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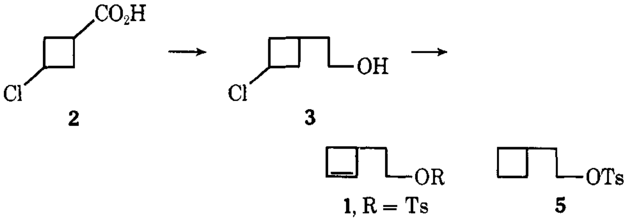
Strained Ring Systems. X.[1] Buffered Acetolysis of 2-(Δ^2-Cyclobutenyl)ethyl and *trans*-3,5-Hexadienyl Tosylates

Sir:

We wish to report the results of our attempt to form the delocalized carbonium ion reported from the acetolysis of *exo*-bicyclo[2.2.0]hex-2-yl tosylate[2] by the π route with 2-(Δ^2-cyclobutenyl)ethyl tosylate (**1**). While double bond participation of the type expected was not observed with **1**, this study developed solution rate data for the cyclobutene → butadiene rearrangement of **1**, and rate and product data from the acetolysis of *trans*-3,5-hexadienyl tosylate (**10**), the simplest system possible with which to observe homodienylic participation.[3]

Tosylate **1** was prepared by Arndt–Eistert chain extension of 3-chlorocyclobutanecarboxylic acid (**2**),[4] followed by hydride reduction to the ethanol **3**, dehydrochlorination to **4** (KO-*tert*-Bu–DMSO),[5] and tosylation.



2 **3**

1, R = Ts
4, R = H

5

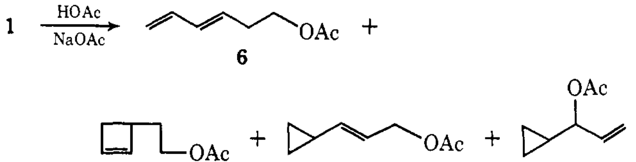
The kinetic results (Table I) for buffered acetolysis of **1** were at first encouraging with a small rate enhancement relative to the saturated derivative **5** (k_1/k_5 = 3.8 at 100°) and the $\Delta S^{\ddagger}$ of the correct magnitude expected for participation. However, analysis of the products derived from **1** made it clear that double bond participation of the type expected had not occurred.

Table I. Buffered Acetolysis Rate Data for 2-(Δ^2-Cyclobutenyl)ethyl OTs (**1**), 2-Cyclobutylethyl OTs (**5**), and *trans*-3,5-Hexadienyl OTs (**10**)

Compd	Temp, °C	10^5k_t,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	85.0	(0.289)[b]		
	100.0	1.36 ± 0.02	27.4 ± 0.4	−7.9 ± 1.1
	120.0	9.70 ± 0.02		
5	85.0	(0.128)[b]		
	100.0	0.488 ± 0.002	23.4 ± 0.3	−20.5 ± 0.7
	120.0	2.57 ± 0.02		
10	85.0	2.85 ± 0.02		
	100.0	12.6 ± 0.1	25.6 ± 0.3	−8.3 ± 0.6

[a] Average k_t from duplicate runs. Errors are the maximum deviation from the average. [b] Extrapolated from rates at higher temperatures.

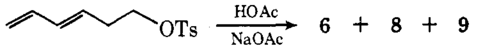
The products from **1** after one solvolytic half-life were a mixture of 49% *trans*-3,5-hexadienyl acetate (**6**), 18% 2-(Δ^2-cyclobutenyl)ethyl acetate (**7**), 29% *trans*-3-cyclopropylallyl acetate (**8**), 2% 1-cyclopropylallyl acetate (**9**), and 2% unidentified materials; no tosylate other than **1** was recovered. After ten solvolytic half-lives, this product composition was 92% **6**, 6% **7**, 1% **8**, and 1% **9**, with a trace of the unidentified materials remaining.



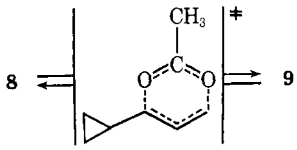
6 **7** **8** **9**

The combined information of (a) formation of these products from **1**, (b) the relative instability of alcohol **4** and acetate **7** to glpc conditions toward rearrangement to their *trans*-3,5-hexadienyl analogs, and (c) the small, negative $\Delta S^{\ddagger}$ suggested that the rate-determining step in the buffered acetolysis of **1** was *not* an ionization process, but rather involved the sum of a cyclobutene → butadiene retrocycloaddition of **3** to *trans*-3,5-hexadienyl OTs (**10**), k_r, and a solvent displacement leading to **7**, k_s.[6]

To examine the validity of this proposal, we have prepared and examined the buffered acetolysis of **10**. The kinetic data and activation parameters for **10** are given in Table I. The products of buffered acetolysis of **10** were varying amounts of acetates **6**, **8**, and **9** dependent on the extent of reaction. The acetate product composition has been determined from 0.25 to 10 solvolytic half-lives for **30** and is plotted in Figure 1. From this plot we can see that the first formed acetate is **9** whose concentration builds and decays rapidly in the early stages of the reaction. The allylic isomer of **9**, **8**, is formed somewhat more slowly and appears to be more stable than **9**. From this and data obtained with pure samples of **8** and **9** an equilibrium exists between these two acetates with K = 9–10 which probably involves **11** as a transition state.



10



11

Plotting the data in Figure 1 as a function of the total composition during the buffered acetolysis gives a "textbook" type of plot shown in Figure 2. Here we see what appears to be a brief induction period in the formation of acetate **6**. This would be expected if

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[1] For paper IX in this series see R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, **35**, 2666 (1970).

[2] R. N. McDonald and C. E. Reineke, *ibid.*, **32**, 1878 (1967).

[3] M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954).

[4] W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962).

[5] M. Hanack and K. Riedlinger, *Chem. Ber.*, **100**, 2107 (1967).

[6] The lack of double bond participation in **1** is a common observation in such 4-pentenyl systems; see A. A. Youssef and S. M. Sharaf, *J. Org. Chem.*, **33**, 2581 (1968).

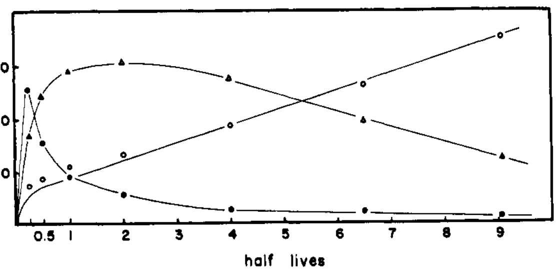

Figure 1. Composition of acetate products from the buffered acetolysis of **10**: *trans*-3,5-hexadienyl acetate (○), 1-cyclopropylallyl acetate (●), and *trans*-3-cyclopropylallyl acetate (△).

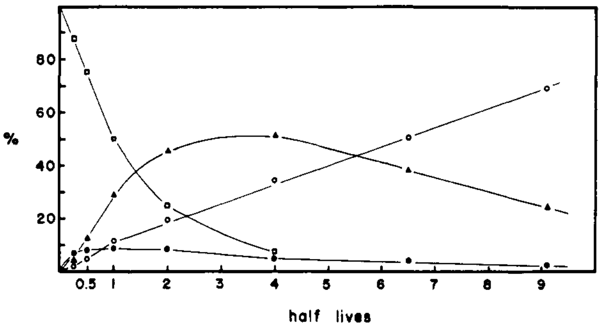

Figure 2. Total composition from the buffered acetolysis of **10**; **10** (□) and the acetate products as defined in Figure 1.

k_t for **10** contained little if any of a k_s (k_2) component. It should also be noted that slopes for the destruction of **8** and the formation of **6** are equal in magnitude beyond several half-lives.

The following general kinetic scheme (Scheme I) was then considered to rationalize the data. As mentioned above, k_2 was considered negligible which simplifies the scheme involving formation of **6** from **10** *via* **8** and **9**. Rate constant k_3 was estimated to be (6.8 ± 0.5) × 10^{-4} sec^{-1} at 100° from the initial rate of disappearance of **9** starting with pure **9**[7] and neglecting k_5. Since $K = k_3/k_4 \approx 10$, k_4 was given as about 7 × 10^{-5} sec^{-1} (100°) in good agreement with $k_4 = 7.3 \times 10^{-5}$ sec^{-1} determined from the initial rate of destruction of pure **8** at 100°. The rate of conversion of **9** to **6**, k_5, was estimated to be 7 × 10^{-5} sec^{-1} at 100° from a plot of the ratio of **8**/**6** *vs.* time starting with pure **9**. Extrapolation to zero time gave the ratio of $k_3/k_5 \approx 10$. From the initial rate of production of **6** from **8**, k_6 was estimated to be 2 × 10^{-5} sec^{-1}. These rate constants, along with those arrived at from computer simulation[9] of the data involving **6**, **8**, and **9** omitting k_6, are given in Table II. Omission of k_6 from the computer calculations gave only qualitative agreement for the rearrangements of **8** and **9** to mixtures of **6**, **8**, and **9** and yielded overestimates of k_4 and k_5, thus establishing the presence of k_6 of about the magnitude determined experimentally.

Scheme I

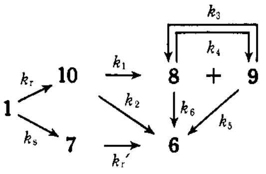

Table II. Certain Rate Constants Associated with Scheme I at 100°

	Exptl 10^5k, sec^{-1}	Computer simulated 10^5k, sec^{-1}
k_1	12.6	
k_2	*a*	
k_3	68 ± 5	70
k_4	7.3	9
k_5	7	10
k_6	2	*b*
K (k_3/k_4)	9–10	7.8

[a] Considered to be negligible. [b] Omitted in computer calculations.

To estimate k_r, the rate of rearrangement of the model acetate **7**, k_r', was examined. These results are given in Table III. The similarity of the rate constants at 100° in buffered acetic acid and in xylene showed the absence of a solvent effect on the rearrangement of **7** to **6**. This rearrangement was then considered to be a thermal cyclobutene ring opening. These rate data would suggest that in the acetolysis of **1**, the major contribution to its k_t is k_r, since $k_t = k_r + k_s$. The product study after one solvolytic half-life for **1** was in agreement with this conclusion; an estimate of k_s for **1** from the amount of **7** formed from **1** is 3 × 10^{-6} sec^{-1} at 100°.[10] This gives a value of $k_r \approx 1.0 \times 10^{-5}$ sec^{-1} for the buffered acetolysis of **1** which suggests that replacement of acetyl in **7** with tosyl in **1** has little effect on the cyclobutene → butadiene conversion, k_r' and k_r, respectively.

Table III. Rearrangement Data for 2-(Δ^2-Cyclobutenyl)ethyl Acetate (**7**) to *trans*-3,5-Hexadienyl Acetate (**6**)

Temp, °C	10^5k,[a] sec^{-1}	$\Delta H^{\ddagger}$,[c] kcal/mol	$\Delta S^{\ddagger}$,[c] eu
85.0	(0.242)[c]		
100.0	1.31 ± 0.01	29.1 ± 0.3	−3.2 ± 0.6
100.0	1.22 ± 0.09[b]		
120.0	10.3 ± 0.1		

[a] 0.022–0.027 *M* ROAc and 0.028 *M* NaOAc. Errors are standard deviations in these single runs. [b] Xylene solvent, 0.031 *M* ROAc. [c] Only data in HOAc–NaOAc used in these calculations.

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(7) Acetate **9** was prepared by acetylation of 1-cyclopropylallyl alcohol.[8]

(8) K. B. Wiberg and A. J. Ashe, *J. Amer. Chem. Soc.*, **90**, 63 (1968).

(9) We thank Professor Kenneth Conrow for developing this computer program.

(10) This estimated k_s is based on *ca.* 21% of **7** formed from **1** with partial rearrangement of **7** to **6**.

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