

Table II. Heats of Formation from the MINDO/3 Calculations

	ΔH_f , kcal/mol
bicyclo[4.2.0]octa-2,4,7-triene (6)	81.1
cis-tricyclo[4.2.0.0 ^{2,5}]octa-3,7-diene (7)	134.4
cyclooctatetraene (8)	63.0
tricyclo[4.2.1.0 ^{2,5}]nona-3,7-dien-9-one (2)	88.0
CO	13.5
highest energy structure in:	
reaction 2	102.2
reaction 3	106.1
reaction 4	118.5

program when used with a minimal STO-3G basis set does not provide a better description of the molecules, and a better calculation with larger basis sets is not possible in our laboratories at this time.

The electron densities were then calculated for each atom, using the MINDO/3 method, and they are shown (in parentheses) in Figure 2 along with the calculated values of the Mulliken bond orders.¹⁶ Because of the objectives of this study, it is important to consider the through space interactions. For ketone 2, significant interactions were found between atoms C7-C9 and C8-C9, with Mulliken bond order values equal to 0.081. All of the other possible interactions were negligible or destabilizing. Of particular interest for later reference is the C1-C6 interaction, where the bond order is -0.039. In bicyclo[4.2.0]octa-2,4,7-triene (6), the bond order for the C1-C3 interaction is -0.023.

In order to compare directly the ketone structure with the reaction products in eq 1, CO was calculated. The minimum energy MINDO/3 bond length is 1.128 Å. This value compares well with previous reports²⁵ and with the experimentally determined distance.²⁶ The electron densities are 3.923 for the carbon atom and 6.077 for the oxygen atom. The Mulliken bond order is 2.004.

The relative energies for the four hydrocarbon structures plus CO obtained from the MINDO/3 calculations appear in Table I. Inspection of these values reveals that 7 is a higher energy species than ketone 2 and suggests that it is not a likely intermediate in the thermal decarbonylation reaction. As a result, the reaction involving 7 will not be considered any further.

All of the degrees of freedom were considered for each system in order to identify those points on the potential energy surface which are of chemical interest.²⁷ For a simple reaction such as this one, these points are energy minimums which correspond to the equilibrium geometries of the products plus reactants and a higher energy point between the two minimums, whose minimum energy will correspond to that of the activated complex for the reaction. This latter point was obtained by varying linearly the coordinates of the system between the values for the reactant and the product. This procedure obviously generates several lines along the surface which connects the reactant and the product. In order to obviate this, intermediate points were selected, and their energy was minimized taking into account all of the degrees of freedom of the molecular species. In this way the reaction path was selected after careful inspection of all of the calculated points.²⁸ It is worth mentioning that in every case, those

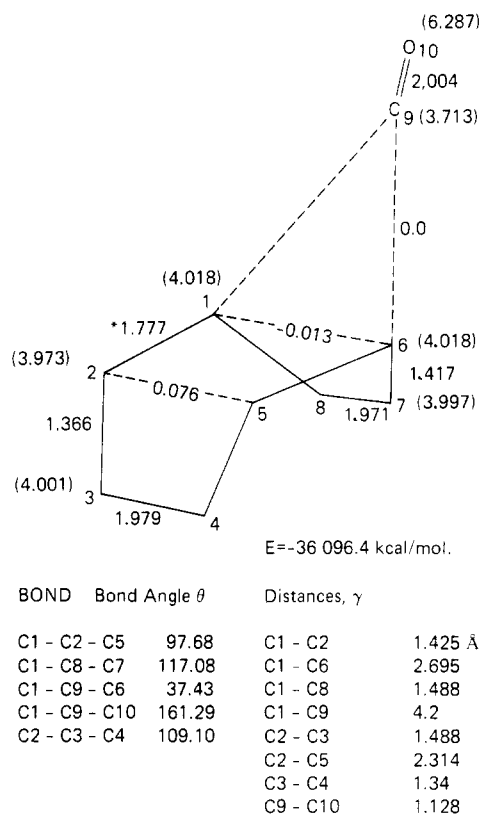
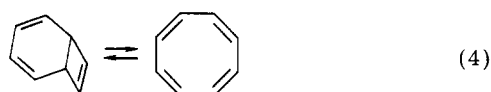
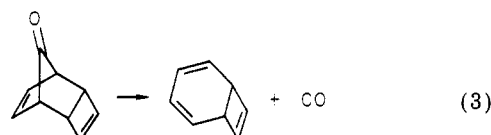
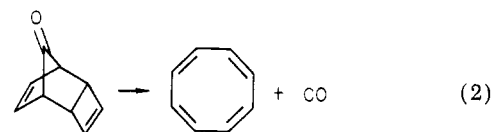


Figure 3. Electron densities and Mulliken bond orders for the higher energy structure in reaction 2 using MINDO/3.

molecular distortions which destroy the plane of symmetry of the system also generated higher energy structures. The heats of formation obtained for these structures are summarized in Table II.

For reaction 2, the greatest change in total energy was



seen when the movement of the CO fragment away from the C₈H₈ structure was accompanied by an increase in the C8-C1-C6-C5 dihedral angle. The energy of the structure was also influenced, although to a much lesser degree, by increasing the C1-C6 plus C2-C5 distances and increasing the C1-C2-C5-C4 dihedral angle. The optimized structure for the highest energy structure along this pathway has the C8-C1-C6-C5 dihedral angle increased to 145.00°. The structure shows enhanced double bond character at C1-C2 and C5-C6 and has a total energy equal to -36096.4 kcal/mol. This makes it 14.2 kcal/mol less stable than compound 2. The results are shown in Figure 3. For reaction 3, the same structural variations were performed as above, except for the C2-C5 bond distance which was not increased. The dihedral angle C8-C1-C6-C9 was increased

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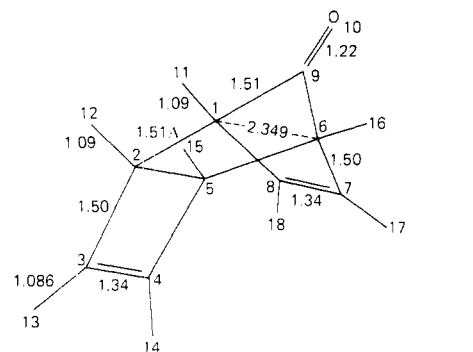
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Table I. Total Energies Obtained from Different Methods

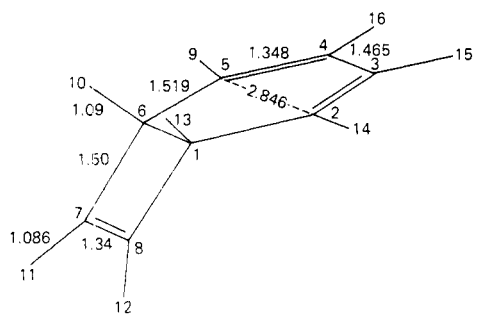
	total energy, kcal/mol				ΔE , kcal/mol ^a
	DPCILO	CNINDO	GAUSSIAN/70	MINDO/3	MINDO/3
bicyclo[4.2.0]octa-2,4,7-triene (6)	-39587.4	-39444.6	-190617.9	-26050.6	+18.2
cis-tricyclo[4.2.0.0 ^{2,5}]octa-3,7-diene (7)	-39619.3	-39492.8	-190578.1	-25997.4	+71.4
cyclooctatetraene (8)	-39495.3	-39340.5	-190600.5	-26068.8	0
tricyclo[4.2.1.0 ^{2,5}]nona-3,7-dien-9-one (2)	-55691.2	-55551.2		-36110.6	+38.6 ^b
CO		-15713.2	-69792.3	-10080.4	

^a Energy differences relative to cyclooctatetraene. ^b The energy of CO was taken into consideration in order to make this comparison.



Bond Angle, θ	Dihedral Angle, φ
C1 - C2 - C5	105.36°
C1 - C2 - H12	114.15
C1 - C3 - C7	109.67
C1 - C3 - H18	125.16
C1 - C9 - C6	106.18
C1 - C9 - C10	128.91
C2 - C3 - C4	94.01
C2 - C3 - H13	132.99
C1 - C2 - C5 - C4	122°
C8 - C1 - C6 - C5	118.13
C8 - C1 - C6 - C9	112.88
H12 - C2 - C1 - C5	126.11
H11 - C1 - C2 - C5	159.22

endo-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one, 2



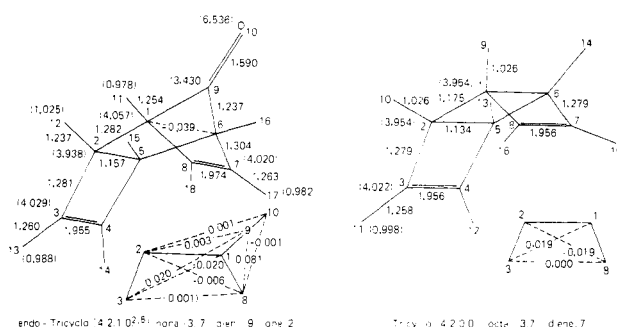
Bond Angle, θ	Dihedral Angle, φ
C1 - C2 - C5	115.50
C1 - C8 - C7	120.81
C2 - C5 - C4	86.22
C8 - C1 - C2	123.69
H10 - C2 - C1	107.94
H11 - C3 - C2	133.11
H16 - C3 - C1	119.87
C1 - C2 - C5 - C4	123°
H10 - C2 - C1 - C5	129.21

Bicyclo[4.2.0]octa-2,4,7-triene, 6

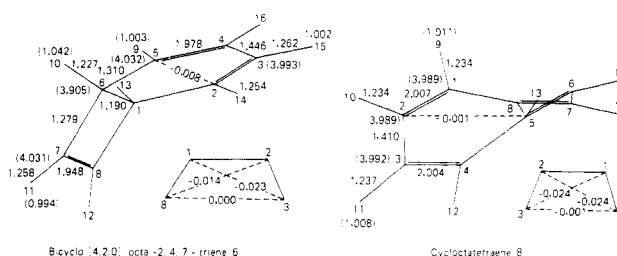
Figure 1. Molecular geometry obtained from MINDO/3 calculations.

has a planar six-membered ring and a dihedral angle (φ) between the rings equal to 123°. This is seen in Figure 1.

For *cis*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (7)¹⁹ and cyclooctatetraene (8), the reported bond angles plus interatomic



endo-Tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one, 2



Bicyclo[4.2.0]octa-2,4,7-triene, 6

Cyclooctatetraene, 8

Figure 2. Electron densities and Mulliken bond orders

distances were used in the initial geometries. The geometry of the most stable structure for tricyclo[4.2.0.0^{2,5}]octadiene (7) agrees well with previous reports.¹⁹ The same cyclobutane-cyclobutene dihedral angle was obtained, 124°, and the bond lengths agree within 0.01 Å with the values reported. In the case of cyclooctatetraene, "tub form", the most stable geometry found has a dihedral angle C1-C2-C5-C4 equal to 140.9°, and the CC bond lengths are 1.340 and 1.476 Å for the double and single bonds, respectively. The CH bond lengths are 1.100 Å, and the C1-C6 distance is 3.079 Å. These results agree within 0.02 Å with the reported values.^{20,21}

The relative stabilities obtained with the different methods can be compared in Table I, where the energy for cyclooctatetraene is used as the basis for comparison. As can be seen, the known order of relative stabilities²² of compounds 6, 7, and 8 is reproduced by the MINDO method, which uses the bond types directly in the parameterization process.²³ Thus this method was adopted for the remainder of this study. The DPCILO and CNINDO methods do not reproduce the known relative stability order. This can be attributed to the limitations of the CNDO parameterization process, especially since molecules with different size rings are involved.²⁴ The ab initio GAUSSIAN/70

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Thermal Decarbonylation of Some Strained Ketones¹M. Rubio, Alfonso Garcia Hernandez, J. P. Daudey,² and R. Cetina R.

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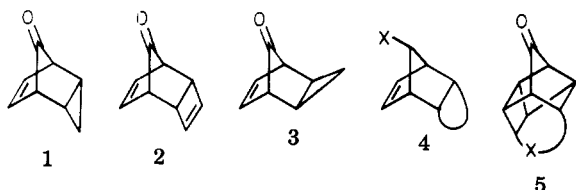
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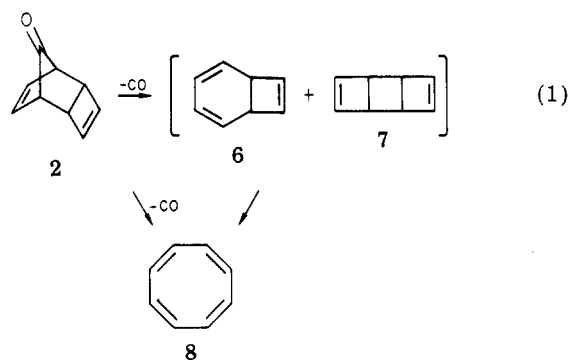
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Norbornen-7-one derivatives are known to undergo facile decarbonylation reactions, and these reactions are sensitive to the presence of endo-fused carbocyclic structures. MO calculations were performed on *endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one in order to determine the importance of electronic participation of the four-membered ring in the decarbonylation reaction.

Strained ketones are known to undergo facile thermal decarbonylation reactions, and the reaction rate is very sensitive to structural changes in the molecule.³⁻⁶ Of particular interest is the norbornen-7-one structural form where changes in the nature of the saturated ethylene bridge strongly influence the reaction rate even though the basic molecular structure about the carbonyl group is minimally changed. For example, there is a large difference in the reactivities of ketones 1,⁵ 2,³ and 3⁵ in de-



creasing order, respectively. Interestingly enough, this same structure-reativity relationship is observed in the solvolytic behavior for the analogous *anti*-7-norbornyl ester derivatives 4.⁷⁻⁹ This comparison suggests that similar electronic demands are made on the strained cyclopropyl (or cyclobutyl) bond in both reactions. A similar effect is seen with the cage ketones, 5, where those changes in the number of carbons in the chain (X) which increase the strain in the cyclobutyl C₂-C₃ bond also increase the reactivity of the ketone.⁴ It seemed appropriate to study the decarbonylation reaction in more detail in order to understand the nature of the participation of the strained bond. In this respect, SCF-MO calculations were performed for the structures involved in eq 1, and these results are compared with the experimental results. While the decarbonylation reaction of 2 is known to give cyclooctatetraene as the only product, our intent was to probe for the possible existence of intermediates in the reaction as are shown in eq 1.



Results

Computations. The molecular geometry of ketone 2 was determined, using DPCILO (Differential Perturbative Configuration Interaction Using Localized Orbitals),¹⁰ and was approached by first combining the known geometries for cyclobutene¹¹ plus norbornene^{12,13} followed by a variation of all the interatomic distances plus bond (θ) and dihedral (φ) angles, until the total energy of the system was minimized. The resulting geometry was then used to calculate the minimum energies, using GAUSSIAN/70,¹⁴ the semiempirical SCF-MO CNINDO,¹⁵ and MINDO/3¹⁶ methods. The results from the MINDO/3 calculations which include additional geometric variations in order to determine the minimum energy structure are shown in Figure 1. It is worth noting that the dihedral angle C8-C1-C6-C9 is 113° and is significantly lower than the reported value of 120°.³

Likewise, the minimum energy structure for bicyclo-[4.2.0]octa-2,4,7-triene (6) was determined as above by combining the known molecular geometries of cyclobutene¹¹ and cyclohexadiene.^{17,18} The resulting structure

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while the CO fragment was moved away from the C₃H₈ structure, and the ring structures were slightly changed. The optimized structure for the highest energy structure along this reaction pathway has the C8-C1-C6-C9 dihedral angle increased to 114.87° with a consequent reduction of the C7-C9 interaction to 0.049. The resulting structure is 18 kcal/mol less stable than compound 2.

For reaction 4, the plane of symmetry of the molecule was again maintained. The energy of the system and the electronic distribution are very sensitive to the motion of the cyclobutene ring and the C1-C6 bond breaking and not sensitive to the deformation of the cyclohexadiene ring. During this process, the cyclobutene double bond remains localized with little change in its electron density. Thus the calculation again points to the cyclic 6π electron intermediate.²⁶ In the highest energy structure along this reaction pathway, the C1-C6 bond order is increased to 0.181.

Rates of Decarbonylation. The rates of decarbonylation for the various ketones in deuterated benzene solution were followed by NMR analysis. The reactions showed good first-order kinetics between 15 and 80% reaction. Listed in Table III are the integrated first-order rate constants. The values represent the average of two or three runs. As can be seen in the table, the values compare well with literature values for those cases where the comparison can be made.

The decarbonylation reactions proceed cleanly to produce a single olefin product quantitatively. Norbornen-7-one (9) produces cyclohexadiene, while *endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (2) and bicyclo[4.2.1]nona-2,4,7-trien-9-one (10) produce cyclooctatetraene. These results are consistent with previous reports.^{3,7}

Discussion

As can be seen, the order of the stabilities for the various compounds obtained from these calculations agrees with the estimates available from various experiments. There is, however, a notable difference in the magnitude of the energy differences. This comparison can be made directly when considering reaction 4 for which a more complete set of data is available. The equilibrium concentration ratio of 6 to 8 is reported equal to 10⁻⁴ at 100 °C, providing an estimate for the ground state energy difference equal to 7 kcal/mol. This value is ca. 1/3 that calculated (18 kcal/mol). In fact for these reactions, the activation energies and ground state energy difference obtained from calculation are consistently greater than those from the experimental data.²²

In considering the decarbonylation reaction of ketone 2, the possible intervention of bicyclo[4.2.1]nona-2,4,7-trien-2-one can be disregarded, since it is less reactive than ketone 2, and its presence in the reaction is not consistent with the clean reaction kinetics observed. The presence of a reaction pathway involving tricyclo[4.2.0.0^{2,5}]octadiene in the overall decarbonylation reaction can also be discarded since this structure is less stable than even the highest energy structures in reactions 2 and 3.

However, the results show that the decarbonylation reaction could proceed with the formation of bicyclo[4.2.0]octadiene (6) (reaction 3). The recovery of cyclooctatetraene as the only reaction product is expected since 6 is readily converted to cyclooctatetraene under these conditions. The estimated rate constant for this reaction, under the present conditions based on the experimental data,²² is 10⁴ s⁻¹.

The calculations show the most favorable reaction pathway for the decarbonylation reaction to be the one that proceeds with participation of the double bond at

Table III. First-Order Rate Constants for the Decarbonylation Reaction of Various Ketones

	temp, °C	10 ⁶ k, s ⁻¹	ΔH [‡] , kcal/mol	ΔS [‡] , eu
	75	16.7 ± 0.04	28.5	1.1
	100	281 ± 7		
	100	350 ^c		
	100	1.48 ± 0.04	34.0	5.6
	125	28.2 ± 0.5		
	125	23 ^b		
	35	130 ^a		
	125	8.15 ^b		
	100	450 ^c		
	125	33000 ^b		
	100	0.009		
	100	0.003 ^c		
	125	0.2		

^a Reference 5. ^b Reference 6. ^c Reference 3.

C7-C8 plus the breaking of the C2-C5 bond to produce cyclooctatetraene directly (reaction 2). However, the energy difference between reactions 2 and 3 is only 4 kcal/mol. This small difference suggests that reaction 3 could be involved in the overall reaction. The optimized structure in Figure 3 implies that the reaction process can be greatly influenced by the character of the strained σ bond at C2-C5. This effect is of course observed in the experimental *k*'s listed in Table II for the various structures. Thus ketone 2, which has a more strained σ bond at C2-C5 than norbornen-7-one, is also more reactive. Likewise in the bicyclo[3.2.1.0^{2,4}]octen-8-one compounds, the isomer with the *endo* cyclopropyl group 1, which has the strained σ bond at C2-C4 in the preferred orientation for interaction with the incipient reaction intermediate, is the more reactive isomer.

In conclusion, our results show that the facile thermal decarbonylation reaction of the various norbornen-7-one structures, such as ketone 2, can be greatly influenced by the character of the strained σ bond at C2-C5. Furthermore, the most favorable reaction pathway for this compound proceeds with opening of the C2-C5 bond to produce cyclooctatetraene directly.

Experimental Section

Norbornen-7-one (9), *endo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (2), and bicyclo[4.2.1]nona-2,4,7-trien-9-one (10) were available from a previous study.⁷ The reactions were followed by NMR analysis of deuterated benzene solutions containing 0.2 M ketone. Sealed NMR tubes containing the reaction solutions were heated at the desired temperature in the absence of light. After the appropriate heating period, the tubes were cooled and analyzed. Seven or eight analyses were made between zero and 85% reaction, and the first-order rate constant calculations were based on the amount of starting material remaining plus product formed.

The reactions proceeded cleanly in every case to produce a single product. In the case of norbornen-7-one (9), the NMR spectra after five reaction half-lives was consistent with the formation of $99 \pm 4\%$ cyclohexadiene. No other products were observed. Ketone 2 produced $101 \pm 4\%$ cyclooctatetraene after eight reaction half-lives, and bicyclo[4.2.1]nona-2,4,7-trien-9-one (10) produced $100 \pm 4\%$ cyclooctatetraene after five reaction

half-lives.

Registry No. 1, 14725-99-6; 2, 38440-48-1; 3, 17876-06-1; 6, 4011-16-9; 7, 6572-53-8; 8, 629-20-9; 9, 694-71-3; 10, 34733-74-9; cyclohexadiene, 29797-09-9; *endo*-tricyclo[4.2.1.0^{2,5}]nona-7-en-9-one, 42948-87-8; (1 α ,4 α ,4 $\alpha\beta$,5 β ,8 β ,8 $\alpha\beta$)-1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalen-9-one, 15914-93-9.

Olefin Inversion. 3. Preparations and Reductions of *vic*-Halohydrin Trifluoroacetates

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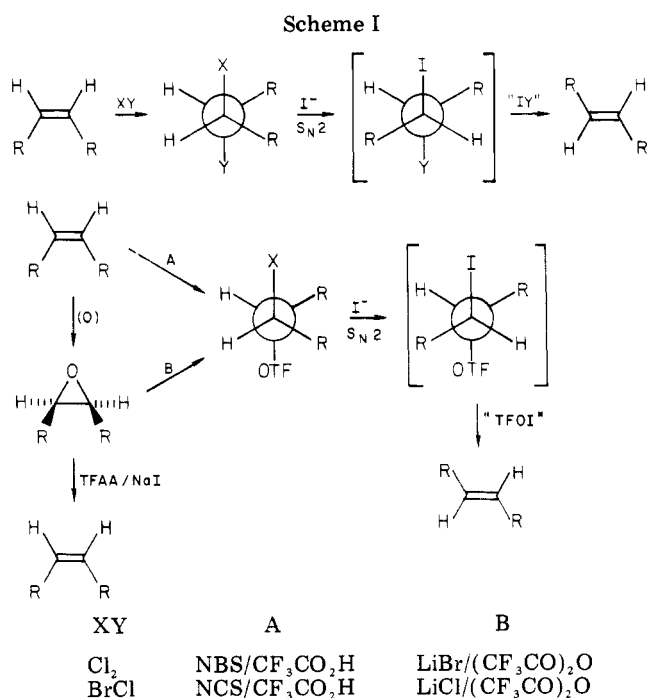
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Treatment of alkenes with *N*-bromo- and *N*-chlorosuccinimide in trifluoroacetic acid resulted in stereospecific anti addition of the elements of trifluoroacetyl hypobromite and hypochlorite, respectively. Heating the *vic*-bromo- or -chlorohydrin trifluoroacetates with NaI in DMF produced olefins with inversion of geometry. Treatment of the adducts with Zn in DMF reduced them to olefins with retention of geometry. Reductive transformations involving the chlorohydrin trifluoroacetates were virtually stereospecific, whereas those involving the bromohydrin trifluoroacetates were >90% stereoselective for NaI reductions and only 60-90% stereoselective for reductions by Zn.

Reductive elimination of vicinal disubstituted compounds employing a wide range of reducing agents has received considerable attention for many years.¹ In particular, sodium iodide induced the elimination of vicinal dibromides,² bromochlorides,³ dichlorides,³ ditosylates,² and dimesylates.² The reductions of *vic*-dibromides proceeded with predominant anti stereochemistry,⁴ and very exacting kinetic studies suggested that the elimination reactions induced by iodide (and other charged nucleophiles) should be viewed reciprocally with electrophilic addition.⁵ If one of the bromine atoms was on a primary (deuterated) carbon, however, S_N2 displacement of bromide by iodide on carbon occurred,⁶ followed by anti elimination of IBr. The resulting deuterated olefin was then the product of a (net) syn elimination. The presumed intermediate iodobromide evidently collapsed by an anti elimination faster than iodide ion could perform another displacement on bound iodine since the product geometry would not otherwise have been preserved. Similarly, diastereomerically pure dichlorides and bromochlorides treated with iodide in DMF resulted in olefins that were the product of (net) syn elimination.³

Additions of halogen to 1,2-disubstituted olefins generally involve clean anti addition. The intervention of a Walden inversion between an anti addition and an anti



elimination constitutes an odd number of inversions and will yield an olefin of opposite configuration (Scheme I). The utility of this route for olefin inversion employing dichlorides and dibromides has been investigated.³ The observation that *vic*-iodohydrin trifluoroacetates eliminated cleanly with anti stereochemistry in the presence of sodium iodide at room temperature⁷ prompted a study of the preparations and reductions of *vic*-bromo- and -chlorohydrin trifluoroacetates. In particular, we wished to know the stereochemistry of iodide- and zinc-promoted

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