Regiochemistry, Stereochemistry, and Mechanism of Addition of Trifluoroacetic Acid to (Z)-Cyclooctene

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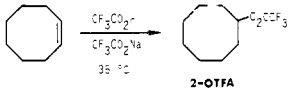
Abstract: The regiochemistry and stereochemistry of addition of CF_3CO_2D to cyclooctene have been established by ^2H NMR analysis of the cyclooctanol derived from the trifluoroacetate product. A complex mixture dominated by (*Z*)-cyclooctanol-*2-d* (**4**-OH) and (*Z*)-cyclooctanol-*4-d* (**8**-OH) was obtained after 99% reaction of the olefin essentially under kinetic control. Determination of the product composition as a function of time and extrapolation to zero, however, established that the trifluoroacetates of **4**-OH and **8**-OH are the exclusive primary adducts. These and complementary results indicate that the reaction proceeds entirely by stereospecific formation of a 1,5-hydride-bridged carbonium ion which is partitioned between nucleophilic solvent attack and, to a lesser extent, reversion to olefin by nearly completely anti vicinal deprotonation or dedeuterionation.

The cyclooctyl cation in superacid solution has been distinctively characterized by NMR spectroscopy as a 1,5-hydrido-bridged species.[1] Stereochemical studies have provided strong support for the same structure as the intermediate in cyclooctyl sulfonate solvolysis,[2] although two probes have failed to reveal major anchimeric assistance.[3] We present here the results of a regiochemical and stereochemical investigation of the addition of trifluoroacetic acid to (*Z*)-cyclooctene which show that this reaction is wholly mediated by the 1,5-hydride-bridged cyclooctyl cation.

Peterson and Allen in 1962 reported that CF_3CO_2H containing NaO_2CCF_3 adds to (*Z*)-cyclooctene (**1**) at 35 °C to produce cyclooctyl trifluoroacetate (**2**-OTFA) (plus minor products of



2-OTFA

higher molecular weight) at a rate 7–25 times faster than that of model alkenes and cycloalkenes.[4] The acceleration, unexpected on steric grounds[3a,5] for rate-limiting protonation, was considered alternatively the result of transannular hydrogen participation or solvation or entropy effects. Allen and Tidwell, on the other hand, have implicated a mechanism of rate-determining carbenium-ion formation from the observation that cyclooctene obeys a linear log/log correlation of rates in CF_3CO_2H and aqueous H_2SO_4 for a group of olefins earlier concluded to follow the Ad_E2 mechanism in aqueous strong acid.[6]

Reactions of other acids with cyclooctene have been recorded with less mechanistic information.[7,8] Instructive additions of other electrophilic[7,9] and free radical[7,9b,10] reagents to **1** have also been reported.[11]

Results

Complete-Addition Products. The regiochemistry and stereochemistry of addition of trifluoroacetic acid to cyclooctene were determined from the reaction of the olefin with CF_3CO_2D in the presence of a small quantity of CH_2Cl_2 (1:10:1 by volume, respectively) at 22 °C. The half-life for consumption of the reactant under these conditions was measured by ^1H NMR spectroscopy to be approximately 78.0 min ($k_1 = 1.48 \times 10^{-4}$ s^{-1}), and control experiments, described below, showed the addition to be essentially under kinetic control through 99% conversion (6.65 half-lives, 519 min). The trifluoroacetate product was isolated after this period and saponified to the alcohol, which was purified via the crystalline *N*-phenylcarbamate and subjected to label-position analysis by 30.7-MHz proton-decoupled ^2H NMR spectroscopy[12] with added shift reagent Ho(fod)$_3$,[2b] Figure 1.

The eight-line spectrum corresponds to a mixture of all but one of the nine possible cyclooctanols-*C-d*, **3**-OH–**11**-OH, Scheme I. From high field downward, the first three peaks were assigned to the *1-d* and *Z*- and *E-2-d* isomers, respectively, by signal enhancements under successive minor additions of authentic **3**-OH[2b] and a 2:1 mixture of **4**-OH + **5**-OH,[2b] together with complementary Ho(fod)$_3$. The next two signals were similarly identified with the *3-d* species after enrichment of the sample with a 1:1:1:1 mixture of **4**-OH + **5**-OH + **6**-OH + **7**-OH, synthesized from 3-bromocyclooctene (**12**) via cyclooctene-*3-d* (**13**). The more upfield of the *3-d* peaks is tentatively assigned to the *Z* epimer, **6**-OH, on the basis of the higher-field shifts ascertained for the

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Scheme I

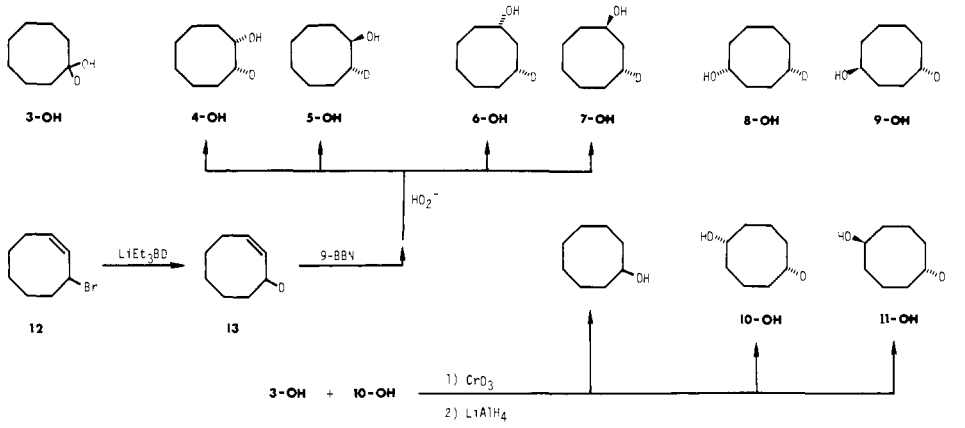


Table I. Dependence of Product Composition on Reaction Time for CF_3CO_2D Addition to Cyclooctene (1)

time, s	% consumption of 1	% ^{2}H NMR signal intensity corresponding to 3-OH	4-OH	5-OH	6-OH	7-OH	8-OH + 10-OH[a]	9-OH + 11-OH	total % minor products[b]	% 4-OH/ % 8-OH
0	0	0[c]	59.5[c]	0[c]	0[c]	0[c]	40.5[c]	0[c]	0[c]	1.47[c]
900	20.0	0.0	57.0	0.4	1.3	0.9	39.1	1.3	3.9	
1800	31.4	0.0	55.4	1.0	2.0	1.0	38.5	2.1	6.1	
3600	45.2	0.0	53.1	1.8	2.7	1.5	37.5	3.3	9.3	
7200	68.3	0.0	50.3	2.5	3.6	2.1	36.4	5.0	13.2	
14400	89.0	0.4	47.3	3.6	4.9	4.2	34.2	5.6	18.7	
31140	99.0	0.7	45.9	3.6	5.9	4.2	33.6	6.1	20.5	

[a] Contribution corresponding to 10-OH shown to be <2% for 99% reaction and concluded to be zero for initial products. [b] Products other than 4-OH and 8-OH, ignoring 10-OH. [c] Extrapolated from the experimental data.

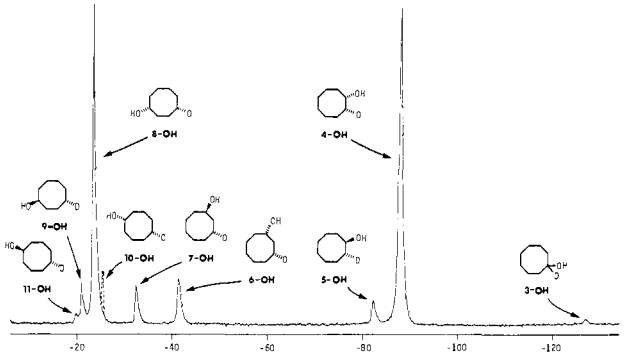


Figure 1. Ho(fod)$_3$-dispersed 30.7-MHz proton-decoupled ^{2}H NMR spectrum of the cyclooctanols (in CCl_4 + $CDCl_3$) derived from CF_3CO_2D addition to cyclooctene (**1**) at 22 °C, with apparent assignments.

Z members of the other three epimeric pairs. The last three signals were associated in decreasing-field order with the *Z-4-d*, **8**-OH;[2b] *E-4-d*, **9**-OH;[2b] and *E-5-d*, **11**-OH isomers by correlation with the spectrum of a synthetic mixture of these alcohols together with the *Z-5-d* species, **10**-OH.[2b] This sample produced four peaks in the same chemical shift region, which were fully assigned from the variation of line intensities as the isomer ratios were changed. The signal for the **10**-OH isomer was found to be slightly upfield from the other three and appeared as a new line, shown as the dashed peak in Figure 1, when **10**-OH (mixed with **3**-OH) was added to the addition-product alcohols. The authentic **11**-OH was generated along with **10**-OH and some undeuteriated cyclooctanol by application of an oxidation–reduction sequence to a mixture of **3**-OH and **10**-OH, prepared by the hydrolysis of cyclooctyl-*1-d* brosylate.[2b] The identification of the major downfield peak as **8**-OH was confirmed by solvolysis in buffered 80% acetone[2b] of the brosylate prepared from the alcohol obtained from the addition reaction. ^{2}H NMR examination of the resultant cyclooctanols showed no appreciable intensification of the lines for 3-OH or **5**-OH as the result of the solvolytic *syn*-1,5-hydroxy transposition,[2b] uniquely consistent with the original **8**-OH assignment.

The stability of the addition products was tested by subjecting cyclooctyl-*1-d* trifluoroacetate (**3**-OTFA) to the addition reaction conditions for 411 min and comparing the starting and recovered esters by ^{1}H NMR. The time was chosen as the mean duration of exposure of the trifluoroacetate products to the acidic medium during the 99% addition reaction.[13] Both samples exhibited only a trace peak at δ 5.10 for protium at C-1, the signal for the treated material appearing slightly but insignificantly stronger. Appreciable solvolysis of the ester would have produced a C-1 proton peak as the result of transannular rearrangement.[2b] Thus the 99% addition reaction was established to be essentially under kinetic control.

While virtually stable to the reaction conditions, the trifluoroacetate products of 99% addition were observed at the same time to have incorporated significantly more than one deuterium atom per molecule. The average deuterium content, D_{av}, was determined by two independent ^{2}H NMR measurements. First the combined ring-*d* signals of the derived cyclooctanol were integrated against an added $CDCl_3$ reference peak. The alcohol was then converted by reaction with $(CD_3CO)_2O$, *N,N'*-dicyclohexylcarbodiimide, and 4-pyrrolidinopyridine to the corresponding acetate-d_3, whose ring and acetyl signal strengths in the Pr(fod)$_3$-dispersed spectrum were compared. Agreement between the two methods was close, the mean result being D_{av} = 1.40.

Initial-Addition Products. Further insight into the addition process was gained by ^{2}H NMR study of the product composition as a function of partial-reaction time. The pertinent data are given in Table I. The contributions of the six lesser peaks in Figure 1 were found to decrease linearly with decreasing fractional consumption of the cyclooctene and to extrapolate to zero at the zero-reaction limit, as shown collectively in Figure 2. Thus, the exclusive primary adducts were indicated to be 59.5% (*Z*)-

(13) Let t_p = the time of exposure to the reaction medium of product ester formed at a given concentration of reactant **1** and $\bar{t}_{99}$ = the time for 99% completion of the addition reaction. Then

$$t_p = \bar{t}_{99} - (1/k) \ln ([\mathbf{1}]_0/[\mathbf{1}])$$

$$t_p = -(0.99[\mathbf{1}]_0)^{-1} \int_{[\mathbf{1}]_0}^{0.01[\mathbf{1}]_0} t_p \, d[\mathbf{1}] = 0.793\bar{t}_{99}$$

Scheme II

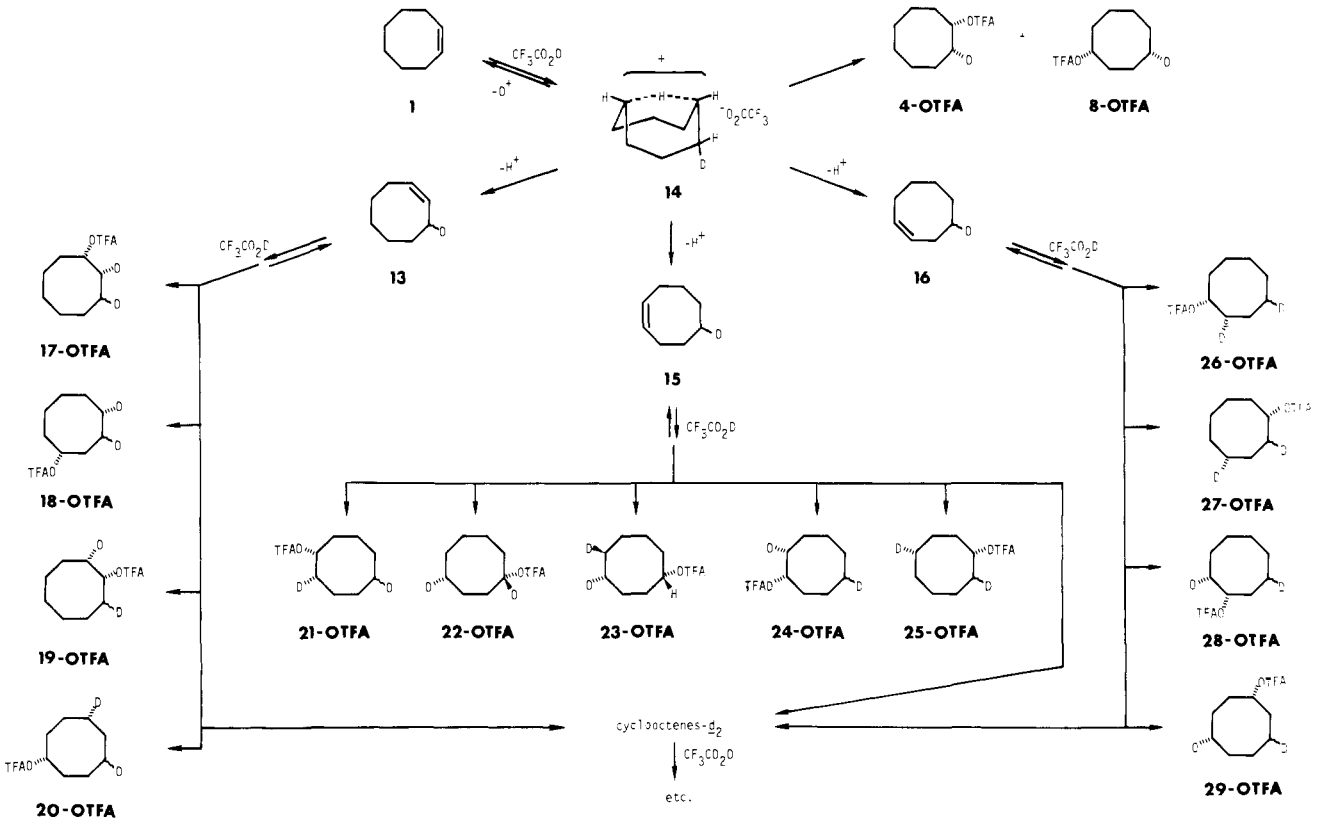
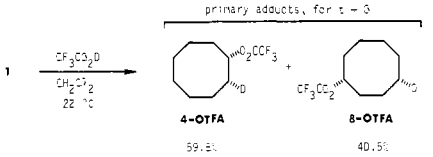


Table II. Deuterium Incorporations in Cyclooctene (1) Recovered from Partial Reaction with CF_3CO_2D

reaction time, s	% consumption of 1	atom % D at position(s) 1 + 2	3	4 + 5	all
1800	31.4	0.16	4.21	8.73	13.10
3600	45.2	0.37	5.98	13.34	19.69
7200	68.3	0.80	9.16	18.80	28.76

cyclooctyl-*2-d* trifluoroacetate (**4**-OTFA) and 40.5% (*Z*)-cyclooctyl-*4-d* trifluoroacetate (**8**-OTFA), eq 1.



(1)

Complementary evidence was acquired by deuterium-content analysis of the cyclooctene recovered from the 30-, 60-, and 120-min partial-addition reactions (31, 45, and 68% olefin consumption, respectively). Separate ^2H NMR signals were observed for deuterium in the vinylic, allylic, and more distal positions, and these were integrated against a quantitative $CDCl_3$ reference peak to measure the abundance of deuterium at these three locations. The data are presented in Table II. Incorporation of deuterium is substantial at the allylic and ultraallylic positions but only slight at the vinylic position. For each location the extent of deuterium uptake is approximately linear with the fraction of cyclooctene consumption and extrapolates reasonably to the origin, Figure 3.

Discussion

The combined data provide strong support for the mechanism outlined in Scheme II.

The identification of **4**-OTFA and **8**-OTFA as the sole primary addition products demonstrates effectively that ester formation occurs wholly through a 1,5-hydride-bridged cation, **14**. The strict

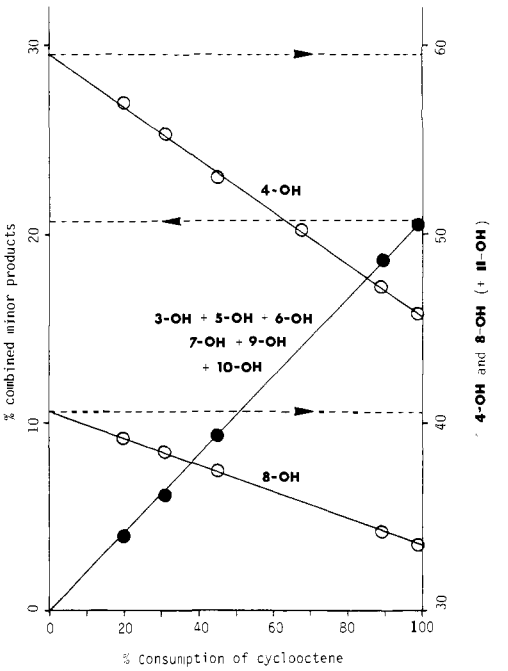


Figure 2. Reaction-time dependence of ^2H NMR signal intensities for cyclooctanol products from CF_3CO_2D addition to cyclooctene.

syn stereochemistry observed for both the 1,2- and 1,4-additions finds no sensible explanation in terms of localized carbenium ion intermediates, eq 2. A model for normal addition of CF_3CO_2D

(2)

to an olefin is afforded by cyclohexene, whose stereochemistry for 1,2-addition is 63% syn and 37% anti.[14] The modest selectivity

(14) Nordlander, J. E.; Haky, J. E.; Kotian, K. D., unpublished observation.

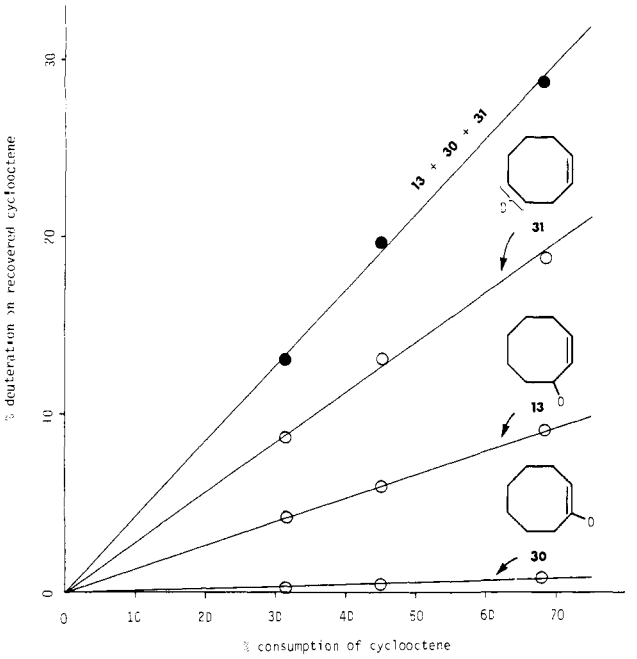


Figure 3. Deuterium incorporations in residual cyclooctene from partial additions of CF_3CO_2D.

Table III. Calculated Product Yields for the Mechanism of Scheme II from Deuterium Incorporation Data

product	%	product	%
4-OTFA	35.69	23-OTFA	1.35
8-OTFA	24.31	24-OTFA[a]	3.97
17-OTFA[a]	3.97	25-OTFA[a]	2.70
18-OTFA[a]	2.70	26-OTFA[a]	3.97
19-OTFA[a]	3.97	27-OTFA[a]	2.70
20-OTFA[a]	2.70	28-OTFA[a]	3.97
21-OTFA[a]	3.97	29-OTFA[a]	2.70
22-OTFA	1.35		

[a] Two epimers.

in that case points to product formation from a carbenium ion with some preference for least-motion ion-pair combination.[15] The minor regioselectivity in the addition to cyclooctene (**4**-OTFA/**8**-OTFA = 1.47) is another evident manifestation of weak ion pairing.[16]

The variation in deuterated cyclooctanol product composition with reaction time under kinetic control, Table I, indicates that carbonium ion **14** undergoes competitive addition and elimination. Vicinal deprotonation is calculated to occur 93% anti to the hydride bridge to produce cyclooctenes-*d* **13**, **15**, and **16**, which undergo second-generation addition. This stereochemical conclusion follows from the 14.3-fold predominance of allylic-*d* isomer **13** over vinylic-*d* isomer **30** in Figure 3 and the relationship of eq 3, from which $k_{anti}{}^{-H}/k_{syn}{}^{-H} = 13.3$. The minor contribution of syn deprotonation of **14** is not included in Scheme II.

$$\frac{\mathbf{13}}{\mathbf{30}} = \frac{k_{syn}{}^{-H} + k_{anti}{}^{-H}}{k_{syn}{}^{-H}} \qquad (3)$$

The elimination stereochemistry constitutes additional evidence for bridged carbonium ion **14**. Anti elimination from **14** should be substantially favored over syn on stereoelectronic grounds, since the exocyclic and bridging C–H bonds being broken can assume a dihedral angular relationship close to 180°.[17] No such marked stereoselectivity is reasonably attributable to alternative equilibrating open cyclooctyl cations, eq 2. Possible stereocontrol of elimination from an open ion by a tightly paired counterion[18] is inconsistent with the experimental absence of any corresponding preference for near-side (C-2,8) over far-side (C-4,6) deprotonation. The yield ratio of near-side and far-side deprotonation products expected from the deduced stereoselectivity and the assumption of no regioselectivity is given by eq 4. The experimental ratio (**13** + **30**)/**31** from Figure 3 for comparison is 0.50.

$$\frac{\mathbf{13} + \mathbf{30}}{\mathbf{31}} = \frac{2k_{syn}{}^{-H} + k_{anti}{}^{-H}}{2k_{syn}{}^{-H} + 2k_{anti}{}^{-H}} = 0.53 \qquad (4)$$

Addition of CF_3CO_2D to the intermediate cyclooctenes-*d* **13**, **15**, and **16** yields the dideuterated esters **17**-OTFA–**29**-OTFA, Scheme II. The product ^2H NMR signals preliminarily identified with cyclooctanols-*1-d*, -(*E*)-*2-d*, -*3-d*, -(*E*)-*4-d*, and -*5-d* (**3**-OH, **5**-OH–**7**-OH, and **9**-OH–**11**-OH), Figure 1, thus emanate instead from the alcohols-d_2 derived from second-generation products **17**-OTFA–**29**-OTFA, as do minor fractions of the peaks corresponding to the first-generation (*Z*)-cyclooctanol-*2-d* (**4**-OH) and -*4-d* (**8**-OH) products. The meager yield of the lone 1-deuterated adduct **22**-OTFA measured by the highest-field absorption in Figure 1 permits the third-generation products to be ignored.

The mechanism of Scheme II is subject to a comprehensive quantitative test. The partitioning of carbonium ion **14** between additions to yield **4**-OTFA and **8**-OTFA and deprotonations to produce **13**, **15**, and **16** is related to the deuterium contents of the final adducts by eq 5. The quotient of rate constants here was

$$\frac{k_{add}{}^{1,2} + k_{add}{}^{1,4}}{k_{elim}} = \frac{3(d_1 \text{ adducts})}{d_2 \text{ adducts}} = \frac{3(2 - D_{av})}{D_{av} - 1} \qquad (5)$$

calculated to be 4.50 from the measured average deuterium content of the end products, $D_{av} = 1.40$. The ratio of regioisomeric nucleophilic capture rates $k_{add}{}^{1,2}/k_{add}{}^{1,4} = 1.47$ is expressed as the relative product yields **4**-OTFA/**8**-OTFA observed at the zero-reaction limit, Table I and eq 1. Combination of these results allows calculation of the yields of the first- and second-generation adducts postulated in Scheme II and from these the relative intensities of the eight composite ^2H NMR signals for comparison with the experimental values in Figure 1.

The derived information is presented in Tables III and IV. The correspondence within 1.1% between columns 4 and 5 in Table IV leaves little doubt that the mechanism of Scheme II is essentially correct.[19]

Nonclassical structure **14** is thus strongly supported for the cyclooctyl cation as a (semi-)stable molecule and as the governing

Table IV. Calculated and Observed ^2H NMR Line Intensities for Cyclooctanols from CF_3CO_2D Addition to Cyclooctene

δ	D position	contributing products	rel intensity calcd[a]	rel intensity obsd
−127.0	1	22-OTFA	0.97	0.7
−87.7	*Z*-2	4-, 17-, 19-, 21-, 24-25-, 26-, 27-, 28-OTFA	45.84	45.9
−82.1	*E*-2	19-, 25-, 27-OTFA	3.35	3.6
−41.3	*Z*-3	17-, 18-, 28-, 29-OTFA	4.76	5.9
−32.4	*E*-3	17-, 18-, 28-, 29-OTFA	4.76	4.2
−25.5	*Z*-5	21-OTFA		
−23.3	*Z*-4	8-, 18-, 20-, 22-, 23-, 24-, 25-, 26-, 27-, 29-OTFA	34.15	33.6
−21.1	*E*-4	20-, 24-, 26-OTFA	6.18	6.1
−19.7	*E*-5	21-, 23-OTFA		

[a] From data in Table III.

(15) Fahey, R. C. *Top. Stereochem.* **1968**, *3*, 237.
(16) See: Nordlander, J. E.; Owuor, P. O.; Haky, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 1288.
(17) Banthorpe, D. V. "Elimination Reactions"; Elsevier: New York, 1963; p 11–13. Bartsch, R. A.; Zavada, J. *Chem. Rev.* **1980**, *80*, 453. Chiao, W.-B.; Saunders, W. H., Jr. *J. Org. Chem.* **1980**, *45*, 1319.
(18) Reference 2b and footnotes 32, 33g,h, 35, and 36 therein. Compare the present lack of regioselectivity in elimination with the substantial preference for near-side deprotonation in cyclooctyl brosylate solvolysis in less electrophilic media.[2b]
(19) The possibility of a 1,3-hydride-bridged cation in place of **14** in Scheme II can be ruled out as possessing a relatively strained quasi-four-membered ring, being experimentally disproven for cyclooctyl solvolysis (Cope, A. C.; Gale, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 3747), and requiring an unreasonable coincidence of nonequivalent deprotonation rates.

intermediate in both solvolysis and acid–olefin reaction. Steric strain relief and transannular bonding are properly seen, we think, as cooperative effects along nucleofugic routes to this ion, and the same bridging evidently also occurs early on the associative pathway investigated here. Further understanding of acid additions to **1** is being sought through the measurement of remote isotope effects.

Experimental Section

General. Melting points in capillary tubes were measured with a Thomas-Hoover apparatus and are uncorrected. Boiling points are uncorrected.

^1H NMR spectra were recorded at 60 MHz on a Varian EM-360A spectrometer, except where otherwise noted. Proton-decoupled ^2H NMR spectra were acquired at 30.7 MHz on a Varian XL-200 spectrometer. The field was shimmed on an analog ^2H signal from $CDCl_3$ obtained by connecting the lock cable to the observe port of the probe, and the instrument was then run unlocked.

Trifluoroacetic Acid. Commercial acid was dried over P_2O_5 and distilled under N_2 immediately before use ($(CF_3CO)_2O$ forerun).

Trifluoroacetic Acid-*d*. The labeled acid was prepared immediately before use from 99.8% D_2O (Norell) and 1.1 equiv of trifluoroacetic anhydride in oven-dried glassware under Ar by the method of DePuy et al.[20]

Cyclooctenes-*d*. Cyclooctene-*1-d* was prepared from 1-bromocyclooctene by the method of Andrews, Baldwin, and Grayston[21] modified by hammering of the lithium into shiny sheets between two polystyrene weighing boats immediately before use. The distilled product was obtained in 56% yield (53-mmol scale), and the vinylic deuterium incorporation was estimated from the ^1H NMR spectrum to be 80%. Cyclooctene-*3-d* (**13**) was prepared in 38% yield by reaction of 9.45 g (50 mmol) of 3-bromocyclooctene (**12**)[22] with 1.2 equiv of $LiEt_3BD$ (Aldrich) in 110 mL of THF for 1.0 h at 0 °C and 12 h at 23 °C, standard workup,[23] and distillation.

Cyclooctanols-*d*. Cyclooctanol-*1-d* (**3**-OH), (*E*)-cyclooctanol-*2-d* (**5**-OH), and the epimeric mixture **4**-OH + **5**-OH were prepared as previously reported.[2b] (*E*)-Cyclooctanol-*4-d* (**9**-OH) was prepared as previously reported,[2b] and a portion was converted likewise to the epimeric **8**-OH + **9**-OH mixture. (*Z*)- and (*E*)-cyclooctanol-*3-d* (**6**-OH and **7**-OH) were prepared in admixture with **4**-OH and **5**-OH by the 9-BBN hydroboration-oxidation[24] of cyclooctene-*3-d* (**13**). The previously reported[2b] solvolysis of cyclooctyl-*1-d* brosylate in 80% aqueous acetone buffered with 2,6-lutidine at 35.5 °C was used to prepare (*Z*)-cyclooctanol-*5-d* (**10**-OH) together with the starting alcohol, **3**-OH. Application again of an oxidation–reduction sequence[2b] yielded the remaining isomeric alcohol (*E*)-cyclooctanol-*5-d* (**11**-OH) along with **10**-OH and unlabeled cyclooctanol.

Additions of CF_3CO_2D to Cyclooctene. To 50 mL of freshly prepared and vigorously stirred CF_3CO_2D under Ar in a creased flask at 22 °C was added 5.0 mL of freshly chromatographed (silica gel) and distilled (under N_2 at ambient pressure) cyclooctene (Cities Service) diluted with 5.0 mL of CH_2Cl_2. After 519 min (99% reaction, see below) the reaction mixture was poured with stirring into 400 mL of ice water and extracted with 4 × 25 mL of pentane (distilled from concentrated H_2SO_4). The dried ($MgSO_4$) pentane solution was concentrated by solvent distillation through a 6-in. Vigreux column (bath temperature <50 °C), and the residual trifluoroacetate ester was saponified by reaction with 75 mL of 3 N KOH in MeOH. The bulk of the methanol was removed by rotary evaporation, 200 mL of water was added, and the cyclooctanol product was extracted into 4 × 25 mL of ether. The solution was dried over $MgSO_4$, the ether removed by rotary evaporation, and the cyclooctanol isolated by vacuum distillation: bp 60–62 °C (1 mmHg) [lit.[25] bp 111.3–111.7 °C (25 mmHg)]. The alcohol was further purified by twofold recrystallization from hexane of the derived *N*-phenylurethane,[26,27] mp 54.7–55.5 °C [lit. mp 57 °C,[26] 56 °C[27]], and cleavage of the latter with 1 molar equiv of $LiAlH_4$ in boiling THF,[28] from which the alcohol was recovered by distillation after acid extraction to remove the *N*-methylaniline byproduct. The expected absence of any rearrangement in this last purification sequence was confirmed by its application to a sample of **5**-OH and observation that the $Ho(fod)_3$-dispersed ^2H NMR spectrum of the recovered alcohol was unchanged.

The addition reaction was also carried out on the same scale for a series of shorter times, 5.0, 15.0, 30.0, 60.0, 120.0, and 240.0 min. Each run was quenched by being poured into ice water as before, and the neutral materials were likewise extracted into pentane, dried, and concentrated. After measurement of the extent of reaction (see below), the crude mixture was treated with KOH in MeOH to saponify the ester. After pentane extraction as before, the unconsumed cyclooctene was separated by distillation, bp 38–40 °C (14 mmHg), and the residual cyclooctanol was purified through the *N*-phenylurethane derivative as described above.

Rate of Addition. The rate constant for the cyclooctene-CF_3CO_2D reaction was approximated as follows. After each of the runs described above was quenched, extracted with pentane, dried, and concentrated, the ratio of unconsumed olefin to trifluoroacetate ester in the resultant solution was measured by integration of the ^1H NMR absorptions at δ 5.10 (>CH–O_2CCF_3) and 5.60 (–CH=CH–) (after it had been demonstrated that negligible deuterium was incorporated into these positions). The fraction of olefin, F_o, was calculated from the ratio of signal intensities, $R = I_{5.60}/I_{5.10}$, by $F_o = R/(2 + R)$. The first-order rate constant was obtained as the slope of the linear least-squares plot of ln $(1/F_o)$ vs. time, 1.480×10^{-4} s^{-1}. The observed time (s) and R pairs were as follows: 300, 19.00; 900, 8.00; 1800, 4.364; 3600, 2.429; 7200, 0.929; 14400, 0.246.

The method used neglects the possible formation of a significant quantity of cyclooctylidenecyclooctane, as suggested by Peterson[4] for the reaction under more concentrated conditions. Isomeric dimeric olefins were contraindicated by the absence of any characteristic vinylic-H absorption after consumption of the cyclooctene.

Stability of Addition Products. A solution of 1.0 mL of cyclooctyl-*1-d* trifluoroacetate (**3**-OTFA), prepared[29] from **3**-OH[2b] and trifluoroacetic anhydride, in 10.0 mL of CH_2Cl_2 was kept at 22 °C for 411 min. The ester was reisolated by addition of the mixture to a large excess of cold water, ether extraction, drying of the extracts with anhydrous $MgSO_4$, and distillation, bp 80 °C (1 mmHg). The 200-MHz ^1H NMR spectrum of the product showed a barely detectable broad singlet at δ 5.10 for protium at C-1. The strength of this signal was perceptibly but not measurably greater than that in the starting ester due to the slightly incomplete deuteriation of the $LiAlD_4$ (Cambridge Isotope Laboratories, Cambridge MA) used in the preparation of **3**-OH.[2b] The **3**-OTFA had therefore undergone negligible isomerization. More extensive rearrangement of this ester was detected after prolonged exposure to trifluoroacetic acid.

^2H NMR Analyses of Product Cyclooctanols. The regio- and stereochemical distribution of deuterium in the cyclooctanol product from each of the addition reactions was determined by the ^2H NMR spectroscopic method developed earlier[2b] but improved by operation at 30.7 MHz and the use of a higher concentration of shift reagent. The standard sample solution consisted of 15 mg of the alcohol and 75 mg of $Ho(fod)_3$ (Norell, stored in a vacuum oven at 57 °C and 30 mmHg) dissolved in 400 μL of CCl_4 containing 0.5% of $CDCl_3$. The chemical shifts of the synthetic isomeric cyclooctanols-*d* under these conditions were **3**-OH, δ -120.2; **4**-OH, -88.2; **5**-OH, -82.3; **6**-OH, -41.7; **7**-OH, -31.8; **10**-OH, -25.5; **8**-OH, -23.4; **9**-OH, -20.5; **11**-OH, -19.3, subject to minor variation with slight inconsistencies in sample concentrations.

The average deuterium content, D_{av}, of the labeled cyclooctanol products of the 99% addition reaction (519 min) was determined by two methods. (1) A drop of the cyclooctanol was weighed in an NMR tube, 10 μL of $CDCl_3$ (Norell, isotopic purity >99.8%, d = 1.500) and 400 μL of CCl_4 (Aldrich, Gold Label) were introduced, and the tube was promptly capped tightly. The ^2H NMR spectrum was recorded (without shift reagent), and comparison of the $CDCl_3$ and combined ring-*d* signal intensities yielded a D_{av} value of 1.42. Two repeat analyses gave values of 1.43 and 1.36. (2) In 15 mL of stirred CH_2Cl_2 under Ar 350 mg (2.71 mmol) of the alcohol was treated with 559 mg (2.71 mmol) of *N,N'*-dicyclohexylcarbodiimide, 40 mg (0.27 mmol) of 4-pyrrolidinopyridine, and 225 mg (2.03 mmol) of $(CD_3CO)_2O$, prepared from acetic-d_3 acid-*d* (Aldrich, Gold Label, isotopic purity 99.5%) by the method of Ellison and Kotsonis.[30] After 12 h the CH_2Cl_2 was evaporated under vacuum

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and the product acetate-d_3 (401 mg, 2.30 mmol, 85%) was obtained by direct distillation, bp 57-59 °C (0.5 mmHg). The 200-MHz ^{1}H NMR spectrum[31] consisted of ring-proton absorptions at δ 1.53-1.75 and 4.92 and a barely detectable signal at δ 2.01 for trace $COCD_2H$. Comparison of the ring (δ 0.5 to -3.1) vs. methyl (δ -17.0) ^{2}H NMR signal intensities for this ester (15 mg in 400 μL of CCl_4 containing 0.5% of $CDCl_3$) in the presence of shift reagent Pr(fod)$_3$ (15 mg) gave D_{av} = 1.395.

^{2}H NMR Analysis of Recovered Cyclooctenes. The unconsumed cyclooctene recovered from the 30-min and 60-min partial addition reactions was analyzed for deuterium incorporation as follows. An integration-reference solution was made up of 10 μL (15.0 mg, 0.125 mmol) of $CDCl_3$ (Norell, isotopic purity >99.8%, d = 1.500) plus 200 μL of CCl_4 (Aldrich, Gold Label); volume additivity was assumed. The ^{2}H NMR spectrum of a sample of 30 μL (25.4 mg, 0.2303 mmol, d = 0.846) of the cyclooctene plus 20 μL of the integration-reference solution (containing 0.0119 mmol of $CDCl_3$) was recorded with integration of the signals for $CDCl_3$, vinylic D, allylic D, and more distal D at δ 7.27, 5.64, 2.16, and 1.52, respectively. The ring-deuterium signal intensities were referenced to the $CDCl_3$ peak intensity to calculate the percentage incorporation of deuterium at these three cyclooctene locations. The average of three such determinations (±1%) is recorded in Table II. The recovered cyclooctene from the 120-min partial addition was analyzed likewise but using 10 μL of the olefin plus 20 μL of the integration-reference solution.

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Registry No. 1, 931-87-3; **3**-OH, 79734-96-6; **3**-OTFA, 87922-05-2; **4**-OH, 55693-43-1; **4**-OTFA, 87922-06-3; **5**-OH, 79734-92-2; **6**-OH, 87922-02-9; **7**-OH, 87922-03-0; **8**-OH, 87922-04-1; **8**-OTFA, 87922-07-4; **9**-OH, 79734-94-4; **10**-OH, 58378-54-4; **11**-OH, 58378-53-3; **13**, 87922-01-8; **30**, 87922-00-7; trifluoroacetic acid, 76-05-1; trifluoroacetic acid-*d*, 599-00-8.

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^{13}C NMR Spectra of Carbanions Derived from 2-Substituted 1,3-Dithianes, 9-Substituted Fluorenes, and Biphenylylmethanes As Related to Structure and Charge Density

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Abstract: The ^{13}C NMR spectra of 1,3-dithianyllithium, (2-methyl-1,3-dithianyl)lithium, (2-phenyl-1,3-dithianyl)lithium, (2-biphenylyl-1,3-dithianyl)lithium, fluorenyllithium, (9-methylfluorenyl)lithium, (9-phenylfluorenyl)lithium, (biphenylylmethyl)lithium, and (dibiphenylylmethyl)lithium in THF solutions have been obtained. Calculations of σ and π charge densities by INDO for the anions of toluene, fluorene, and biphenylylmethane in sp^2 and sp^3 states of hybridization are used to evaluate degrees of charge delocalization into phenyl substituents adjacent to these carbanions. The dithiane series appears to have sp^3-hybridized and localized carbanions with no indication of dπ-pπ bonding. (9-Phenylfluorenyl)lithium and (biphenylylmethyl)lithium offer excellent examples of little or no delocalization of charge by resonance and maximum delocalization, respectively. The use of correlations of charge density ($\sigma + \pi$) vs. chemical shift offers new evaluations of such delocalization.

Introduction

Since the initial investigation of carbon-lithium bonding by Waack et al. using ^{13}C NMR techniques,[1,2] carbon-13 NMR has become a valuable tool in studying the properties of carbanions. It has been used to evaluate structure,[3,4] solvent effects,[5] ion pairing,[6-9] hybridization,[1,10,11] charge density,[9,12-14] and resonance effects.[15] Although care is obviously necessary in using appropriate compounds[16] for comparison and controlling the variables of the investigation, ^{13}C NMR can be used very fruitfully to study electronic structures of carbanions.

The usual method of determining the hybridization for carbon using ^{13}C-H coupling constants does not apply for carbanions.[17-19]

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