Anal. Calcd for $C_{32}H_{20}N_4$: C, 83.46; H, 4.38; N, 12.17. Found: C, 82.99; H, 4.49; N, 12.44.

In order to determine the relative reactivities of *cis*-1,2-diphenyl-, *trans*-1,2-diphenyl- and 1,1,2-triphenylbenzocyclobutene toward tetracyanoethylene, 0.2 mmol of each hydrocarbon was dissolved in 1 ml of toluene contained in three separate flasks. To each solution was added 0.1 mmol of tetracyanoethylene and the time required for disappearance of the bright yellow color noted. Times required were as follows (two separate runs): 1,1,2-triphenyl derivative (4–6 min); *trans*-1,2-diphenyl derivative (60–65 min); *cis*-1,2-diphenyl derivative (5–5.5 days).

Sulfur Dioxide Adduct of 1,1,2-Triphenylbenzocyclobutene.—A solution of 0.15 g of the benzocyclobutene in 50 ml of liquid sulfur dioxide was heated in a sealed tube at 90–95° for 15 hr. Evaporation of the solvent gave 0.17 g (94.4%) of the adduct, mp 167–174°. Recrystallization from ethanol–benzene (2:1) gave the sulfone as tiny white crystals: mp 173–175° (gas evolution and yellowing), lit.[15] mp 174–174.5°; nmr δ^{CDCl_3} 5.15 (s, 1 H, CH) and 7.3 (m, 19 H, aromatic); ir λ_{max}^{Nujol} 7.61, 8.81 μ (SO_2). The ultraviolet curve matched that published by Kloosterziel and Backer[15] for 1,1,3-triphenyl-1,3-dihydroisobenzothiophene sulfone.

Registry No.—1,1,3,3-Tetraphenyldihydroisoindole, 18554-09-1; 2-nitroso-1,1,3,3-tetraphenyldihydroisoindole, 18554-10-4; 2-amino-1,1,3,3-tetraphenyldihydroisoindole, 18554-11-5; acetyl derivative of 2-amino-1,1,-3,3-tetraphenyldihydroisoindole, 18554-12-6; 2-nitroso-1,1,3-triphenyldihydroisoindole, 18554-13-7; 2-amino-1,1,3-triphenyldihydroisoindole hydrochloride, 18554-14-8; benzal derivative of 2-amino-1,1,3-triphenyldihydroisoindole hydrochloride, 18554-15-9; IV, 18554-16-0; α,α,α′-triphenyl-*o*-xylene, 18554-17-1; tetracyanoethylene adduct of 1,1,2-triphenylbenzocyclobutene, 18598-44-2.

Acknowledgment.—This work was supported by a grant (NSF-GP-4283) from the National Science Foundation.

[15] H. Kloosterziel and H. J. Backer, *Rec. Trav. Chim. Pays-Bas*, **71**, 1235 (1952).

The Solvolysis of Some Substituted Cyclohexyl Methanesulfonates[1]

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In connection with other studies from these laboratories on the effect of polar substituents on the rate of solvolysis of derivatives of substituted cyclohexanols,[2,3] it was desirable to examine the reactivity of some simple cyclohexyl methanesulfonates. Though methanesulfonates have been widely used in carrying out chemical transformations in the steroid and sugar families, relatively few rate measurements have been made with them. Robertson and his coworkers, in their definitive studies of solvent isotope effects, have examined the solvolysis of simple alkyl methanesulfonates.[4] The rate for isopropyl methanesulfonate is about one-half the rate for isopropyl tosylate in water. Cyclopentyl methanesulfonate solvolyzes somewhat more slowly in methanol than does the tosylate,[5] and comparisons of the relative rates of acetolysis of cholestanyl and 4,4-dimethylcholestanyl sulfonates can be made from the reported kinetic measurements of deSousa and Moriarity[6] and of Biellman and Ourisson.[7] The tosylate and methanesulfonate show nearly identical rates.

We have prepared and measured the rate of acetolysis of *cis*- and *trans*-4-*t*-butylcyclohexyl methanesulfonates and of *cis*- and *trans*-4-methylcyclohexyl methanesulfonates. The rate measurements are summarized in Table I, with derived thermodynamic parameters in Table II.

TABLE I

RATES OF ACETOLYSIS OF 4-SUBSTITUTED CYCLOHEXYL METHANESULFONATES

Substituent	Temp, °C	10^6k_1, sec^{-1}	k_{rel} (70°)	k_{OMs}/k_{OTs}[a]
Unsubstituted	50	2.42 ± 0.03		1.23[b]
	70	28.7 ± 0.6	1.16	
	70	28.8 ± 0.6		
trans-4-Methyl	50	1.49 ± 0.88		1.15[c]
	70	19.3 ± 0.3	0.78	
cis-4-Methyl	50	3.88 ± 0.32		1.18[c]
	70	48.8 ± 1.0	1.97	
	70	48.0 ± 3.0	1.94	
trans-4-*t*-Butyl	50	1.91 ± 0.02		1.20[b]
	70	24.8 ± 0.7	1.00	
cis-4-*t*-Butyl	50	7.19 ± 0.25		1.26[b]
	70	75.8 ± 2.2	3.06	

[a] Rate ratio methanesulfonate/tosylate at 75.7°, the only temperature at which data for the 4-methylcyclohexyl tosylates are available. [b] Tosylate data: S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955). [c] Tosylate data: H. Kwart and T. Takeshita, *ibid.*, **86**, 1161 (1964).

TABLE II

ACTIVATION PARAMETERS

Substituent[a]	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
trans-4-*t*-Butyl	27.6 ± 0.2	+0.5 ± 0.6
cis-4-*t*-Butyl	25.3 ± 0.4	−3.8 ± 1.1
trans-4-Methyl	27.6 ± 0.4	−0.1 ± 1.2
cis-4-Methyl	27.2 ± 0.7	+0.5 ± 2.2
Unsubstituted	26.6 ± 0.2	−2.1 ± 0.7

[a] Substituent on cyclohexyl methanesulfonate.

These rate measurements may be compared with previously determined rates for the corresponding tosylates, and the data are summarized in the last column in Table I. It is to be noted that the methanesulfonates solvolyze at rates which are very similar to those of the corresponding tosylates. In the present, unhindered cyclohexyl derivatives, the methanesulfonates, solvolyze about 20% faster than the tosylates.

Conformational Analysis.—One of the primary pur-

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[1] Supported in part by grants from the National Science Foundation (GP-1572 and GP-6133X).

[2] D. S. Noyce and B. Weinstein, *J. Org. Chem.*, to be submitted.

[3] D. S. Noyce and Byron E. Johnston, *ibid.*, to be submitted.

[4] K. T. Leffek, R. E. Robertson, and S. E. Sugamori, *Can. J. Chem.*, **39**, 1989 (1961); R. E. Heppolette and R. E. Robertson, *ibid.*, **44**, 677 (1966).

[5] F. J. Chloupek and G. Zweifel, *J. Org. Chem.*, **29**, 2092 (1964).

[6] R. M. deSousa and R. M. Moriarity, *ibid.*, **30**, 1509 (1965).

[7] J. F. Biellman and G. Ourisson, *Bull. Soc. Chim. Fr.*, 341 (1962).

poses of the present study was to examine the possibility of carrying out conformational analysis of the equilibrium distribution of conformational isomers in substituted cyclohexyl systems of the type under study. We have examined the infrared spectra of the methanesulfonates, and find that there is a strong band at 931 cm^{-1} for *trans*-4-methylcyclohexyl methanesulfonate, and a doublet at 931 and 941 cm^{-1} for *trans*-4-*t*-butylcyclohexyl methanesulfonate. In the spectrum of *cis*-4-*t*-butylcyclohexyl methanesulfonate a prominent band at 906 cm^{-1} is reproduced in the spectrum of *cis*-4-methylcyclohexyl methanesulfonate, which shows in addition a minor band at 928 cm^{-1}. Assigning the low frequency band to the axial C–O bond, and the high-frequency band to the equatorial C–O bond, and also noting that in the *t*-butyl derivatives the bond intensities are the same within 2%, it is possible to calculate from the observed spectrum of cyclohexyl methanesulfonate a conformational equilibrium. This calculation gives the result that cyclohexyl methanesulfonate is 69% in the equatorial conformation. We have also examined the conformational equilibrium in the case of cyclohexyl methanesulfonate by nmr techniques. Using the peak shift method for the methinyl hydrogen,[8] *A* values in both carbon tetrachloride and acetic acid solvent may be obtained.

Through the kindness of Professor Jensen and his collaborators[9] we have been able to verify these results with low-temperature nmr spectral determination of the *A* value for the methanesulfonate group. The data obtained by these several different methods are summarized in Table III.

TABLE III

A VALUES

Method	Methanesulfonate	Tosylate
Infrared (CCl_4)	0.53 ± 0.10	
Nmr chemical shift in CCl_4	0.48 ± 0.10	0.6[a]
in acetic acid	0.41 ± 0.10	
Low-temperature nmr[b]	0.56 ± 0.03	0.515 ± 0.021

[a] Ref 8. [b] Measurements at 100 MHz kindly carried out by F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, **90**, 344 (1969).

In considering the kinetic method of determining *A* values it is to be noted that the data for the 4-methylcyclohexyl methanesulfonates give a satisfactory answer for the *A* value of the methanesulfonate group using the method of Winstein and Holness,[10] though the *t*-butylcyclohexyl methanesulfonates do not. This is perhaps another manifestation of the suggested small distortion of the cyclohexane ring by the "locking" *t*-butyl group, which has previously been suggested by Kwart and Takeshita.[11]

We would like to suggest that methanesulfonates may be more generally useful than has heretofore been indicated by their utilization in kinetic studies. A further feature which may well increase their utility is the fact that the methanesulfonate is undoubtedly formed from the alcohol by a different mechanism[12,13] than is the tosylate. We have found that the conditions required for the formation of the methanesulfonate are far milder than those required for the formation of tosylates.

Experimental Section[14]

***cis*- and *trans*-4-*t*-Butylcyclohexanol.**—Commercial 4-*t*-butylcyclohexanol (Dow Chemical Co.) was separated as described by Winstein and Holness[10] *via* the acid phthalate to give a sample of pure *trans*-4-*t*-butylcyclohexanol, and by chromatography on neutral grade III Woelm alumina to give a sample of pure *cis*-4-*t*-butylcyclohexanol.

***trans*-4-*t*-Butylcyclohexyl Methanesulfonate.**—Methanesulfonyl chloride (5.12 g) and *trans*-4-*t*-butylcyclohexanol (6.36 g) were combined in dry benzene (75 ml). The solution was stirred vigorously and the temperature was maintained at 5–10° while triethylamine (4.53 g) in benzene (50 ml) was added over a period of 10 min. The solution was immediately filtered to remove the amine hydrochloride, and the clear filtrate was washed with cold 10% HCl and with saturated $NaHCO_3$. The benzene was removed under vacuum, and the remaining solid (8.8 g, 92.5%), mp 72–74°, was crystallized from hexane to give pure *trans*-4-*t*-butylcyclohexyl methanesulfonate, mp 74–75°.

Anal. Calcd for $C_{11}H_{22}O_3S$: C, 56.37; H, 9.46; S, 13.68. Found: C, 56.54; H, 9.27; S, 13.52.

***cis*-4-*t*-Butylcyclohexyl methanesulfonate** was prepared in the same fashion (89% yield, mp 94.0–94.5°).

Anal. Found: C, 56.13; H, 9.27; S, 13.64.

***trans*-4-Methylcyclohexanol** was purified as the 3,5-dinitrobenzoate[15] and ***cis*-4-methylcyclohexanol** was purified as the *p*-nitrobenzoate.[15] ***trans*-4-Methylcyclohexyl methanesulfonate** was prepared as above, and crystallized from benzene, mp 38.5–39.0°.

Anal. Calcd for $C_8H_{16}O_3S$: C, 49.96; H, 8.39; S, 16.67. Found: C, 49.68; H, 8.17; S, 16.48.

Similarly, ***cis*-4-methylcyclohexyl methanesulfonate** was prepared. A liquid at room temperature, this sulfonate ester was purified by low-tempeature (−60°) crystallization from methanol.

Anal. Found: C, 49.81; H, 8.36; S, 16.51.

Cyclohexyl methanesulfonate was prepared in similar fashion. Distillation from a small amount of calcium carbonate, bp 97–98° (0.05 mm), afforded pure material in 76% yield.

Anal. Calcd for $C_7H_{14}O_3S$: C, 47.17; H, 7.92; S, 17.99. Found: C, 47.48; H, 7.89; S, 17.74.

Product Analysis.—The products resulting from the solvolysis of both *cis*- and *trans*-4-*t*-butylcyclohexyl methanesulfonates at 70° in acetic acid solutions contained 0.05 *M* sulfonate, 0.10 *M* sodium acetate and 0.10 *M* acetic anhydride. Analysis was carried out using an Aerograph A-90-P instrument, with a 5-ft 20% Carbowax 20M on 60–80 mesh Chromosorb W column. Comparisons of retention times with those for authentic samples of all products were made, and the thermal conductivities were calibrated. The results obtained are listed in Table IV. Since this work was completed, a very careful study of the solvolysis of the 4-*t*-butylcyclohexyl *p*-toluenesulfonates has been reported by Whiting, *et al.*,[16] and our results show a very close correspondence to those reported (Table 7 of ref 16).

Kinetic Methods.—The kinetics were determined by the usual sealed ampoule technique. Solutions were prepared in purified acetic acid with sulfonate ester approximately 0.05 *M*, with added sodium acetate and acetic anhydride each 0.10 *M*. At

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(8) E. L. Eliel and M. H. Gianni, *Tetrahedron Lett.*, 97 (1962).

(9) We wish to express our appreciation to Dr. C. H. Bushweller and Dr. B. H. Beck for providing us with the measurements reported here.

(10) See Table I, footnote *b*.

(11) See Table I, footnote *c*.

(12) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **86**, 287 (1964).

(13) W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).

(14) All melting points are corrected; boiling points are uncorrected. Routine infrared spectra were determined on a Perkin-Elmer Model 237 Infracord; analytical spectra were taken on a Perkin-Elmer Model 421 spectrophotometer. Nmr spectra were determined with a Varian Associates Model A-60 spectrometer. Elemental analyses were determined by the Microanalytical Laboratory, Department of Chemistry, University of California.

(15) L. M. Jackman, A. K. Macbeth, and J. A. Mills, *J. Chem. Soc.*, 1717 (1949).

(16) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.*, *B*, 355 (1968).

Table IV

Products from the Acetolysis of *t*-Butylcyclohexyl Methanesulfonates

Product	% from *cis*	% from *trans*
4-ene	85.0	75.0
3-ene	0.9	1.5
trans-4-OAc	8.1	0.1
cis-4-OAc	1.2	19.8
trans-3-OAc	4.6	0.3
cis-3-OAc	0.4	1.1

appropriate times aliquots were titrated with standardized perchloric acid in acetic acid to the bromophenol blue end point. Rate constants were calculated by a modified LSKIN2 computer program.[17]

Registry No.—*trans*-4-*t*-Butylcyclohexyl methanesulfonate, 18508-90-2; *cis*-4-*t*-butylcyclohexyl methanesulfonate, 18508-91-3; *trans*-4-methylcyclohexyl methanesulfonate, 18508-92-4; *cis*-4-methylcyclohexyl methanesulfonate, 18508-93-5; cyclohexyl methanesulfonate, 16156-56-2.

[17] D. F. DeTar and C. E. DeTar, Florida State University. We are grateful to Mr. Howell A. Hammond for his assistance in modifying these programs.

A Facile Synthesis of 1,4-Cyclooctadiene

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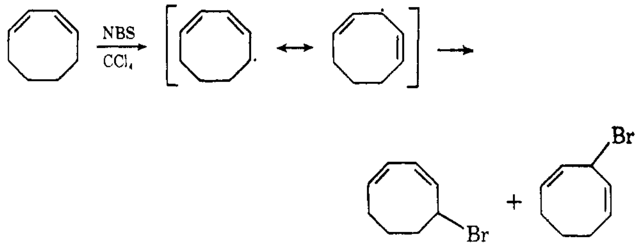
The chemical reactions of both 1,3- and 1,5-cyclooctadiene have been studied in some detail.[1] The chemistry of the corresponding 1,4 isomer, however, has been largely neglected, possibly due to the inaccessibility of this compound.

Although some preparations of 1,4-cyclooctadiene have been reported,[2-6] a facile synthesis which gives a substantial quantity of the pure compound is still lacking. In this paper, we wish to describe a simple synthetic procedure which utilizes a readily available and inexpensive starting material and which affords 1,4-cyclooctadiene of high purity.

The synthesis is based upon the partial rearrangement of 1,3-cyclooctadiene during bromination with N-bromosuccinimide (NBS). Treatment of the bromination product with lithium aluminum hydride affords approximately a 50:50 mixture of 1,3- and 1,4-cyclooctadiene. It therefore appears that the intermediate radical, formed in the NBS reaction, undergoes an allylic rearrangement in the manner illustrated.



On the basis of previous studies made by Jones,[4] we have found that, at room temperature, 1,3-cyclooctadiene is inert to silver nitrate while the 1,4 isomer readily forms a silver nitrate complex. 1,4-Cyclooctadiene can thus be conveniently and selectively separated from the lithium aluminum hydride reduction mixture by extraction with 50% silver nitrate at room temperature. Regeneration of the 1,4-diene from its silver nitrate complex is accomplished by treatment with cold concentrated ammonium hydroxide. Ether extraction of the resultant ammonium hydroxide solution followed by distillation affords pure (>99% by vpc analysis) 1,4-cyclooctadiene.

Experimental Section[7]

Bromination of 1,3-Cyclooctadiene.—To 105.4 g of freshly distilled 1,3-cyclooctadiene[8] in 400 ml of carbon tetrachloride was added 175 g of NBS and 1.25 g of benzoyl peroxide. The mixture was refluxed, with stirring, for 17 hr, then cooled and the succinimide removed by filtration. The filtrate was washed with two 600 ml-portions of 10% $NaHCO_3$ and 600 ml of H_2O and then dried ($MgSO_4$). The solvent was removed under reduced pressure (20 mm) through a Vigreux column. The residue was then distilled through a short-path distillation column to give 97.1 g (53% based on 1,3-cyclooctadiene) of a bromide mixture, bp 25–52° (0.3 mm). The nmr spectrum of the distillate suggested that it was a mixture of 2,4-cyclooctadien-1-yl bromide and 2,7-cyclooctadien-1-yl bromide.

Lithium Aluminum Hydride Reduction of the Bromination Product.—To a suspension of 15 g of lithium aluminum hydride in 250 ml of anhydrous ether was added, dropwise and with stirring, 97.1 g of the bromide mixture in 25 ml of ether. Following complete addition, the solution was refluxed overnight. After cooling, 40 ml of H_2O was cautiously added, dropwise and with stirring, to the externally cooled solution. Sulfuric acid (20%, 100 ml) was then added in a similar manner, followed by 400 ml more of the acid added at room temperature. Stirring was continued until all of the white precipitate, formed on H_2O addition, had dissolved. The aqueous portion was separated and extracted with 250 ml of ether. The latter was added to the original organic layer and the combined extracts were washed with two 400 ml-portions of 10% $NaHCO_3$ and 400 ml of H_2O and dried ($MgSO_4$). The ether was removed by distillation. The crude diene mixture (50.5 g, 90% based on the bromide mixture) was analyzed by vpc (TCEP, 65°) and found to be approximately a 50:50 mixture of two compounds with slightly different retention times. Each compound was isolated by

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[1] See, for example, A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, **81**, 1643 (1959); R. S. H. Liu, *ibid.*, **89**, 112 (1967); I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

[2] K. Ziegler and H. Wilms, *Ann. Chem.*, **567**, 1 (1950).

[3] L. E. Craig, R. M. Elofson, and I. J. Ressa, *J. Amer. Chem. Soc.*, **75**, 480 (1953).

[4] W. O. Jones, *J. Chem. Soc.*, 312 (1954).

[5] W. Grimme, *Chem. Ber.*, **98**, 756 (1965).

[6] U. S. Rubber Co., Netherlands Patent 6,607,898 (1966); *Chem. Abstr.*, **67**, 11922 (1967).

[7] Nmr spectra were determined on a Varian A-60 spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Gas chromatography was performed on an F & M Model 720 thermal conductivity gas chromatograph using a 4-ft column containing 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P. Boiling points are uncorrected.

[8] We are grateful to the Columbian Carbon Co. for a generous sample of this compound.