcyclooctanol was converted into the *trans* isomer in good yield.

3-*t*-Butylcyclooctyl Acetate (III).—Alcohol II, 1.7 g, was heated under reflux with 1.1 g of acetic anhydride in 5 ml of pyridine for 12 hr. The solution was cooled and treated with 10% hydrochloric acid until no pyridine odor remained. The solution was then extracted with ether, and the ether extracts were washed with water, sodium bicarbonate, and water and dried. The residual oil showed a weak OH bond in the infrared, and was therefore dissolved in pentane, and the solution was passed through a calcium chloride column twice. The residual oil was distilled: bp 110–111° (3 mm); $n^{25}D$ 1.4566; ir 5.75 (CO), 7.28 (*t*-butyl), and 8.0 μ (acetate).

Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.34; H, 11.59. Found: C, 74.65; H, 11.51.

Pyrolysis of Acetate III.—3-*t*-Butylcyclooctyl acetate was pyrolyzed by dripping the neat liquid under a positive pressure of nitrogen onto a 7 × 0.5 in. column packed with glass helices heated at 511°. The effluent vapor was condensed in a Dry Ice trap. The condensate was taken up in ether, which was washed with sodium carbonate and water and dried. After evaporation of the solvent, the residual oil was distilled twice. The final fraction was collected at 68–80° (6 mm). The infrared spectrum was free of OH or CO absorption. Vpc analysis is discussed below.

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.38; H, 13.11.

A mixture of 3- and 4-*t*-butylcyclooctene was prepared by an unambiguous route: pyrolysis of 3-*t*-butylcyclooctyl acetate. Hydrogenation of this mixture gave *t*-butylcyclooctane, which was identified by comparison with authentic sample on vpc.

Vapor Phase Chromatography of the Acetate Pyrolysis Product.—A 7-ft column packed with 25% of the tricyanoethylation product of glycerol on firebrick at 100° was used. The product from the acetate pyrolysis was resolved into three major peaks, with retention times of 4.55, 10.20, and 16.15 min. The first peak is believed to be an acyclic diene, analogous to that found earlier by Bloomquist from the pyrolysis of cyclooctyl acetate.[18]

(15) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7043 (1967).
(16) A. C. Cope and D. M. Gale, *ibid.*, **85**, 3747 (1963).
(17) A. C. Cope, M. R. Kinter, and R. T. Keller, *ibid.*, **76**, 2757 (1954).
(18) A. T. Blomquist and P. R. Taussig, *ibid.*, **77**, 6399 (1955).

The peaks at 10.2 and 16.15 min are assigned the 4- and 3-*t*-butylcyclooctene structures, respectively.

3-*t*-Butylcyclooctyl *p*-Nitrobenzoate.—The oily product from the lithium aluminum hydride reduction of 1.0 g of 3-*t*-butylcyclooctanone was dissolved in 60 ml of dry pyridine, and 10.6 g of *p*-nitrobenzoyl chloride was added with shaking. After standing for 6 hr, the solution was poured into water and the precipitate was collected and carefully recrystallized from ethanol and then from pentane, mp 94–95°. Further recrystallization did not raise the melting point.

Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16. Found: C, 68.29; H, 8.43.

3-*t*-Butylcyclooctanol.—A 3-g sample of the above *p*-nitrobenzoate was refluxed with a solution of 5 g of potassium hydroxide in 100 ml of 95% ethanol for 2 hr. The mixture was poured into water, and the solution was extracted with ether. The ether extracts were washed and dried, and the ether was evaporated. The residual oil was triturated with a small amount of pentane, whereupon it crystallized. The material was twice recrystallized from pentane, yield 1.5 g, mp 45–46°.

Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.21; H, 13.00.

Preparation and Solvolysis of 3-*t*-Butylcyclooctyl Tosylate.—A solution of 0.5 g of 3-*t*-butylcyclooctanol (crystalline) in 20 ml of dry pyridine was cooled to 0° and 1 g of tosyl chloride was added. After standing at 5° for 16 hr, the solution was poured into ice-water and the white crystals were collected on a filter, washed with water, and dried under vacuum at room temperature. The crystalline tosylate melted sharply at 68.5–69°.

The freshly prepared tosylate (0.8 g) was added to a solution prepared from 5 ml of glacial acetic acid and 0.2 g of sodium acetate (anhydrous). The solution was heated under reflux for 16 hr, and was then poured into water. The mixture was extracted with pentane, the pentane extracts were washed and dried, and the solvent was evaporated. The residue was subjected to vpc analysis.

The vpc conditions were as follows: column, 20 ft, containing 30% SE-30 on Chromosorb W at 175°, followed by 200°. The results are given in Table II.

TABLE II

VPC ANALYSIS OF SOLVOLYSIS PRODUCTS FROM 3-*t*-BUTYLCYCLOOCTYL TOSYLATE

Fraction	Assigned structure (-cyclo-octene)	Temp, °C	Retention time, min	Peak areas	Olefin fraction, %
1	?	175	29.1	1.05	3.10
2	3-*t*-Butyl	175	31.1	0.42	1.24
3	1-*t*-Butyl	175	33.2	1.44	4.25
4	4-*t*-Butyl	175	35.7	30.98	91.41
5	Acetate	200	123.	66.11	...

General Procedure for Kinetic Experiments.—The methods previously employed[7] were used with some exceptions. Preparation of 80% ethanol was carried out by dilution of 95% ethanol with distilled water sufficient to make the solvent 80% ethanol by volume. Kinetic runs in acetic acid were carried out manually as previously described.[7] These tended to be laborious and somewhat inaccurate. Since there was available a Sargeant pH-Stat, it was decided to repeat all the kinetic runs in 80% ethanol with the aid of this device. In all but the slowest runs, the solvolysis was allowed to proceed for at least two half-lives. In cases where the half-lives of the reaction were more than 3 days, the rates were followed for a single half-life.

The data were obtained as a plot of milliliters of titrant *vs.* time. The plots were smoothed with a French curve, and points were taken from the smoothed graph. Between 10, and 75 points were taken in each case. The logarithm of the concentration was then plotted *vs.* time, and the rate constants were determined graphically in the usual way.

It was found that for highest precision, some modification in the use of the equipment was necessary. An external voltage regulator was used to alleviate pen drift owing to variance in the line voltage. It was also necessary to construct a cover to more tightly seal the reaction vessel from the atmosphere, otherwise the absorption of carbon dioxide was troublesome. In addition, a grid was placed around the reaction vessel to eliminate errors owing to changes in atmospheric capacitants. With these precautions, the relative rate constants obtained are believed accurate to about 1%.

3-*t*-Butylcyclooctanol-1-*d*.—The deuterated alcohol was prepared as described for its hydrogen analog, and was obtained as a viscous liquid, which solidified after seeding and trituration with pentane. The pentane was evaporated and left a crystalline mass, which at room temperature was contaminated with a small amount of liquid. The infrared spectrum showed the expected hydroxyl band at 3325 cm^{-1} and a sharp C–D stretching band at 2120 cm^{-1}. The acetate was prepared as described for the nondeuterated analog, and its ir showed strong absorption at 2160, 1730, and 1250 cm^{-1}.

Preparation and Solvolysis of 3-*t*-Butylcyclooctyl-1-*d* Tosylate.—The tosylate was prepared as previously described for the hydrogen analog and the crystals were collected, dried, and treated with refluxing acetic acid containing sodium acetate as previously. A similar work-up gave a residual oil, which upon vpc gave fractions of the same retention times as previously, although the ratios were somewhat different. Fractions 1–5 in Table II in this case gave the following peak areas: 2.29, 16.02, 4.21, 40.65, and 36.83. Fractions 2, 4, and 5 were collected by vpc.

Fraction 2 gave the following data: ir 3020, 2240, 1650, 1398, and 1370 cm^{-1}; nmr a multiplet at δ 5.30–5.75 (1 H) with a doublet of triplets at δ 5.45 predominating, a broad region at δ 1.06–2.44 (11 H), and a sharp singlet at δ 0.88 (9 H). It was assigned the structure of 3-*t*-butylcyclooctane. The relatively large amount of this fraction may be noted. In all other solvolyses (with nondeuterated material) this fraction accounted for only about 1% of the total olefins. Whether the discrepancy is due to deuteration or to some unrecognized experimental factor is not known.

Fraction 4 gave the following data: ir 3030, 2260, 1655, 1400, and 1370 cm^{-1}; nmr a triplet of triplets at δ 5.45 (1 H), a broad region at δ 1.00–2.50 (11 H), and a sharp singlet at δ 0.88 (9 H). It was assigned the structure of 4-*t*-butylcyclooctene.

Fraction 5 gave the following data: ir 2160, 1730, and 1250 cm^{-1}; nmr a sharp singlet at δ 2.0 (3 H), a broad methylene region at δ 1.00–1.94 (13 H), and a sharp singlet at δ 0.87 (9 H). It was assigned the structure of 3-*t*-butylcyclooctyl acetate.

Registry No.—I, 23804-51-5; I *p*-nitrophenylhydrazone, 23804-52-6; II, 23809-66-7; III, 23809-67-8; 4-*t*-butylcyclooctene, 23796-85-2; 3-*t*-butylcyclooctene, 23809-68-9; 3-*t*-butylcyclooctyl *p*-nitrobenzoate, 23809-69-0; 3-*t*-butylcyclooctyl tosylate, 23809-70-3.