Kinetics of Cyclopropane Formation by 1,3-Deoxystannylation. A Kinetic Isotope Effect as a Probe for the Mechanism of Neighboring Group Participation[1]

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Abstract: 1-Aryl-3-trimethylstannyl 3,5-dinitrobenzoates, ($Me_3SnCH_2CH_2CHAr(ODNB)$, **4H**, undergo solvolysis in 2,2,2-trifluoroethanol to form arylcyclopropanes and trimethylstannyl dinitrobenzoate. The rates for nine substituents on Ar are correlated by σ^+ with a ρ value of -3.63 at 100 °C. The rates for a series of model compounds, $Me_3CCH_2CH_2CHAr(ODNB)$, **5H** (six substituents), are also correlated by σ^+ with a ρ value of -4.90. In each case the rate for a given **4H** is greater than that for the corresponding **5H**. The Winstein-Grunwald m values for **4H** and **5H** in aqueous acetic acid at 100 °C are 0.41 and 0.46, respectively. Measurements of the rates of solvolyses in trifluoroethanol of the 2,2-d_2 analogues of **4H** and **5H** revealed kinetic isotope effects of 0.94 and 1.08, respectively. These results are taken as evidence that the mechanism for the rate acceleration observed in the **4H** series is due to direct participation of the C–Sn σ electrons in the transition state of the rate-determining step of the 1,3-elimination reaction.

A given nonradical 1,3-elimination leading to the formation of a cyclopropane can be envisioned as occurring by any of three general mechanisms. One is a two-step process involving the formation of a carbanion at the electrofugic center, followed by an intramolecular nucleophilic displacement reaction at the nucleofugic center. An important group of examples includes 1,3-dehydrohalogenation of 3-halopropyl ketones to form cyclopropyl ketones.[2] A second mechanism is a concerted process in which bonds to the electrofugic and nucleofugic groups are being broken as the ring-forming carbon–carbon bond is forming. Possible examples are the 1,3-destannoxylations of 3-trimethylstannyl tosylates[1] and mesylates,[3] which proceed hundreds of times faster in polar solvents than model compounds lacking the trimethylstannyl group. Cyclopropane formation by the treatment of 3-chloropropylboron dichloride[4] with base may fall into either of these two mechanistic categories. The third mechanism is a two-step process in which formation of a carbonium ion at the nucleofugic center is followed by an electrophilic attack at the electrofugic center. An example which may belong in this category or in the preceding one is the aluminum chloride catalyzed formation of cyclopropane from 3-bromopropyltrimethylsilane.[5]

The 1,3-destannoxylation reaction has proved to be convenient for study and, as a part of our approach to the general problem, we have chosen to examine the solvolytic formation of arylcyclopropanes according to eq 1. The presence of the

$$Me_3SnCH_2CH_2\underset{\displaystyle Ar}{\underset{|}{C}}HOCOAr' \longrightarrow Me_3SnOCOAr' + ArCH\begin{cases}CH_2\\ |\\ CH_2\end{cases} \qquad (1)$$

benzylic nucleofugic center suggests the possibility of the third of the above mechanisms, and would provide results which could be compared with previous investigations on solvolyses of benzylic systems.

Results and Discussion

Syntheses. The substrates used were prepared by the scheme shown in eq 2, which involved preparation of 1-arylallyl alcohol by reaction of the aryl aldehyde with vinylmagnesium chloride, followed by hydrostannation of the resulting allylic alcohol. The product was then converted to the substrate for solvolysis by reaction with 3,5-dinitrobenzoyl chloride. Alcohol precursors of model 3,5-dinitrobenzoates in which the trimethylstannyl group was replaced by the *tert*-butyl group were prepared from *n*-butylmagnesium or 3,3-dimethylbutylmagnesium bromide and the aryl aldehyde. Yields were uniformly satisfactory and no noteworthy difficulties were encountered. Deuterated substrates for the kinetic isotope effect studies were prepared according to eq 3 for the organotin derivatives, followed by dinitrobenzoate formation as in eq 2. For the model compound **1** in which Me_3Sn is replaced by Me_3C the procedure was the same with the exception that NaOH was needed to catalyze the exchange reaction.

$$CH_2{=}CHMgCl + ArCHO \longrightarrow \underset{\displaystyle Ar}{\underset{|}{CH_2{=}CHOH}}$$

$$\xrightarrow{Me_3SnH} \underset{\displaystyle Ar}{\underset{|}{Me_3SnCH_2CH_2CHOH}} \xrightarrow{Ar'COCl} \underset{\displaystyle Ar}{\underset{|}{Me_3SnCH_2CH_2CHOCOAr'}}$$

1 **2** (2)

$$I + CrO_3 \longrightarrow Me_3SnCH_2COPh \xrightarrow[\text{dioxane}]{D_2O,\ Na_2CO_3} Me_3SnCH_2CD_2COPh$$

$$\xrightarrow{LiAlH_4} Me_3SnCH_2CD_2CHOHPh \qquad (3)$$

Course of Reaction. Because these 1,3-eliminations have not been widely studied it was considered desirable to establish whether they do, in fact, proceed to give the arylcyclopropanes quantitatively. Phenylcyclopropane isolated from a solvolysis of the appropriate 3,5-dinitrobenzoate **2** (R = Ph) was shown to be equimobile in the GLC with an authentic sample, and to show the same NMR spectrum. Five other cyclopropanes from solvolyses were characterized by NMR as shown in Table I, all showing the characteristic high-field signals from the ring methylenes along with the other expected signals. The yield of phenylcyclopropane was shown to be quantitative by the internal standard GLC method. Yields for this product and the five others listed in Table I were also determined by extracting the hydrocarbon into carbon tetrachloride. A known weight of methylene chloride was added and the area of the signals from its protons were compared with those from the aromatic protons of the product. A control experiment with phenylcyclopropane showed this to yield valid results. No other hydrocarbon, such as olefin, was observed as a product.

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Table I. Yields and NMR Parameters of Selected Arylcyclopropanes Formed under Solvolysis Conditions[a]

substituent	10^3 concn, M	T, °C	time, h	yield, %	NMR parameters[b,c] CH_2CH_2 (m)	CH (m)	CH_3 (s)	Ar
p-MeO	19.1	25	0.5	95	0.83	1.83	3.73	6.79 (AB)
p-Me	12.1	100	0.17	90	0.76	1.76	2.28	6.91 (s)
m-Me	11.4	100	1	90	0.79	1.79	2.29	6.86 (m)
H	11.5	100	1	85	0.79	1.84		7.08 (m)
p-Cl	9.0	100	3	90	0.78	1.81		7.04 (AB)
m-CF_3	8.9	100	28	70	0.86	1.93		7.26 (m)

[a] Spectra on CCl_4 solutions. [b] Chemical shifts in parts per million downfield from tetramethylsilane. Areas correspond to expected numbers of protons. [c] Multiplicities shown in parentheses: m = multiplet; s = singlet; AB = AB quartet.

Table II. Rate Constants and Activation Parameters for Solvolysis of 1-Aryl-3-trimethylstannyl 3,5-Dinitrobenzoates in Trifluoroethanol

substituent	T, °C	k_1, s^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
p-MeO	0.9	6.8×10^{-5}	19.9	−4.5
	25	1.52×10^{-3}		
	40	7.5×10^{-3}		
p-Me	41	8.51×10^{-5}	20.0	−13.4
	55	3.64×10^{-4}		
	65	8.54×10^{-4}		
	75	2.12×10^{-3}		
m-Me	55	6.63×10^{-5}	20.6	−15.0
	65	1.58×10^{-4}		
	75	4.35×10^{-4}		
H	55	2.28×10^{-5}	20.4	−17.2
	65	6.85×10^{-5}		
	75	1.85×10^{-4}		
p-F	55	2.62×10^{-5}	20.5	−17.1
	65	6.15×10^{-5}		
	75	1.71×10^{-4}		
m-MeO	55	1.77×10^{-5}	21.4	−15.2
	65	4.05×10^{-5}		
	75	1.25×10^{-4}		
p-Cl	55	9.25×10^{-6}	20.9	−17.9
	65	2.41×10^{-5}		
	75	6.22×10^{-5}		
m-Cl	65	4.49×10^{-6}	22.2	−17.4
	75	1.25×10^{-5}		
	85	3.07×10^{-5}		
m-CF_3	65	1.70×10^{-6}	22.2	−19.4
	75	4.28×10^{-6}		
	85	1.16×10^{-5}		

The low yield of *m*-trifluoromethylphenylcyclopropane may be attributed to a side reaction which was observed to occur with the less reactive substrates. This involved the exchange reaction between substrate and trimethylstannyl 3,5-dinitrobenzoate, eq 4.[6] This reaction is most pronounced when the

$$\mathrm{Me_2SnCH_2CH_2CHODNB} + \mathrm{Me_3SnODNB\cdot} \longrightarrow \underset{\mathrm{ODNB}}{\underset{|}{\mathrm{Me_2SnCH_2CH_2CHODNB}}} + \mathrm{Me_4Sn} \quad (4)$$
$$\mathrm{Ar} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{Ar}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{3}$$

substrate is of low reactivity; when the initial concentration of substrate is high (because reaction 4 is first order in both substrate and a reaction product, whereas the solvolysis is first order in substrate only); and when the reaction has progressed to such a degree that an appropriate concentration of trimethylstannyl 3,5-dinitrobenzoate has accumulated. The bisdinitrobenzoate formed in reaction 4 is unreactive in cyclopropane formation because the dinitrobenzoyloxydimethylstannyl group is a much poorer electrofuge than the trimethylstannyl group. In the kinetic studies the effect of reaction 4 could be minimized by using low initial concentrations of substrate.

Kinetics. The kinetics of the 1,3-eliminations of the 1-aryl-3-trimethylstannyl 3,5-dinitrobenzoates were studied in trifluoroethanol using either an NMR or spectrophotometric method for analysis. In the NMR method the extents of reaction were estimated from the peak heights of the trimethylstannyl protons of the unreacted ester and of trimethylstannyl 3,5-dinitrobenzoate. In the spectrophotometric method samples were quenched and extracted with hexane. The concentration of arylcyclopropane was then determined by measurement of the absorbance of the dinitrobenzoate function of the substrate in the hexane solution at an appropriate wavelength in the region 250–270 nm. Rate constants were obtained by the method of least squares and correlation coefficients of 0.99 or greater were obtained in most cases. Values agreeing within 5% from two or more experiments are gathered in Table II. Activation parameters for the nine substrates are also included in the table. The rate constants are well correlated by the Hammett equation using the Brown-Okamoto[7] σ^+ constants. These are plotted for rates at 100 °C (see below) in the upper line of Figure 1 yielding a ρ value of −3.63 with a correlation coefficient of 0.990. This high negative value of ρ indicates substantial positive charge development at the benzylic carbon in the transition state of the slow step, and the correlation with σ^+ reflects delocalization of the charge into the benzene ring.

The activation parameters gathered in Table II show a curious behavior. When the *p*-methoxy substituent is compared with *p*-methyl the change in rate appears to be due primarily to a more negative entropy of activation in the latter case. The enthalpies of activation are more or less constant down the series toward the deactivating substituents, *m*-chloro and *m*-trifluoromethyl, which display larger enthalpies of activation than the others.

In view of the large negative ρ value for the solvolysis it was of interest to establish whether the trimethylstannyl group had any effect at all on the rate of ionization at the benzylic carbon. A suitable series of model compounds was needed. In order to assess the effect of steric bulk of the trimethylstannyl group on the solvolysis rate, models in which this was replaced by a *tert*-butyl group (1-phenyl-4,4-dimethylpentyl dinitrobenzoate) and by an ethyl group (1-phenylpentyl dinitrobenzoate) were prepared, and their rates of solvolysis in trifluoroethanol at 100 °C measured. The rate constants observed were 2.42×10^{-5} and 2.18×10^{-5} s^{-1}, respectively. The similarity of these rates suggests that use of the *tert*-butyl analogue as a model should be satisfactory on steric grounds. If this is incorrect then absolute values in the series discussed below would be in doubt, but trends due to changes in substituents on the phenyl ring should have quantitative validity. Six members of the 1-aryl-4,4-dimethylpentyl 3,5-dinitrobenzoate series were subjected to solvolysis with the results at 100 °C gathered in Table III, and displayed in the lower Hammett plot in Figure

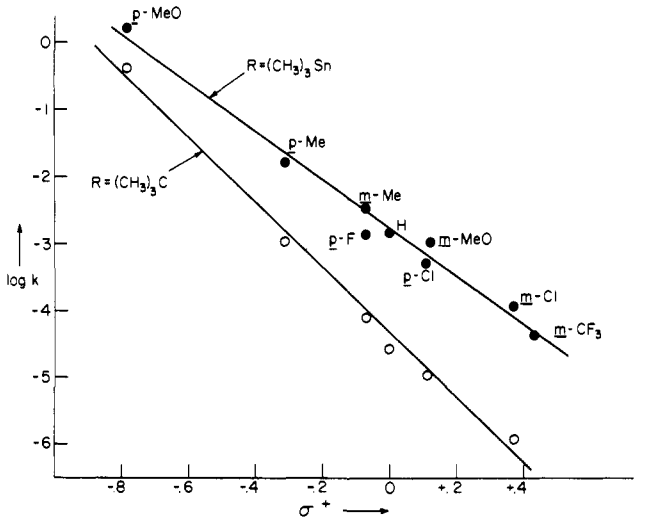


Figure 1. Hammett plots for solvolysis of $RCH_2CH_2CH(Ar)ODNB$ in trifluoroethanol at 100 °C. σ values from H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

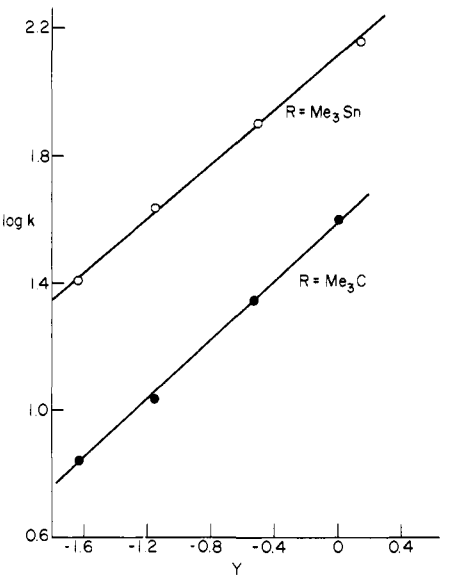


Figure 2. Grunwald–Winstein plot of data from Table IV.

Table III. Rate Constants for Solvolysis of 1-Aryl-4,4-dimethylpentyl Dinitrobenzoates in Trifluoroethanol at 100 °C

substituent	concn, 10^3 M	lutidine, 10^2 M[a]	R(o/e)[b]	k, s^{-1}
p-MeO	5.00			4.07×10^{-1} [c]
p-Me	37.6	6.6	0.13	1.07×10^{-3}
m-Me	38.9	7.0	0.23	7.67×10^{-5}
H	42.7	1.2	0.30	2.68×10^{-5}
p-Cl	39.2	7.4	0.26	1.06×10^{-5}
m-Cl	33.6	9.1	0.26	1.2×10^{-6}

[a] Added to prevent complications due to acid formed in solvolysis. [b] Ratio to olefin to trifluoroethyl ether in product. [c] Extrapolated from data at lower temperatures: 10^4k (s^{-1}) 2.32 at 20 °C; 7.45 at 30 °C; 21.3 at 45 °C; $\Delta H^{\ddagger}$ = 19.5 kcal/mol; $\Delta S^{\ddagger}$ = −8.25 eu.

Table IV. Solvolyses of $RCH_2CH_2CH(p\text{-}MeOC_6H_4)ODNB$ in $AcOH/H_2O$

R	T, °C	concn, 10^2 M	$[H_2O]$, M	Y[a]	10^4k, s^{-1}
Me_3Sn	41	5.0	0	−1.63	2.54
Me_3Sn	41	5.0	1.11	−1.15	4.33
Me_3Sn	41	5.0	3.52	−0.049	7.95
Me_3Sn	41	5.0	7.7	+0.16	14.2
t-Bu	40	6.8	0	−1.63	0.695
t-Bu	40	6.8	1.09	−1.15	1.06
t-Bu	40	6.8	3.42	−0.52	2.22
t-Bu	40	6.8	6.57	+0.02	3.93

[a] Obtained by interpolation of values from ref 8.

1. The value of ρ is −4.90 with a correlation coefficient of 0.996. Two characteristics of the plots in the figure are noteworthy: the linearity of each suggests that there is no change in mechanism as the electronic effect of the aryl group is changed, and the rates for the trimethylstannyl analogues are uniformly greater than those of the model compounds, the difference increasing as the aryl substituent becomes more electron withdrawing. The factors by which the presence of the trimethylstannyl group accelerate the reaction rate vary from 3.9 for *p*-methoxy to 95 for *m*-chloro. The difference between the two ρ values is +1.27, and might be taken as a ρ value for acceleration by the trimethylstannyl group.

As a further probe into the apparent similarity in the nature of the transition states for the 1-*p*-anisyl-3-trimethylstannylpropyl and 1-*p*-anisyl-4,4-dimethylpentyl 3,5-dinitrobenzoates solvolyses the rates were measured in aqueous acetic acid of varying compositions with the results collected in Table IV, and displayed in Figure 2 as a Winstein-Grunwald plot.[8,9] The slopes are very similar: 0.41 for the trimethylstannyl derivative and 0.46 for the model compound.

Aqueous acetic acid was chosen as the solvent system for the above experiments in order to obtain a comparison with the data of Davis and Black,[3] who used it to obtain an estimate of the effect of solvent ionizing power in the solvolysis of 3-trimethylstannylpropyl mesylate. They obtained an m value of 0.35. Other data of theirs suggest a relatively low degree of positive charge at the electrofugic center in the transition state, while our substituent effects show a relatively large positive charge in the transition state.

Mechanism of Trimethylstannyl Accelerating Effect. Data presented above indicate that the steric bulk of the trimethylstannyl group does not play a significant role in increasing the rate of solvolysis over that of a corresponding model compound. Thus, one must seek the source in electronic effects. One possibility is the through-bond inductive effect. If we take the σ^* value of Me_3Sn to be −0.5,[10] then the magnitude felt at the electrofugic center will be −0.16 if we assume that it is transmitted to the extent of about 40% through each of the intervening methylene groups.[11] Then for the unsubstituted phenyl substituted substrate in which an acceleration by a factor of 52 is observed one calculates an unreasonably high value of −10.7 for ρ^*. This is particularly unlikely when one considers that it is superimposed upon stabilization of the transition state by delocalization of the developing positive charge by the phenyl group.

The other alternatives which can be distinguished conceptually involve direct participation of the C–Sn bonding electron pair in affecting the observed reaction rate. In the currently accepted solvolysis scheme of eq 5[12] P represents the

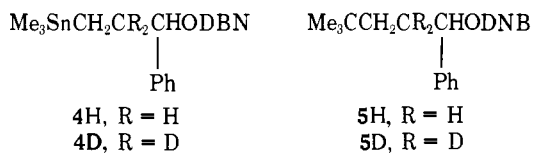
$$\begin{array}{ccccccc} R\text{—}ODNB & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & R^+, {}^-ODNB & \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} & R^+\|{}^-ODNB & \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} & R^+ + {}^-ODNB \\ \downarrow k_{p\Delta} & & \downarrow k_{p1} & & \downarrow k_{p2} & & \downarrow k_{p3} \\ P & & P & & P & & P \end{array} \quad (5)$$

reaction products, arylcyclopropane and trimethylstannyl 3,5-dinitrobenzoate. One mechanism which must be considered has all of the reaction proceeding via the ionization step identified by the rate constant k_1, followed by a product-forming step identified by k_{P1}, for example, If k_{P1} (leading to arylcy-

clopropane) is much larger than k_{-1} then the overall rate is given by k_1. If internal return occurs, as expected, the overall rate will be less than k_1.[13] The difference in rates between the model compound and the trimethylstannyl derivative will then be a measure of the internal return. This difference would be expected to increase as the substituents on the phenyl group become more electron withdrawing because of the increased reactivity (and diminished selectivity between return and product formation from the intermediate benzylic carbocation). The rates of ionization would be correlated by σ^+.[7] The same would be true for the model series as long as no change in mechanism occurs with changes in substituents. Thus both reactions show good σ^+ correlations because the rate-determining steps are the same, but the ρ values differ because the product-forming steps differ.

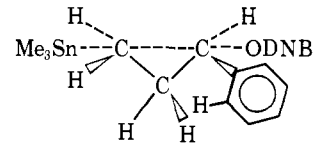
Another mechanism involves a form of neighboring group participation in which the step identified by $k_{P\Delta}$ is rate determining. This may lead to product as indicated or to an intermediate cation stabilized by the trialkylstannyl group, and has been considered previously.[1,3] Analogous behavior of a benzylic system was first discovered by Gassman and Fentiman in the solvolysis of 7-arylnorbornyl-7-*p*-nitrobenzoates and the corresponding 2-norbornenyl analogues.[14] Both solvolyzed at similar rates with *p*-dimethylamino and *p*-methoxy as substituents, but with electron-withdrawing substituents the norbornenyl analogues solvolyzed faster than the norbornyls and the difference increased with capacity of the substituent for the electron withdrawal. This phenomenon has seen application as a probe for σ and π participation in solvolyses[15] and delocalization in carbocations.[16] However, This "tool of increasing electron demand" does not provide a distinction between the two mechanism of acceleration under consideration here.

A choice could be made on the basis of the β-hydrogen kinetic isotope effects which were determined for the phenyl analogues of the trimethylstannyl **4** at 55 °C and model compounds **5** at 65 °C. Sets of three experiments yielded the following rate constants (s^{-1}): **4H,** $4.00 \pm 0.04 \times 10^{-5}$; **4D,** 4.25



$\pm 0.02 \times 10^{-5}$; **5H,** $7.47 \pm 0.07 \times 10^{-7}$; **5D,** $6.92 \pm 0.01 \times 10^{-7}$. Thus the secondary kinetic isotopes k_H/k_D are 0.94 for compounds **4** and 1.08 for compounds **5.** The observation of a normal isotope effect for the latter compound and an inverse effect for **4** is a strong indication of difference in mechanism.

The β kinetic isotope effect in S_N1 solvolyses has been elegantly shown to be due mainly to hyperconjugative interactions between the hydrogens and the developing vacant p orbital.[17] The observation of an inverse isotope effect in the deoxystannylation is in excellent accord with the mechanism involving participation by the C–Sn σ orbital as suggested by Davis and Black.[3b] If we assume that the stereochemistry at both reacting sites is inversion, as in the case of the 3-mesyloxy-7-trimethylstannylnorbornanes, the transition state passes through a configuration resembling **6** on the way to product or a corner-stannylated cyclopropane. As the dinitrobenzoate ionization proceeds and the benzylic cationic center begins to form the axis of the electron-deficient orbital and the plane of the benzene ring must be normal to each other for maximum delocalization. This results in substantial nonbonded interaction between a β proton and an ortho hydrogen. Also, eclipsing interactions between the vicinal protons of the developing cyclopropane ring increase. These changes have the effect of



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constricting the bending vibrations of the β hydrogens in particular, and may be the cause of the inverse isotope effect. The incipient ionization of the carbon–tin bond provides the stabilization needed to increase the reaction rate by 50-fold while that provided by delocalization into the benzene is decreased as indicated by the lower value of ρ for the deoxystannylation as compared to the simple solvolysis.

We conclude that the 1,3-deoxystannylation reaction procedes by a concerted process in which the negative charge developed in the transition state on the departing dinitrobenzoate anion is balanced in large part by positive charge on the benzylic carbon and the attached benzene ring, and in smaller part by the tin atom of the departing trimethyltin cation. A geometry resembling **6** involving inversion at both reaction sites is consistent with this conception, but knowledge of the stereochemistry will be required in order to establish whether it is uniquely required.

Experimental Section

Commercially available reagents were used in the syntheses and as solvents without further purification. Ultraviolet spectra were obtained with a Cary Model 14 instrument. NMR spectra were obtained with a Varian A-60 or HA-100 instrument as needed. Melting points are uncorrected. Elemental anslyses were performed on all of the dinitrobenzoates by Instranal Laboratory, Inc. Three C values agreed within ±0.3% and the remainder within ±0.2%; H analyses agreed within ±0.15%.

1-Arylprop-2-en-1-ols. The synthesis of 1-(*p*-fluorophenyl)-2-en-1-ol is given as a typical procedure for all of these alcohols but one. To 50 mL of a 2 M solution of vinylmagnesium chloride in tetrahydrofuran (THF) was added 11.1 g (0.09 mol) of *p*-fluorobenzaldehyde at a rate to maintain a temperature of 50 °C in the reaction flask, and the mixture was stirred for an additional 1 h. Saturated ammonium chloride (5 mL) was added, the resulting precipitate was filtered off and washed with ethyl ether, and the combined organic layers were concentrated in a rotary evaporator. The residue provided 11.4 g (84%) of product, bp 64–66 °C (0.5 Torr). Yields of the other alcohols were as follows (substituent on benzene ring indicated): *p*-OCH_3, *p*-CH_3, 79%; *m*-CH_3, 81%; none, 90%; *p*-F, 84%; *p*-Cl, 88%; *m*-OCH_3, 87%; *m*-Cl, 77%.

1-*m*-Trifluoromethylphenylprop-2-en-1-ol was prepared in a similar fashion by the reaction of *m*-trifluoromethylphenylmagnesium bromide with acrolein, 60% yield, bp 50–55 °C (0.05 Torr).

The purity of the alcohols was at least 97% as indicated by GLC, and the NMR spectra were consistent with the expected structures. They were used in the next step without further characterization or purification.

1-Aryl-3-trimethylstannyl-1-propanols. Pyrex tubes containing the above propenols and a 5% excess of trimethylstannane were irradiated neat in a Rayonet[18] reactor using 313-nm lamps. The course of the reaction was monitored by GLC using a 6 ft × 1/8 in. column of UCW 98 on Chromosorb at 230 °C until the hydrostannation was complete (about 20 h). The products were obtained by distillation and were characterized by the NMR spectra as shown in Table V.

1-Aryl-3-trimethylstannyl-1-propyl 3,5-Dinitrobenzoates. In the general procedure 5.0 mmol of 1-aryl-3-trimethylstannyl-1-propanol was added to 20 mL of pyridine in a flask cooled by an ice–water bath. Then 7.5 mmol of 3,5-dinitrobenzoyl chloride was added. The mixture was stirred for 5 h and poured into 200 mL of water. In the cases of the unsubstituted and the *p*-fluoro, p-chloro, and *m*-trifluoromethyl substituted alcohols the ester appeared as a precipitate, which was washed after filtration with dilute aqueous sodium carbonate, aqueous hydrochloric acid, and water. It was then recrystallized from a minimum volume of absolute ethanol.

When the ester appeared as an oil the aqueous layer was decanted off and dissolved in ethyl ether. The ether solution was washed successively with 150 mL of 10% aqueous sodium carbonate, 150 mL of

Table V. Yield and NMR Data[a] for 1-Aryl-3-trimethylstannyl-1-propanols

	chemical shift (multiplicity)[b]								
substituent	Me_3Sn (s)	CH_2 (m)	CH_2 (m)	OH (s)	CH_3 (s)[c]	CH (t)	Ar	yield,[d] %	bp °C (Torr)
p-MeO	0.03	0.72	1.72	2.0	3.72	4.33	6.9 (AB)	73%	118–121 (0.02)
p-Me	0.03	0.68	1.75	2.25	2.28	4.32	7.03 (s)	76%	96–98 (0.02)
m-Me	0.03	0.73	1.77	2.25	2.30	4.32	7.0 (s)	71%	130–132 (0.02)
H	0.03	0.73	1.77	2.40		4.35	7.17 (s)	74%	97–100 (0.02)
p-F	0.03	0.70	1.77	2.57		4.35	7.03 (m)	75%	94–95 (0.05)
p-Cl	0.05	0.70	1.77	2.23		4.38	7.2 (s)	76%	110–112 (0.07)
m-MeO	0.03	0.72	1.78	2.32	3.70	4.35	6.9 (m)	71%	112–117 (0.02)
m-Cl	0.05	0.72	1.78	2.32		4.4	7.17 (m)	74%	115–118 (0.04)
m-CF_3	0.05	0.72	1.8	2.37		4.48	7.47 (m)	69%	103–107 (0.07)

[a] 10% in CCl_4; parts per million from Me_4Si; expected areas observed. [b] Left to right $(CH_3)_3SnCH_2CH_2(OH)C(Ar)H$. [c] Substituent on benzene ring. [d] Elemental analyses for C and H agreed within the accepted limits with theory.

Table VI. NMR Data for 1-Aryl-3-trimethylstannyl-1-propyl-3,5-dinitrobenzoates[a,b]

substituent	Me_3Sn (s)	CH_2 (m)	CH_2 (m)	CH_3 (s)[c]	CH (t)	Ar	ODNB
p-MeO	0.09	0.73	2.2	3.75	5.83	7.03 (AB) 4	9.05 (br, s)
p-Me	0.10	0.73	2.17	2.33	5.85	7.20 (AB) 4	9.08 (br, s)
m-Me	0.10	0.75	2.17	2.38	5.85	7.18 (brs) 4	9.08 (br, s)
H	0.10	0.77	2.23		5.90	7.35 (brs) 5	9.08 (s)
p-F	0.10	0.72	2.15		5.87	7.23 (m) 4	9.07 (m)
p-Cl	0.10	0.77	2.17		5.85	7.33 (s) 4	9.08 (m)
m-MeO	0.09	0.75	2.17	3.78	5.83	7.05(m) 4	9.15 (br, s)
m-Cl	0.11	0.75	2.20		5.85	7.33 (m) 4	9.10 (m)
m-CF_3	0.11	0.83	2.23		5.97	7.63 (m) 4	9.10 (br, s)

[a] 10% in CCl_4; chemical shifts in parts per million downfield from internal tetramethylsilane; multiplicity in parentheses. [b] Protons identified left to right $(CH_3)_3SnCH_2CH_2CH(Ar)OCOC_6H_3(NO_2)_2$; correct areas observed. [c] Substituent on Ar.

Table VII. NMR Data for 1-Aryl-4,4-dimethylpentyl-3,5-dinitrobenzoates.[a]

	chemical shift (multiplicity)[b]							
substituent	*t*-Bu (s)	CH_2 (m)	CH_2 (m)	CH_3[c] (s)	CH (t)	Ar	ODNB (m)	mp, °C
p-MeO	0.90	1.22	1.98	3.73	5.87	7.03 (AB)	9.03	81–82
p-Me	0.95	1.25	2.02	2.37	5.93	7.23 (AB)	9.08	79–80
m-Me	0.92	1.20	2.00	2.35	5.90	7.18 (m)	9.07	63–65
H	0.90	1.20	1.98		5.92	7.33 (m)	9.07	100–101
m-Cl	0.92	1.25	2.03		5.92	7.32 (m)	9.07	92–94
p-Cl	0.92	1.20	2.0		5.90	7.33 (s)	9.07	61–63
rel area	9	2	2	3	1		3	

[a] Parts per million from TMS, 10% in carbon tetrachloride; expected areas observed. [b] Left to right as in $(CH_3)_3CCH_2CH_2CH(Ar)OCOC_6H_3(NO_2)_2$; s = singlet, t = triplet, m = multiplet, AB = AB quartet. [c] Aryl substituent.

3 N hydrochloric acid, and twice with water, and concentrated. The residual oil was purified further by column chromatography on silica gel (activity II–III) using 50/50 benzene/cyclohexane as eluent. Four of the remaining five esters were obtained as crystals in this way, only the *m*-chlorophenyl ester remaining as an oil. Data are gathered in Table VI.

1-Aryl-4,4-dimethyl-1-pentanols. 3,3-Dimethyl-1-bromobutane was prepared by free-radical addition of hydrogen bromide in benzene to 3,3-dimethyl-1-butene. The Grignard reagent was prepared from 19.0 g (0.125 mol) of the bromide and 3.0 g (0.125 mol) of magnesium in 50 mL of ethyl ether. Benzaldehyde (9.3 g, 0.088 mol) in 25 mL of ether was added at a rate which maintained reflux, and the reaction mixture stirred for 0.5 h, whereupon it was hydrolyzed by addition of 5 mL of saturated ammonium chloride. The mixture was filtered and the precipitate washed with ether; the ether extracts were combined with the filtrate, dried over calcium chloride, concentrated, and distilled, yielding 13.2 g (78%), bp 88–89 °C (0.1 Torr), of product which crystallized on standing, mp 50 °C. The other substituted alcohols were prepared in the same manner with the following results (substituent, yield, melting point or boiling point): *p*-CH_3O, 76%, mp 42 °C; *p*-Cl, 75%, mp 79–80 °C; *p*-CH_3, 42%, bp 79–80 °C; *m*-CH_3, 70%, bp 88 °C (0.02 Torr); *m*-Cl, 79%, bp 100–103 °C (0.02 Torr).

The NMR spectra of the alcohols showed the expected chemical shifts, multiplicities, and areas as follows, with the chemical shift range for the series given in parts per million for each type of proton: $(CH_3)_3C$, 0.83–0.85 (s); CH_2CH_2, 1.37–1.40 (m); OH, 1.95–2.22 (s); CH, 4.37–4.45 (t); Ar, 6.95–7.20; *p*-CH_3, 2.30; *m*-CH_3, 2.32; all (s).

1-Aryl-4,4-dimethylpentyl 3,5-dinitrobenzoates. These esters were prepared in the same way as the trimethylstannyl analogues described above. They were characterized more thoroughly than the precursor alcohols; NMR and data are given in Table VII.

3-Oxo-3-phenyl-1-propyltrimethylstannane. To a solution of 17.5 g (0.35 mol) of chromium trioxide in 125 mL of water was slowly added 16 mL of 17 M sulfuric acid. The resulting solution was cooled to room temperature and added dropwise to 12 g (0.04 mol) of 1-phenyl-3-trimethylstannyl-1-propanol dissolved in 50 mL of acetone. The solution was cooled in an ice–water bath and 20 mL (0.03 mol) of the chromium trioxide solution was added with stirring until the solution turned orange. The stirring was continued for 3 h; the organic layer was separated and the green aqueous layer was extracted three times with 30-mL portions of carbon tetrachloride. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed. The ketone was distilled under reduced pressure, yield 5 g (55%), bp 110–112 °C (0.06 Torr). The purity was 95% as indicated by GLC analysis (15 ft × ⅛ in. 10% Apiezon L Chromosorb W 60/80 column, programmed between 50 and 200 °C): NMR (CCl_4, ppm) 7.4 (m, 5 H), 3.2 (t, 2 H), 1.0 (t, 2 H), 0.65 (s, 9 H), $J(^{119}SnCH)$ = 59 Hz; IR (CCl_4) 1680 cm^{-1} (C=O).

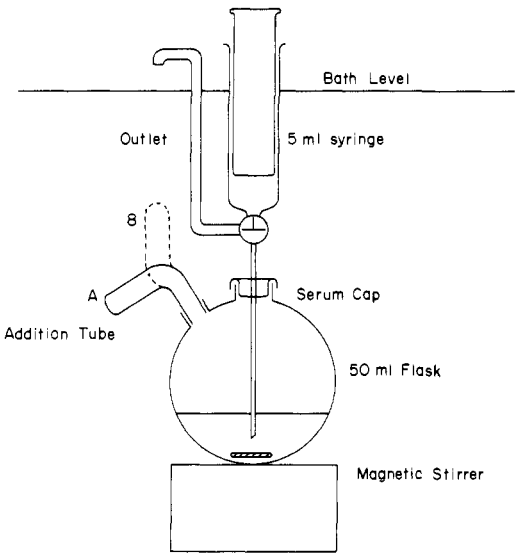

Figure 3. Apparatus for conducting kinetic measurements with more reactive substrates.

1-Phenyl-2,2-dideuterio-3-trimethylstannyl-1-propanol. To a solution of 2.4 g (8 mmol) of 3-oxo-3-phenyl-2,2-dideuterio-1-propyltrimethylstannane in 25 mL of anhydrous ether was added dropwise a slurry of lithium aluminum hydride (1.47 g, 38.7 mmol) in anhydrous ether (25 mL) over a period of 0.5 h. After the solution was refluxed for an additional 1 h the excess $LiAlH_4$ was destroyed, the ether layer was filtered and dried over anhydrous magnesium sulfate, and the solvent was removed: yield 2.1 g (87%); IR (CCl_4) 3500 (O-H) and 2100 cm^{-1} (C-D); mass spectrum (70 eV) *m/e* 285 (loss of OH) and 165 (Me_3Sn^+); NMR (CCl_4, ppm) 7.35 (m, 5 H), 2.23 (no signal), 0.77 (m, 2 H), 9.08 (s, 3 H), 5.90 (s, 1 H), 0.10 (s, 9 H), J (^{119}SnCH) = 59 Hz.

3-Oxo-3-phenyl-2,2-dideuterio-1-propyltrimethylstannane. To a solution of 4.46 g (15 mmol) of 3-oxo-3-phenyl-1-propyltrimethylstannane in 15 mL of 1,4-dioxane 1.067 g (10 mmol) of anhydrous sodium carbonate and 2.6 mL of deuterium oxide of 99.8% purity (Stohler) (2.873 g, 143.6 mmol) were added and refluxed for 20 h. The aqueous layer was separated, washed with 75 mL of petroleum ether, and combined with the organic layer which was dried over anhydrous magnesium sulfate and the solvent was distilled off. Repetition of the deuteration (using 10 mL of 1,4-dioxane, 0.4 g of anhydrous sodium carbonate, and 1.4 mL of deuterium oxide) gave 3.6 g (82%) of deuterated product: IR (CCl) 2100 (C-D) and 1680 cm^{-1} (C-O); NMR (CCl_4, ppm) 7.5 (m, 5 H), 0.9 (pentuplet, 2 H), 0.5 (s, 9 H), J (^{119}SnCH) = 59 Hz; 91.7% deuteration by NMR integration.

1-Phenyl-2,2-dideuterio-3-trimethylstannyl-1-propyl 3,5-Dinitrobenzoate. The procedure was the same as above except that 1-phenyl-2,2-dideuterio-3-trimethylstannyl-1-propanol was used instead of 1-phenyl-3-trimethylstannyl-1-propanol: yield 93%; mp 81–82 °C; NMR (CCl_4, ppm) 3,5-ODNB 9.1 (s, 3 H), C_6H_5 7.25 (s, 5 H), C*H*OH 5.75 (t, 1 H), CD_2, 2.23 (no signal), 6.78 (pentuplet, 2 H), $(CH_3)_3$, 0.1 (s, 9 H), J (^{119}SnCH) = 59 Hz.

1-Phenyl-4,4-dimethyl-1-pentanone. To a solution of 21.3 g (0.213 mol) of chromium trioxide in 125 mL of water was slowly added 16 mL of 17 N sulfuric acid. The resulting solution was cooled to room temperature and added dropwise to a 250-mL Erlenmeyer flask containing 11 g (0.057 mol) of 1-phenyl-4,4-dimethyl-1-pentanol dissolved in 100 mL of acetone. The contents of the flask were cooled in an ice-water bath and the chromium trioxide solution (30 mL, 0.038 mol) was added with stirring until the solution turned and remained orange for 2 h. The organic layer was separated and the green aqueous layer was extracted three times with 40-mL portions of carbon tetrachloride. The organic layer and carbon tetrachloride washings were combined and dried over anhydrous magnesium sulfate, solvents were removed on a rotary evaporator, and the ketone was distilled under reduced pressure, bp 78–80 °C (0.1 Torr). On standing the compound solidified to a pasty mass: yield 9.9 g (91%); IR (CCl_4) 1640 cm^{-1} (C=O); NMR (CCl_4, ppm) $(CH_3)_3C$ 0.86 (s), CH_2 1.46 (m), CH_2 2.76 (m), Ar 7.36 (br s).

1-Phenyl-2,2-dideuterio-4,4-dimethyl-1-pentanone. To a solution of 1.8 g (0.009 mol) of 1-phenyl-4,4-dimethyl-1-pentanone in 15 mL of 1,4-dioxane, a solution of 1 g of sodium hydroxide in 1.8 mL of deuterium oxide (Stohler, 99.8%) was added and refluxed at 100 °C for 6 h over an oil bath. The solution was then extracted with 60 mL of petroleum ether and dried over anhydrous magnesium sulfate. The solvents were removed in a rotary evaporator and the NMR data confirmed the completion of deuteration: yield 1.7 g (99%); IR (CCl_4) 2325 (C-D), 1680 cm^{-1} (CO); NMR (CCl_4, ppm) $(CH_3)C$ 0.9 (s), CH_2 1.5 (t), Ar 7.3 (m).

1-Phenyl-2,2-dideuterio-4,4-dimethyl-1-pentanol. To a slurry of 1.56 g (0.041 mol) of lithium aluminum hydride in 40 mL of anhydrous ethyl ether was added dropwise a solution of 4.7 g (0.025 mol) of 1-phenyl-2,2-dideuterio-4,4-dimethyl-1-pentanone in 20 mL of anhydrous ethyl ether over a period of 20 min. After refluxing for an additional 1 h the excess lithium aluminum hydride was destroyed, the ether layer was filtered and dried over anhydrous magnesium sulfate, and solvent was removed under a rotary evaporator: yield 4.5 g (98%); mp 48 °C; IR (CCl_4) 3300–3400 (br) (OH), 230 cm^{-1} (C-D); NMR (CCl_4, ppm) $(CH_3)_3C$ 0.91 (s), CH_2 1.75 (t), CD_2 no signal, CH 4.5 (t), OH 3.35 (s), Ar 7.28 (br s[4]); mass spectrum (70 eV) *m/e* 194.

1-Phenyl-4,4-dimethylpentyl 3,5-Dinitrobenzoate and 1-Phenyl-2,2-dideuterio-4,4-dimethylpentyl 3,5-Dinitrobenzoate. These esters were prepared in the same way as the trimethylstannyl analogues described above. These were characterized more thoroughly than the precursor alcohols, mp 100–101 °C. NMR data of 1 (CCl_4, ppm): $(CH_3)_3C$ 0.90 (s), CH_2 1.20 (m), CH_2 1.98 (m), CH 5.92 (t), Ar 7.33 (s), ODNB 9.07 (s). NMR (CCl_4, ppm) $(CH_3)_3C$ 0.96 (s), CH_2 1.25 (m), CD_2 no signal, CH 5.97 (t), Ar 7.46 (s), ODNB 9.05 (s).

Product Identification. Samples (10 mL) of 1-aryl-3-trimethylstannylpropyl 3,5-dinitrobenzoate in trifluoroethanol were sealed in ampules and heated at 100 °C for at least 8 solvolysis half-lives. The contents was then distributed between 15 mL of carbon tetrachloride and 25 mL of 10% aqueous sodium chloride. The organic layer was concentrated to 0.35–0.25 mL and transferred into an NMR tube as quantitatively as possible by washing with the solvent. The identities of the arylcyclopropanes were established by the characteristic NMR spectra displayed in Table I. The yields were determined by adding a known weight of methylene chloride and comparing the areas under the aryl proton signals with those under those of the methylene chloride protons. The intensities per proton were shown to be identical within experimental error by comparison of an authentic mixture of phenylcyclopropane and methylene chloride with the results shown in Table I. A further check on the NMR method was made by solvolyzing 1-phenyl-3-trimethylstannylpropyl 3,5-dinitrobenzoate and determining the yield of phenylcyclopropane after the extraction and concentration procedure using the usual internal standard GLC method. The results obtained with the two methods agreed within the experimental error of ca. ±3%. The products from the other aryl derivatives used in the NMR analyses were examined by GLC using a column 6 ft × 1/4 in. with Apiezon L on Chromosorb isothermally at 145 °C. Only a single peak was observed in each case. Except for the *m*-trifluoromethyl analogue the retention time was greater than that of phenylcyclopropane.

The trimethylstannyl 3,5-dinitrobenzoate was characterized by its NMR spectrum, which was the same as that of an authentic sample. The fact that the yields of arylcyclopropanes were less than quantitative can be ascribed in part to losses in the procedure described, and in part to the incursion of the exchange reaction of eq 4 with the *m*-trifluoromethylphenyl and *m*-chloro derivatives. Signals due to the products of this reaction (tetramethyltin and 1-aryl-3-(3,5-dinitrobenzoyloxydimethylstannyl) 3,5-dinitrobenzoate were evident in the NMR spectra, especially when the solvolysis was conducted with higher (ca. 0.02 M) concentrations of substrate.

Kinetics. A. NMR Procedure. This method was used for those substrates (*p*-CH_3, *m*-CH_3, H, *p*-F, and *p*-Cl) with which no interference by reaction 4 was observed before 1 half-life of solvolysis. A solution 0.02–0.05 M in substrate was dissolved in trifluoroethanol; about 0.72 mL was placed in an NMR tube fitted with a tightly fitting stopper and placed in the constant temperature bath. The spectrum was recorded at suitable intervals and the peak heights of the trimethylstannyl proton signals of the substrate and trimethylstannyl 3,5-dinitrobenzoate were recorded four times and averaged. The ratio of the figure for the substrate to the sum of the two (A_s/[A_s + A-$Me_3SnODNB$]) gave the fraction of unreacted starting material, from which the rate constant could be computed by the method of least

squares. Correlation coefficients were always 0.998 or greater and usually 0.999.

B. UV Procedure. This method was used with the less reactive substrates because the lower concentrations needed to minimize interference from reaction 4 rendered the NMR method too insensitive. The strong absorption of the dinitrobenzoate moiety, ca. 2.3×10^4 in the 200–260-nm region, was exploited. Absorbances were usually measured at 240 nm at which interference due to the arylcyclopropane was absent. Samples ca. 2×10^{-3} M in substrate were dissolved in the solvent; 2-mL aliquots were sealed in ampules under reduced pressure and immersed in the constant temperature bath. Samples were removed at suitable intervals and transferred, with rinsing of the ampule with hexane, into a separatory funnel so that its total volume was about 40 mL. This was washed twice with 5% aqueous sodium chloride to remove trimethylstannyl 3,5-dinitrobenzoate and made up to volume in a 50-mL volumetric flask. The absorbance was read and the data from six to ten samples were used to compute the rate constant. When applied to the same substrate the UV and NMR methods gave the same results within experimental error.

C. Rapid Reaction Procedure. 1-*p*-Anisyl-3-trimethylstannylpropyl 3,5-dinitrobenzoate was shown initially to have a half-life of solvolysis of about 3 min at 40 °C. In order to obtain rapid sampling the apparatus shown in Figure 3 was used. Enough substrate to make a solution 0.004 M was placed in the addition tube, which was attached in position A. The assembly with solvent in the flask was placed in the constant temperature bath. After temperature equilibration the substrate was added by turning the addition tube to position B. The solvent was stirred until the substrate was completely dissolved before sampling was begun. The stopcock was turned into the position which allowed about 2 mL of solution to be drawn into the syringe. It was then turned into the position shown in the figure and the sample forced through the 2-mm i.d. outlet tube into a vial to which had been added 9 mL of hexane and 2 mL of 5% aqueous sodium chloride, and was then weighed. The resulting solvent mixture was shaken vigorously for 0.5 min and stored in an ice-water bath, if necessary, until it could be weighed again to determine the aliquot size. The layers were separated, the hexane layer was washed again with the saline solution and made up to volume, and the absorbance was read at 247.5 nm.

D. Titrimetric Procedure. A simple titrimetric procedure using a pH meter was initially used for the model compounds. Good first-order rate plots ($r \leq 0.98$) were obtained over 2 half-lives with the following results: 1-phenylpentyl 3,5-dinitrobenzoate, $k = 2.18 \times 10^{-5}$ s^{-1} at 100 °C; 4,4-dimethyl-1-phenylpentyl 3,5-dinitrobenzoate, $k = 2.42 \times 10^5$ s^{-1} at 100 °C and 8.8×10^{-7} s^{-1} at 65 °C; $\Delta H^{\ddagger} = 23$ kcal/mol, $\Delta S^{\ddagger} - 19$ eu. Infinity titers were only about 90% of the expected values, presumably owing to reversibility of the solvolysis.

E. Modifications for Model Compounds. Because of the difficulty mentioned above further solvolyses were conducted in the presence of 2,6-lutidine to drive the reaction to completion, which was indeed observed. The NMR method used with the organostannyl derivatives was adopted with two modifications. A solution of 5% aqueous sodium carbonate was used for the water extraction to remove the 3,5-dinitrobenzoic acid. The peak heights due to the protons of the *tert*-butyl groups in the substrate and of the products, which were trifluoroethyl ether and the olefin formed by elimination, were monitored. These could be separated on the HA-100 instrument because their chemical shifts were 0.90, 0.84, and 0.93 ppm, respectively. For the more reactive *p*-methoxy derivative the special apparatus was used, and aqueous sodium carbonate again used in the extraction process. Proportions of olefin and ester shown in Table III were estimated from the respective *tert*-butyl proton peak heights.

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π,π-Biradicaloid Hydrocarbons. The Pleiadene Family. 3.[1] A Facile Symmetry-Forbidden Thermal Conversion of a Polycyclic Butadiene Moiety to a Cyclobutene

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Abstract: The orbital symmetry "forbidden" thermal electrocyclic ring closure of the "biradicaloid" hydrocarbon 7,12-dimethylpleiadene (**2c**) to 6b,10b-dimethyl-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**1c**) proceeds readily below room temperature, $E_{act} = 21.3 \pm 0.6$ kcal/mol, $\log A = 15.6 \pm 0.5$ (s^{-1}).

Thermal interconversions of butadienes and cyclobutenes generally have a reputation for strict adherence to the orbital-symmetry rules.[2] We presently report an unusually facile butadiene → cyclobutene thermal ring closure, **1c** → **2c**, proceeding along the "forbidden" disrotatory pathway and discuss the factors which make it unique.

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