bution of isomers. In the presence of Fe(II) the decomposition of MCPBA is instantaneous even at −20 °C in the absence of cyclohexanol. Accordingly, the initial formation of a reactive intermediate upon reaction of MCPBA with Fe(II) is required.

(7) Quantitative analysis of the data lead to the conclusion that cis diol formation proceeds with 89% retention while trans diol is formed with 98% retention (Table II).

(8) Hydroxylation with retention of configuration and with a substantial isotope effect has been observed for chromate[8a] and ozone[8b] oxidations of alkanes suggesting mechanistic similarities to the process reported here: (a) K. B. Wiberg and G. Foster, *J. Am. Chem. Soc.*, **83**, 423 (1961); (b) G. A. Hamilton, B. S. Ribner, and T. M. Hellman, *Adv. Chem. Ser.*, **No. 77**, 15 (1967).

(9) Processes involving hydrogen abstraction by locally generated, free hydroxyl or carboalkoxy radicals and recombination in the solvent cage must also be considered as possible explanations for the observed regioselectivity and stereospecificity (cf. ref 3b), but it is not apparent how such a recombination process could occur without concomitant involvement of the metal.

(10) Exchange rates for aqueous Fe(III) are ca. 10^3; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, p 152.

(11) J. T. Groves and M. Van Der Puy, *J. Am. Chem. Soc.*, **97**, 7118 (1975).

(12) The carbon dioxide produced upon peracid reductive decarboxylation may be regarded as a barrier to electron transfer from the carbon radical to Fe(III). Thus, loss of stereochemistry by intracomplex rotations occurs in the time required for the neutral molecule to diffuse from the molecular cavity. Various aspects of this process are under further study.

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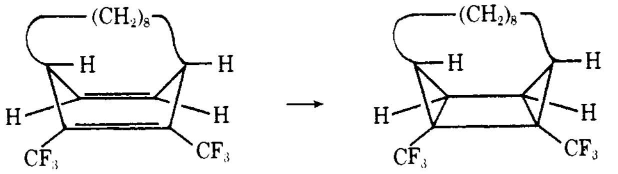
Metathesis. Diene and Cyclobutane Interconversions[1]

Sir:

The remarkable olefin disproportionation reaction commonly referred to as olefin metathesis has received extensive attention in recent years.[2] In particular, the mechanism of these astounding interconversions has been the topic of intensive discussion.[2] The intervention of a "concerted" switching of carbons through a "quasicyclobutane" transition state,[3] the intermediacy of a metallocyclopentane,[4] and the generation of metallocyclobutanes[5] have all been proposed as parts of various mechanistic explanations. A key point in practically every mechanistic discussion has been the failure of olefins and cyclobutanes to interconvert under metathesis conditions. It has been noted that "cyclobutanes are not products of the reaction, and olefins are not converted into cyclobutanes under the disproportionation reaction conditions," [3] and "no cyclobutane has been found to evolve from the reaction." [5] In general, most recent publications[5] have invoked the intermediacy of metallocyclobutanes as a rationale for the data obtained. To some extent, it was indicated that other mechanisms, such as those involving a "quasicyclobutane" transition state, were no longer acceptable. We now wish to report that, in certain cases, cyclobutanes can be converted quantitatively into olefins[6] and more importantly that *in one case two nonconjugated olefinic groups can be converted into a cyclobutane in close to quantitative yield by a commonly accepted metathesis catalyst.*

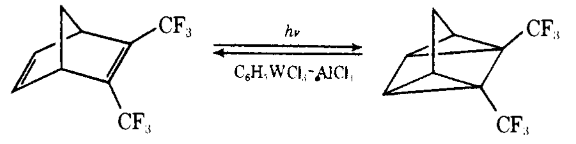
Although there is little difference in the free energy of a cyclobutane as compared to the free energy of two isolated double bonds, the comparable difference between a cyclobutane and a metal-complexed diene system is less well established. In principle, a cyclobutane ring should not be capable of any significant degree of stabilization through complexation with a metathesis catalyst. Thus, in order for a cyclobutyl system to be isolated from a metathesis reaction, a cyclobutane derivative in which the cyclobutyl moiety is more stable than the corresponding metal-complexed diene is required. In considering these principles, we decided that such a system might be available in the inside-outside bicyclic structures that have been of recent interest in our laboratories.[7] We have previously established[7] that 11,12-bis(trifluoromethyl)-(i,o)-bicyclo[8.2.2]tetradeca-11,13-diene (**1**) was readily converted into 1,12-bis(trifluoromethyl)-(i,o)-tetracyclo[10.2.0.0^{2,14}.0^{11,13}]tetradecane (**2**) on irradiation. Furthermore, **2** showed excellent thermal stability and was not converted back to **1** on treatment with various transition metal complexes, which were known to convert derivatives of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane into derivatives of bicyclo[2.2.1]hepta-2,5-diene.[6] These observations indicated to us that **2** might be considerably more stable than **1**. If **2** were much more stable than **1**, it should serve as an excellent substrate for testing whether cyclobutanes can be isolated from dienes in the presence of metathesis catalysts.



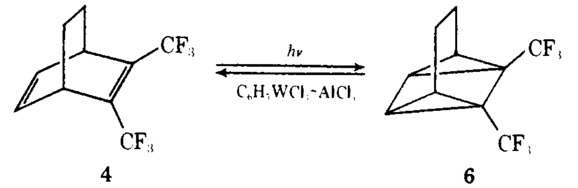
1 **2**

In order to test this concept, a sample of **1** was treated with approximately 0.1 equiv of the 1:1 complex[5,8,9] derived from phenyltungsten trichloride and aluminum trichloride in an argon atmosphere. After stirring for 5 min, the reaction was quenched by bubbling air through the solution.[10,11] Vapor phase chromatographic analysis of the resultant solution indicated that it contained only **1** and **2** in the ratio of 2:98. Analysis vs. an internal standard indicated that the conversion of **1** into **2** had occurred in quantitative yield. Isolation of this isomerization product indicated that it was identical in all respects (VPC retention times, ir, NMR) to a sample of **2** prepared via the irradiation of **1**.[12]

In order to establish that our observations were not due to the presence of the trifluoromethyl groups on **1**, we exposed 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (**3**) and 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (**4**) to the metathesis catalyst described above. These dienes appeared to be unreactive under the reaction conditions. However, when their photoproducts **5** and **6** were exposed to the catalyst system, they were rapidly converted into the dienes **3** and **4**, respectively.



3 **5**



4 **6**

In addition to constituting the first example of a metal complex promoted conversion of a diene into a highly strained polycyclic ring system, the catalytic transformation of **1** into **2** firmly establishes that cyclobutanes can be generated from dienes in the presence of metathesis catalysts. The conversion of **5** and **6** into **3** and **4**, respectively, demonstrates that unless the molecule is suitably designed, the normal course of events would lead to the transformation of a highly strained cyclobutyl moiety into a diene system. The implications of these observations relative to the mechanistic picture of olefin metathesis are difficult to access. While it is established that cyclobutanes can be formed in high yield in carefully constructed structural situations under metathesis conditions, our results in no way implicate cyclobutane containing intermediates for all olefin metathesis reactions. Clearly, the sum of data which are currently available would implicate a variety of different mechanistic paths.

We are continuing to investigate the mechanism of these useful olefin disproportionation reactions.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

References and Notes

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(6) Ample precedent exists for this portion of our findings. See H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967); P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968); L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).

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(9) The catalyst system was prepared from 0.66 g of aluminum trichloride and 1.86 g of phenyltungsten trichloride in 100 ml of carefully deoxygenated chlorobenzene. The formation of the catalyst system was carried out in Schlenk apparatus under an argon atmosphere. After 15 min of reaction time, the catalyst preparation was centrifuged and the clear supernatent liquid was used as the active catalyst-containing solution.

(10) On exposure to air the activity of the cayalyst system is destroyed immediately. A flocculent precipitate was formed when a solution of the active catalyst was exposed to air. This precipitate was removed by filtration prior to VPC analysis of the reaction mixture.

(11) The activity of the catalyst system deteriorated with time. In our hands, the phenyltungsten trichloride–aluminum trichloride catalyst system retained its activity for approximately 36 h.

(12) Control reactions established that neither phenyltungsten trichloride nor aluminum trichloride alone promoted the conversion of **1** into **2**.

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Influence of Neighboring Phenyl Participation on the α-Deuterium Isotope Effect on Solvolysis Rates. Neophyl Esters

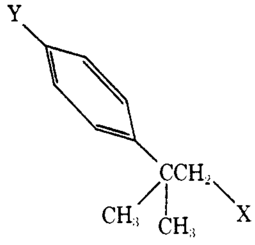
Sir:

Winstein and co-workers[1-3] originally suggested that the rearranging solvolyses of neophyl esters (I) are accelerated by nucleophilic participation of neighboring phenyl in the displacement of the leaving group leading to a phenyl-bridged cationic intermediate. For example, despite the expected electron withdrawing and rate retarding inductive effect of the phenyl ring, neophyl p-toluenesulfonate (I, Y = H; X = OTs) at 50 °C acetolyzes 460 times faster than neopentyl p-toluenesulfonate.[1] Further, substituents in the phenyl ring have marked effects on the solvolysis rate, e.g., the acceleration of acetolysis at 50 °C with p-methoxy relative to the unsubstituted compound is a factor of 122.[2] Because these and other results conclusively demonstrate that for these compounds solvolysis proceeds via participation in the rate determining ionization, we have measured α-deuterium (α-d) effects on the rates of solvolysis of some substituted neophyl esters in order to establish unambiguously what influence participation has on the α-d rate effect and to probe the variation of transition state structure with changes in substituent, solvent, and leaving group.

Table I. Solvolysis Rates and α-d Rate Effects for Neophyl Esters, 25 °C[a]

Ring substituent	Leaving group[b]	k_H, 10^{-5} s^{-1}			$k_H/k_{\alpha\text{-D}}$ per D[c]		
		97T	70T	48E	97T	70T	48E
p-MeO	OMs	34.46	29.15	10.67	1.113	1.117	1.119
p-Me	OMs		4.451			1.120	
None	OMs		0.3965			1.128	
None	OTr	45.16	40.90	7.548	1.128	1.134	1.134
m-CF_3	OTr		0.2346			1.099	

[a] Rates were measured conductometrically;[13] standard error is 0.1% in the isotope effect. [b] OMs is methanesulfonate, OTr is 2,2,2-trifluoroethanesulfonate. 97T is 97 wt % 2,2,2-trifluoroethanol–3 wt % water, 70T is 70 wt % 2,2,2-trifluoroethanol–30 wt % water, 48E is 48 vol % ethanol–52 vol % water. [c] Isotope effect per α-d atom; the square root of the ratio of the rate constant for solvolysis of the undeuterated compound divided by the rate constant for the α-d analogue prepared via $LiAlD_4$ reduction of the corresponding carboxylic acid.



I

Ando and co-workers[4] have measured α-^{14}C, β-^{14}C, and phenyl-*1*-^{14}C effects for acetolysis and trifluoroacetolysis of neophyl p-bromobenzenesulfonate and have concluded that the results are consistent with participation. In particular, modest phenyl-*1*-^{14}C effects (2.34% in HOAc) and medium-sized α-^{14}C (9.31% in HOAc) indicate an involvement of the two atoms similar to that expected in an S$_N$2 reaction.[5]

In order to measure the isotope effects as accurately as possible with the conductometric method, we have used principally aqueous ethanolic and trifluoroethanolic solvent mixtures at 25 °C with both methanesulfonate and trifluoroethanesulfonate leaving groups to obtain convenient reactivity and to assess the effect of leaving group change in the reaction. These results are shown in Table I.

First, the α-d effects are all below 1.135 and thus significantly less than the value of 1.15–1.16 shown by 3,3-dimethyl-2-butyl sulfonates in a wide variety of solvents and which we associate with rate determining unassisted ionization.[6] Therefore phenyl participation, as expected, lowers the α-d effect because bonding of the phenyl ring to the α-carbon partially compensates for the reduction in α-CH bending force caused by ionization of the leaving group.

In order to show that the α-d effects in the neophyl ester