Stereochemistry of Thermal and Electron Impact Induced Eliminations from Cyclic Acetates and Malonates

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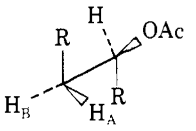
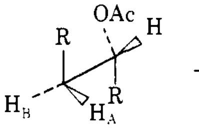
Abstract: Deuterium labeling experiments demonstrate that the pyrolytic elimination of acetic acid from the equatorial acetate *trans*-4-*tert*-butylcyclohexyl acetate proceeds via elimination of the cis axial hydrogen atom, as predicted on theoretical grounds. In contrast, the stereochemistry of the electron impact induced process involves predominant elimination of the trans equatorial hydrogen. The dichotomy is consistent with a nonconcerted mass spectral process, although a concerted process leading to a severely twisted ionized alkene cannot be excluded. The latter explanation cannot account for the observed trans elimination observed in the mass spectrum of diethyl *trans*-4-*tert*-butylcyclohexylmalonate, however. Both thermal and electron impact induced eliminations from the axial acetate *cis*-4-*tert*-butylcyclohexyl acetate occur with predominant cis elimination. The electron impact induced loss of *tert*-butylcyclohexene from diethyl *cis*-4-*tert*-butylcyclohexylmalonate occurs with clean cis stereochemistry. This result is fully consistent with predominant fragmentation from the most stable chair conformers. The similarities between the mass spectra of the unlabeled axial and equatorial acetates are due primarily to the formation of a common intermediate ion, and not to ring opening prior to fragmentation.



$\rightarrow \mathrm{M} - \mathrm{H_AOAc} > \mathrm{M} - \mathrm{H_BOAc}$

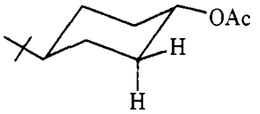
Ia



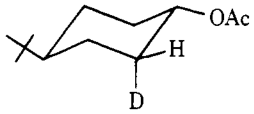
$\rightarrow \mathrm{M} - \mathrm{H_BOAc} > \mathrm{M} - \mathrm{H_AOAc}$

Ib

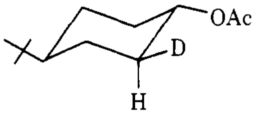
The fragmentation reactions of radical cations in the mass spectrometer often bear a formal similarity to the reactions of neutral molecules in condensed phases.[1] In a few cases, it has been established that the similarity is deep seated. For example, acetates eliminate acetic acid, either thermally or after electron impact; deuterium labeling experiments demonstrate that both occur with predominant loss of the β-hydrogen atom.[2,3] More subtly, it has been established that the predominant stereochemistry of β-hydrogen elimination from compounds such as I is the same for both reactions.[4,5] In each case, the predominant reaction corresponds to a transition state with an anti orientation of the bulky R groups. These experiments elegantly demonstrate that the structures of the reacting molecular ions are unrearranged and substantially undistorted. However, the multiplicity of conformers available for reaction in these acyclic systems leaves mechanistic questions that can only be answered by an acetate whose conformation is constrained, and which has two stereochemically distinct hydrogen atoms available for abstraction. Then, the choice of hydrogen abstracted should reflect steric and stereoelectronic factors within the two competing transition states for reaction of that conformer and thus should be more readily interpretable. A system fulfilling these criteria is *trans*-4-*tert*-butylcyclohexyl acetate (II). The bulky *tert*-butyl group should largely freeze the cyclohexyl ring into the indicated chair conformation,[6] and the equatorial acetate group can react with abstraction of either an equatorial or an axial hydrogen atom. Thus, the diastereomerically labeled acetates *trans*-4-*tert*-butylcyclohexyl-*cis-2-d* (III) and -*trans-2-d* acetate (IV) were prepared. Electron impact induced loss of deuterioacetic acid from III generates a peak at *m/e* 118; conversely, loss of protioacetic acid generates a *m/e* 119 peak. After correcting for isotopic impurities, statistical effects, isotope effects, and the occurrence of a small amount of 1,3- and 1,4-elimination,[3b] the ratio of these peak heights is related to the relative rates of abstraction of cis axial and trans equatorial hydrogen atoms. Similarly, the deuterium content of the alkene isolated after pyrolysis is relatable to the relative rates of cis and trans hydrogen elimination. Comparison of the pyrolytic and electron impact induced results should provide insight into the degree of mechanistic similarity of the two reactions. For these experiments to be readily interpreted, two conditions must be fulfilled. First, the cyclohexyl ring structure must remain intact before fragmentation. If processes such as α-cleavage (eq 1) precede fragmentation the stereochemical distinctions between axial and equatorial hydrogens are lost. Such processes have been reported for other cyclohexyl derivatives[7] and have in fact been invoked as a possible explanation for the nearly superimposable mass spectra of *cis*- and *trans*-4-*tert*-butylcyclohexyl acetate.[8] Second, the cyclohexyl ring must remain largely in the most stable chair conformation, and not flip into, for example, a boat-like conformer before fragmentation. Such a process, already reported for certain related compounds,[9] would complicate interpretation of these experiments. Fortunately, the results described below suggest that neither process is predominant



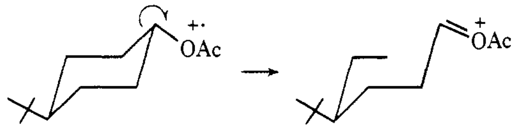
II



III



IV



(1)

Table I. Pyrolyses of Stereospecifically Labeled 4-*tert*-Butylcyclohexyl Acetates

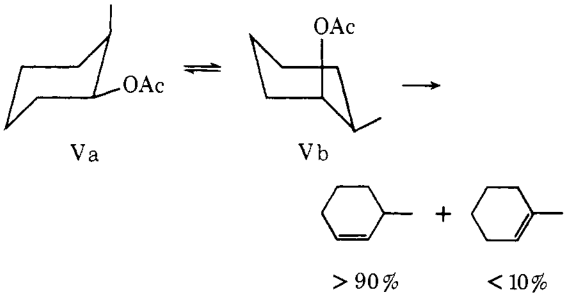
Compound	% isotopic purity[a]	(HOAC loss)/ (DOAC loss)[b]
III	97 d_1 3 d_0	2.2
IV	78 d_1 22 d_0	50
X	81 d_1 19 d_0	1.9
XI	95 d_1 5 d_0	46

[a] Determined by analysis of the mass spectrum of the trimethylsilyl derivative of the corresponding alcohol. [b] Corrected for unlabeled acetate.

among the molecular ions of *trans*-4-*tert*-butylcyclohexyl acetate which eliminate acetic acid.

Results and Discussion

A priori, the elimination of acetic acid from *trans*-4-*tert*-butylcyclohexyl acetate might involve abstraction of a cis axial hydrogen (axial, equatorial elimination) or a trans equatorial hydrogen (equatorial, equatorial elimination). Naively, it might be argued that both processes would be comparably facile, since the acetate group is equidistant from both sets of gauche hydrogen atoms. Nevertheless, it is generally considered that the pyrolytic eliminations proceeds via the axial, equatorial pathway.[2a,c-e,10] Experimental support of this hypothesis is not strong, however. The most frequently cited observation is that the pyrolysis of *cis*-2-methylcyclohexyl acetate produces more than 90% Δ^2-1-methylcyclohexene and less than 10% of the Δ^1 isomer (eq 2).[11] Since the conformer Va must produce at least 50% 1-methylcyclohexene on equatorial, equatorial elimination, the small amount of that alkene produced is taken to indicate preferential axial, equatorial elimination. However, this interpretation does not take into account the existence of the lower energy conformer Vb ($\Delta G° = -1.0$ kcal/mol).[12]



(2)

This conformer, which at 450° would comprise ca. 70% of the equilibrium mixture, can only produce the Δ^2 isomer for obvious geometrical reasons. Because there is evidence suggesting that axial acetates react more rapidly than equatorial acetates,[2a] the observed product distribution is not inconsistent with equatorial, equatorial elimination. Since the special preparative utility of acetate pyrolysis stems in large part from its stereospecific nature, since the reaction has been used as a diagnostic of alcohol stereochemistry,[13] and since it is the basis of comparison for the electron-impact induced reaction, it is particularly important that the stereochemical preferences of the reaction be established. The data appearing in Table I do so in an unambiguous manner.

If the pyrolysis reaction occurs with clean elimination of the cis axial hydrogen, and if an isotope effect of 2.0 is assumed,[2a] the predicted ratio of acetic acid loss to deuterioacetic acid is 2.0 for the axially deuterated acetate III. In fact, the observed ratio (determined by analysis of the mass spectrum of the alkene product) is 2.2. Conversely, the equatorially deuterated acetate IV eliminates acetic acid 50 times as readily as deuterioacetic acid. Thus, elimination of the cis axial hydrogen is by far the predominant process. The small amount of apparent trans equatorial elimination may indicate the intervention of a small amount of nonstereospecific radical elimination[2a] or may simply demonstrate that the deuterium labeling procedures are not 100% stereospecific. (It should be pointed out that these pyrolyses set a lower limit on the stereochemical purity of these derivatives. Even if all of the observed trans elimination is ascribed to nonstereospecific labeling, both compounds are over 93% labeled as indicated, if an isotope effect of 2.0 is assumed.)

Table II. Electron-Impact Induced Loss of Acetic Acid from Stereospecifically Labeled 4-*tert*-Butylcyclohexyl Acetates

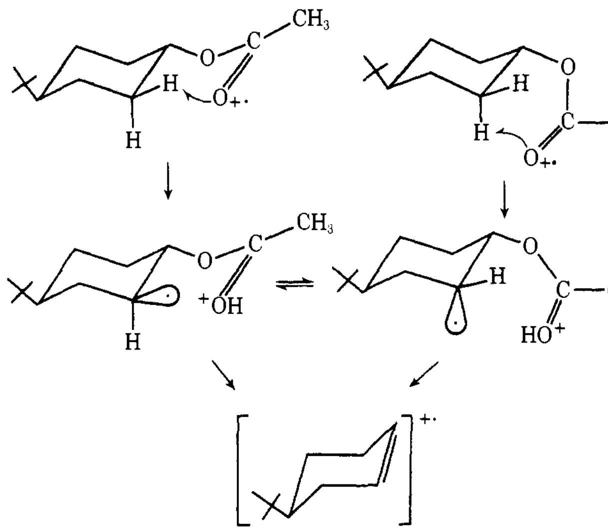
Compound	Ionizing voltage (eV)[a]	$(m/e)^b$ 139	$(m/e)^b$ 138	(HOAC loss)/ (DOAC loss)[b,c]
III	70	93%	7%	13
	12	90%	10%	9.0
IV	70	70%	30%	2.3
	12	70%	30%	2.3
X	70	69%	31%	2.2
	12	71%	29%	2.5
XI	70	86%	14%	6.1
	12	83%	17%	4.9

[a] Ionizing voltages are nominal. [b] All data are corrected for isotopic impurities and the occurrence of a small amount of 1,3 elimination. The extent of the latter process was evaluated by consideration of the mass spectra of *cis*- and *trans*-4-*tert*-butylcyclohexyl-*2,2,6,6-d*$_4$ acetate. Cf. ref 3b. [c] Ratios are the average of at least five determinations and are considered reproducible ±10%.

The observed predominant cis elimination is not unexpected on theoretical grounds. If, as is generally acknowledged,[2] the pyrolytic reaction is concerted, the transition state for elimination must involve a movement of the groups to be eliminated toward coplanarity. Since movement together of cis-1,2 placed groups leads to a flattening of the chair toward the flexible form against a relatively soft potential barrier,[6] and since the elimination leads smoothly to a cis double bond, the reaction should be facile. Conversely, movement together of trans-1,2 placed groups requires increased puckering of the chair against a potential barrier which is quite steep[6] and leads to an impossibly strained trans double bond. Clearly, this process should be less favorable.

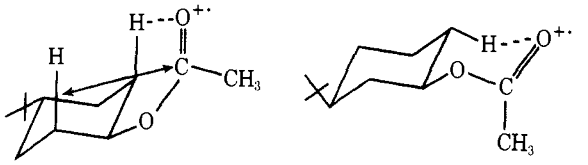
Table II contains data relating to the stereochemistry of the electron impact induced elimination. Strikingly, the *predominant stereochemistries of the thermal and the electron impact induced eliminations are opposite.* Thus, *trans*-4-*tert*-butylcyclohexyl-*trans-2-d* acetate (labeled with a trans equatorial deuterium) eliminates protioacetic acid and deuterioacetic acid in the ratio of 2.3 to 1 at 70 eV; the corresponding ratio for *trans*-4-*tert*-butylcyclohexyl-*cis-2-d* acetate is over five times as high (13 to 1).

A number of explanations might be adduced for this dichotomy. The most attractive relates to the concerted or stepwise nature of the elimination. If the reaction is stepwise, and if abstraction of either hydrogen generates a common intermediate radical, the relative amount of cis and trans elimination would be determined by the relative energies of the transition states for hydrogen abstraction. Removal of either cis or trans hydrogen would generate a radical site at the β-carbon atom (eq 3). Regardless of the identity of the abstracted hydrogen, the planar free radical[14] could expel acetic acid with smooth formation of a cisoid ionized carbon-carbon double bond.



(3)

The geometrical requirements for abstraction of a γ-hydrogen by an acetate carbonyl group are not well known. However, the formally similar McLafferty rearrangement of ketones has received much more attention.[15] Although the subject remains controversial, the balance of recent opinions seems to favor a stepwise mechanism for this rearrangement.[16,17] Thus, the optimal geometric requirements for the McLafferty rearrangement (an interatomic distance between the γ-hydrogen and the receptor oxygen of less than 1.8 Å,[18] and planarity of the carbonyl group and the carbon-hydrogen bond to be broken[17,19]) and for the abstraction of a hydrogen atom by an acetate group should be similar. Inspection of models indicates that both geometric requirements can be fulfilled for abstraction of either the cis axial or trans equatorial hydrogen without distortion of the cyclohexyl ring system. Thus, if the reaction is stepwise, trans elimination need not involve the energetically prohibitive moving together of trans equatorial substituents, or the generation of a strained ionized double bond. The explanation for the *preferred* trans elimination is less clear. Consideration of models indicate that the transition state for axial hydrogen abstraction may be more congested than the transition state for equatorial hydrogen abstraction. In the former case, a 1,3-diaxial interaction between the carbonyl group and the hydrogen at C-6 exists.



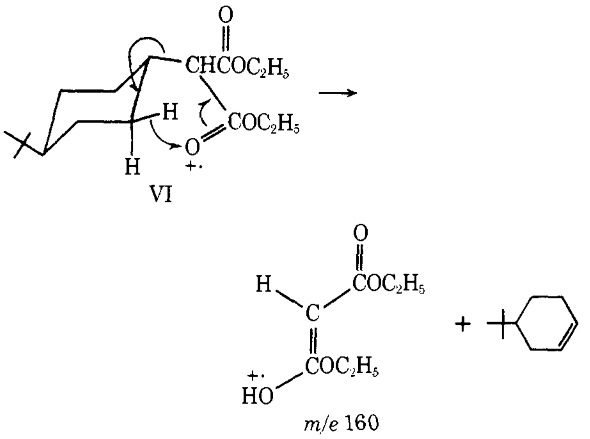
An alternative explanation of these results exists and cannot be excluded. If the p orbitals of the ionized double bond can be sufficiently skewed without prohibitive energetic cost, the elimination could occur trans in a concerted manner without any unfavorable deformation of the cyclohexyl ring system. There is, in fact, considerable evidence that indicates that ionized alkenes are, in fact, appreciably twisted. Spectroscopic data on Rydberg states of ethylene suggest an angle of about 30° between the p orbitals.[20] Calculations using the SCF CNDO/2 method indicate an equilibrium angle of 37° for the p orbitals of $C_2H_4^+$; the twisted geometry is predicted to be 0.1 eV more stable than the planar geometry and 0.9 eV more stable than the perpendicular form.[21] If the geometry of ionized 4-*tert*-butylcyclohexene is similar to that of ionized ethylene, electron impact induced elimination of a trans hydrogen may be less unfavorable than for the pyrolytic process; less movement together of the trans equatorial groups may be required in the transition state. Nevertheless, this argument does not predict *preferential* elimination of the trans hydrogen unless the preferred geometry involves skewing by 60° or more. In that case, the concerted elimination of the trans hydrogen involves the energetically more favorable spreading apart of the trans equatorial groups. In the absence of accurate knowledge concerning the preferred geometry of the 4-*tert*-butylcyclohexene radical ion, this possibility cannot be excluded.

Table III. Electron-Impact Induced Loss of 4-*tert*-Butylcyclohexene from Stereospecifically Labeled Diethyl 4-*tert*-Butylcyclohexylmalonates

Compound	Ionizing voltage (eV)[a]	(*m/e*)[b] 160	(*m/e*)[b] 161	($C_9H_{17}D$ loss)/(C_9H_{18} loss)[c]
VII	70	92%	8%	11.5
	12	93%	7%	13
VIII	70	55%	45%	1.2
	12	53%	47%	1.1
XIII	70	55%	45%	1.2
	12	58%	42%	1.4
XIV	70	>98%	<2%	>50
	12	>98%	<2%	>50

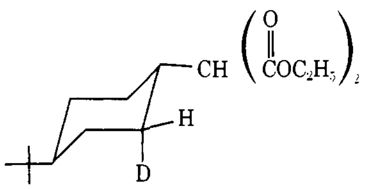
[a] Ionizing voltages are nominal. [b] All data are corrected for isotopic impurities and the occurrence of a "McLafferty +1" peak. The mass spectra of diethyl *trans*-4-*tert*-butylcyclohexyl-2′,2′,6′,6′-d_4-malonate and diethyl *cis*-4-*tert*-butylcyclohexyl-2′,2′,6′,6′-d_4-malonate indicated that the McLafferty rearrangement was >98% site specific. [c] Ratios are the average of three determinations and are considered reproducible ±10%.

Therefore, it appeared worthwhile to investigate the stereochemistry of an elimination occurring with charge retention on the heteroatom and generation of a neutral alkene. The base peak in the mass spectrum of diethyl *trans*-4-*tert*-butylcyclohexylmalonate (VI) corresponds to such a process (eq 4).[22] Table III contains data relating to the electron-impact induced elimination of neutral *tert*-butylcyclohexene from diethyl *trans*-4-*tert*-butylcyclohexyl-*cis*-2′-*d*-malonate (VII) and -*trans*-2′-*d*-malonate (VIII). *The predominant mode of tert-butylcyclohexene elimination is also trans.* Thus, VIII (labeled with a trans equatorial deuterium) eliminates labeled alkene and unlabeled alkene in the ratio of 1.2 to 1 at 70 eV; the corresponding ratio for VII (labeled with a cis deuterium) is ca. ten times as high. Since the most stable geometry of a ground electronic state alkene is planar,[23] and since a planar trans double bond in a six-membered ring would be highly strained, this result provides more convincing evidence for the existence of a nonconcerted McLafferty rearrangement.

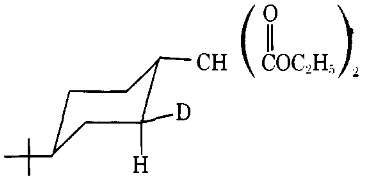


(4)

The stereospecificity of electron impact induced elimina-



VII

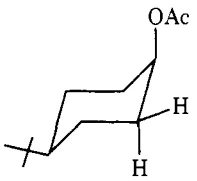


VIII

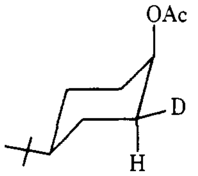
tion from II and VI is lower than the stereospecificity of acetate pyrolysis. This is not unexpected; if the mass spectral eliminations are stepwise, the difference in energy between the transition states leading to cis and trans eliminations is probably small. The stereospecificity of the electron impact induced elimination from the malonate VI is, however, considerably higher than from the acetate II. This is probably due largely to the occasional occurrence of ring opening prior to loss of acetic acid (eq 1), with consequent loss of stereochemistry. An analogous process is not possible for the malonate VI. It appears unlikely that much of the cis acetic acid elimination can be attributed to a competing pyrolytic process. All acetate mass spectra were obtained using a direct insertion technique and source temperatures below 50°. In contrast, the acetates survived vapor phase chromatography at 170° without detectable elimination. It also appears unlikely that much cis acetic acid elimination can be attributed to partial hydrogen–deuterium randomization prior to fragmentation, since the stereospecificity of the elimination remains virtually unchanged from 70 eV to threshold.[24] Generally, hydrogen–deuterium randomization has been observed (and predicted) to be increased at low ionizing voltages.[25]

It should be emphasized that the predominant trans elimination observed in the electron impact induced elimination cannot simply be attributed to the conformational mobility of the cyclohexyl ring system. Whatever conformation of the ring system is implicated, concerted elimination of the trans hydrogen necessitates the introduction of a highly strained transoid double bond into a six-membered ring.

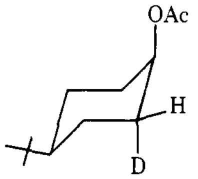
In an effort to better understand the comparatively low stereospecificity observed in the mass spectral elimination of acetic acid from *trans*-4-*tert*-butylcyclohexyl acetate, the stereospecificity of elimination from *cis*-4-*tert*-butylcyclohexyl acetate (IX) was investigated. If the cyclohexyl ring remains intact and locked in the most stable chair conformer, *cis*-4-*tert*-butylcyclohexyl acetate must eliminate acetic acid with clean cis stereochemistry; only the cis equatorial hydrogen is geometrically accessible to the axially oriented acetate carbonyl. Such behavior was, in fact, observed during the pyrolytic reaction (Table I); only a small amount of deuterium is eliminated from the trans axially deuterated derivative XI.



IX



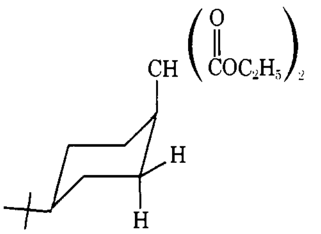
X



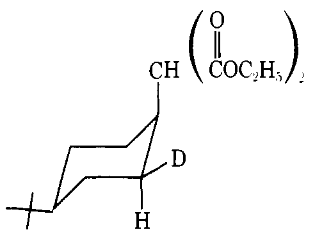
XI

The electron impact induced elimination also occurs with predominant cis stereochemistry, although the stereospecificity is rather low (Table II); the trans labeled acetate XI eliminates ca. half as much deuterium as the cis labeled acetate X. This observation suggests the intervention of appreciable amounts of ring cleavage prior to fragmentation and/or appreciable fragmentation through boat conformers. (Since the axial isomer is more strained than the equatorial isomer, both processes may be more favorable for IX than for II.) Although these results do not permit an assessment of the relative importance of these two processes, they do raise the possibility that the stereospecificity of the elimination from ions of *trans*-4-*tert*-butylcyclohexyl acetate in which the cyclohexyl ring is intact and in the stable chair conformation may be higher than simple inspection of the data in Table II indicates.

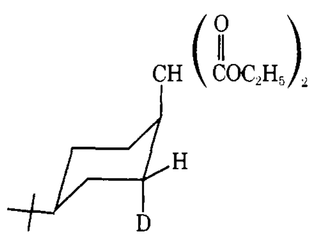
Boat-like conformers have already been implicated in other electron impact induced eliminations from cyclohexyl systems.[9] The results obtained in the present study are, however, fully consistent with fragmentation occurring predominantly from the most stable chair conformation. Although boat and twist boat conformers cannot be ruled out, they appear less plausible in certain cases. For example, the data for the electron impact induced elimination of *tert*-butylcyclohexene from the malonates XIII and XIV appear in Table III. *No detectable trans elimination occurs from the axial malonates.* There are accessible boat-like conformers of the axial malonate XII in which the malonate group can approach the trans hydrogen closely, yet no trans elimination is observed. Either these conformers are not implicated significantly in the fragmentation or they undergo cis elimination. The latter explanation seems unlikely in light of the very predominant trans elimination observed from the equatorial malonate VI (where, in most conformations, both cis and trans hydrogens are accessible). If the former explanation is correct, it would be surprising if other boat-like conformations participated extensively in the fragmentation reactions.



XII



XIII



XIV

Conclusions

These experiments shed considerable light on the stereochemistry of thermal and electron impact induced eliminations proceeding through cyclic transition states. The pyrolysis experiments unambiguously demonstrate that both axial and equatorial acetates react with essentially complete cis elimination. In contrast, although the electron impact induced elimination proceeds predominantly cis from the axial acetate, the elimination from the equatorial acetate is predominantly trans. This discrepancy is attributed to the stepwise nature of the electron impact induced process, although a concerted process leading to a severely twisted alkene radical ion cannot be excluded.

The latter explanation cannot be invoked to explain the electron impact induced predominant trans elimination of 4-*tert*-butylcyclohexene from diethyl *trans*-4-*tert*-butylcyclohexylmalonate. The elimination of 4-*tert*-butylcyclohexene from diethyl *cis*-4-*tert*-butylcyclohexylmalonate is exclusively cis. These experiments demonstrate that the cyclohexyl ring structure of these acetates remains largely intact and that stereochemical relationships are largely preserved before acetic acid elimination occurs. Thus, the similarity of the spectra of the unlabeled acetates[8] must be due primarily to the formation of a common intermediate, ionized 4-*tert*-butylcyclohexene, which then fragments further to produce most of the lower mass peaks. The malonate results are fully consistent with predominant elimination of 4-*tert*-butylcyclohexene from the most stable chair conformations. These experiments reaffirm the utility of stereospecific deuterium labeling as a probe into the mechanism of electron-impact induced reactions; the stereochemistry of Ei eliminations from conformationally immobile systems may eventually become a reliable probe into the stepwise or concerted nature of these reactions. Finally, these results demonstrate again the sensitivity of mass spectral fragmentations toward subtle stereochemical differences and support the use of deuterium labeling in conjunction with mass spectrometry as a tool for structure elucidation.[26]

Experimental Section

Mass spectra were obtained on an A.E.I. MS902 mass spectrometer using a direct insertion probe; source temperatures were maintained at 30-50° to minimize pyrolytic reactions. Electron voltages are nominal. Pyrolyses were accomplished by injecting 20-μl samples of pure acetate onto a 3-m unpacked glass column by a 15 ml/min flow of helium. Under these conditions essentially all of the acetate was converted to alkene. The deuterium content of the 4-*tert*-butylcyclohexene was determined by analysis of the mass spectra of the alkene after purification by gas chromatography. All gas chromatography was performed on a Hewlett-Packard 5750 instrument containing a 10 ft × 0.25 in. column packed with 10% Carbowax 20M on 80-100 Chromosorb P.

***trans*-4-*tert*-Butylcyclohexyl-*cis*-2-*d* Acetate (III), *cis*-4-*tert*-Butylcyclohexyl-*cis*-2-*d* Acetate (X), and *cis*-4-*tert*-Butylcyclohexyl-*trans*-2-*d* Acetate (XI)** were prepared from the corresponding alcohols by the acetic anhydride-pyridine procedure[27] and were purified by preparative gas chromatography prior to use. The corresponding alcohols, prepared according to literature procedures,[28] were thoroughly characterized. Gas chromatography, thin layer chromatography (Al_2O_3, benzene eluent), and NMR spectroscopy confirmed the axial or equatorial nature of the hydroxyl groups. Melting points of the *p*-nitrobenzoate derivatives and of the alcohols themselves confirmed the location of the hydroxyl group.

***trans*-4-*tert*-Butylcyclohexyl-*trans*-2-*d* Acetate (IV).** A solution of 120 mg (0.77 mmol) of *cis*-4-*tert*-butylcyclohexyl-*cis*-2-*d* acetate[28] in 10 ml of reagent acetone was stirred under nitrogen at 0°. Jones reagent[29] was carefully added (care was taken to maintain the solution at less than 10°) until the orange color of unreacted chromic acid persisted. After 20 min, the excess reagent was destroyed by the addition of 2-propanol. The mixture was diluted with 20 ml of water, and washed three times with ethyl ether. The combined organic layers were washed with water, saturated sodium bicarbonate solution, and water, dried (M_gSO_4), and concentrated under reduced pressure to 5 ml. The solution of crude 4-*tert*-butylcyclohexanone-*trans*-2-*d* was immediately added to a cooled slurry of $LiAlH_4$ (1.0 g) in ethyl ether (50 ml). After the mixture had stirred overnight, the excess hydride was carefully decomposed by the addition of 10% hydrochloric acid. After washing the organic phase with 10% hydrochloric acid and water, it was dried and concentrated to dryness. Two recrystallizations (hexane) of the residue gave 65 mg (54%) of *trans*-4-5-butylcyclohexanol-*trans*-2-*d*, mp 81-81.5° (lit.[30] mp 81-82°). Gas chromatography demonstrated that the product was over 99% equatorial alcohol. This observation was confirmed by NMR spectroscopy (δ 3.35 ppm, $W_{1/2}$ = 19 Hz). The alcohol was converted into the acetate IV according to the usual procedure.

Diethyl *trans*-4-*tert*-Butylcyclohexyl-*cis*-2′-*d*-malonate (VII), Diethyl *trans*-4-*tert*-Butylcyclohexyl-*trans*-2′-*d*-malonate (VIII), Diethyl *cis*-4-*tert*-Butylcyclohexyl-*cis*-2′-*d*-malonate (XIII), and Diethyl *cis*-4-*tert*-Butylcyclohexyl-*trans*-2′-*d*-malonate (XIV) were prepared by analogy to the procedure of Stork and White.[31] Thus, for example, 20 ml of absolute ethanol were placed in a 50-ml three-necked round-bottom flask equipped with a reflux condenser and dropping funnel and maintained under a nitrogen atmosphere. After 0.115 g (5 mmol) of metallic sodium had dissolved, 0.800 g (5 mmol) of diethyl malonate (dissolved in 5 ml of ethanol) was added. After 15 min, 0.062 g (0.2 mmol) of *cis*-4-*tert*-butylcyclohexyl-*trans*-2-*d*-tosylate (mp 77-78°, lit.[31] mp 77.5-78.5°) dissolved in 5 ml of ethanol was added. After 5 hr at reflux, the solution was cooled and acidified. The mixture was extracted with several portions of ether; the ether layers were combined, washed with water, dried (M_gSO_4) and concentrated sub vacuo. A preliminary distillation removed most of the unreacted diethyl malonate. The product, diethyl *trans*-4-*tert*-butylcyclohexyl-*cis*-2′-*d*-malonate was isolated by preparative gas chromatography. The isolated yield (27%) was 0.016 g (0.053 mmol). The product exhibited ir and NMR spectra and VPC retention times (on the standard Carbowax column, and on a 10 ft × 0.25 in. U CON on 80-100 Chromosorb W-AW) identical with those of authentic[31] unlabeled diethyl *trans*-4-*tert*-butylcyclohexylmalonate. The mass spectra exhibited a molecular ion at *m/e* 299.

Gas chromatography permitted facile separation of cis and trans malonate. In every case, the reaction proceeded with >98% inversion of configuration at the tosylate bearing carbon.

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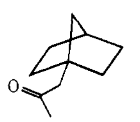
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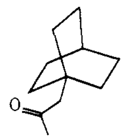
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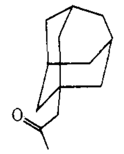
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Mechanistic Photochemistry of 1-Adamantylacetone

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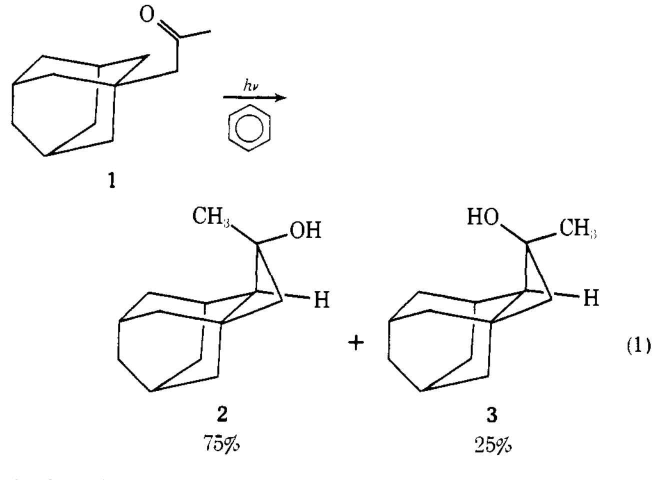
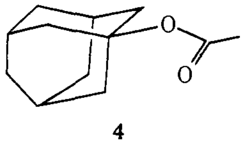
Abstract: Irradiation of 1-adamantylacetone (**1**) results in essentially a quantitative yield of two cyclobutanols, **2** and **3**. Quantum yields for the formation of **2** and **3** from the S_1 and T_1 states of **1** in benzene and methanol are reported. Formation of cyclobutanols from the excited triplet state of **1** is much more efficient in methanol than in benzene. The cyclobutanol product ratio, **2**:**3**, is 1.0-1.8 for the T_1 reaction and approximately 5 for the S_1 reaction. The observed stereoselectivity from the excited singlet state reaction is consistent with the intermediacy of a short-lived 1,4 biradical which undergoes rehybridization, resulting in a preference for rotation and closure to yield **2** rather than **3**. The reactivity of the S_1 and T_1 states of **1** toward intramolecular γ-hydrogen abstraction is determined by fluorescence measurements and Stern-Volmer treatments of 1,3-pentadiene quenching of cyclobutanol formation, respectively.

We[2] and others[3] have recently reported that irradiation of 1-adamantylacetone (**1**) results in nearly quantitative formation of two cyclobutanols, **2** and **3** (eq 1). Neither of the Norrish type II photoelimination products, acetone and adamantene, was observed on photolysis of **1**, although Gano has subsequently reported trapping adamantene in low yields from irradiation of ester **4**.[4] The absence of adamantene among the photoproducts of 1-adamantylacetone[2-4] and the structure assignments for **2** and **3**[2,3] have been discussed in some detail elsewhere. We report here our studies of solvent and multiplicity effects on the efficiency and stereochemistry of cyclobutanol formation from **1**.[5]

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Results and Discussion

The quantum yields for formation of **2** and **3** in benzene and methanol given in eq 2 were determined using benzo-

$$1 \xrightarrow{h\nu} 2 + 3 \qquad (2)$$

	2	3
	0.010	0.0033
MeOH	0.027	0.012

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