(12) Diene **5:** NMR (220 MHz, $CCl_4$) $\delta$ 5.55–5.95 (m, $H_2$–$H_5$), 2.18–2.78 (major peaks at 2.27 and 2.53, $H_1$, $H_6$), 1.0–2.1 (major peaks at 2.0 and 1.4, $H_7$–$H_{10}$); uv (hexane) $\lambda_{max}$ 240 nm ($\epsilon$ 6940). Diene **6:** NMR (220 MHz, $CCl_4$) $\delta$ 5.58 (5 line m, $H_3$, $H_5$), 5.40 (d, $H_2$, $H_6$, $J_{23} = J_{56} = 11$ Hz), 2.93 ($H_{4a}$, m of at least 14 lines consistent with a d ($J_{4a,4b} = 19$ Hz) of t (4 Hz) of t (2 Hz)), 2.69 (broadened s, $H_1$, $H_7$), 2.49 (d of t, $H_{4b}$, $J_{3,4b} = J_{4b,5} = 6.5$ Hz), 1.48–1.82 (m, major peaks at 1.6 and 1.7, $H_8$–$H_{10}$); uv (hexane) end absorption ($\epsilon_{220\ nm}$ 120).

(13) N. L. Allinger and V. B. Zalkow, *J. Am. Chem. Soc.*, **83**, 1144 (1961). We thank Professor Allinger for sending us copies of the ir spectra of **7** and its trans isomer.

(14) We thank Professor R. B. Bates for providing us with a sample of the reaction mixture from the catalytic hydrogenation of azulene, which turned out to be >90% **7**.

(15) NMR and uv data were essentially identical with data reported by L. M. Dané, J. W. de Haan, and H. Kloosterziel, *Tetrahedron Lett.*, 2755 (1970).

(16) (a) F. J. Kronzer and V. R. Sandel, *J. Am. Chem. Soc.*, **94**, 5750 (1972). (b) Further discussion will be found in a forthcoming review: S. W. Staley in "Pericyclic Reactions", A. P. Marchand and R. P. Lehr, Ed., Academic Press, New York, N.Y., 1976.

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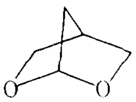
## 2,6,7-Trioxabicyclo[2.2.1]heptane

*Sir:*

We recently reported the synthesis of bicyclic acetals **1** and **2**, and noted that their rates of dichloracetic acid catalyzed hydrolysis exceeded those of an acyclic reference compound by factors of $10^6$ and $10^5$, respectively.[1]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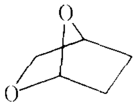
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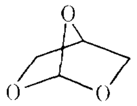
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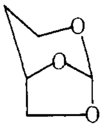
We now report the synthesis of 2,6,7-trioxabicyclo-[2.2.1]heptane[2] and note that, despite expected high ring strain, it undergoes acetic acid catalyzed hydrolysis at a rate slightly *less* than those of acyclic model compounds.

Compound **3** was prepared in 73% yield by the interchange reaction of glycerol with ethyl orthoformate in dilute dioctyl phthalate solution at 110–140° with a trace of anhydrous *p*-toluenesulfonic acid as catalyst with vigorous stirring at 0.1 mm. The bicyclic compound distilled out as formed and was condensed in a liquid nitrogen-chilled receiver. Alternatively the first two molecules of ethanol could be removed without catalyst or dilution as described by Crank and Eastwood[3] and the final molecule of ethanol removed as above using dibutyl phthalate. This technique avoids oligomerization of very acid-sensitive compounds such as **3**, which may account for its absence from the chemical literature to the present time. The hydrolysis rate constant for **3**, given in Table I, is smaller than those for trimethyl and triethyl orthoformates by factors of 2 and 1.5, respectively.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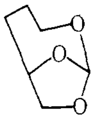
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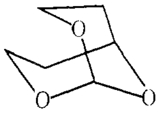
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To extend this finding, orthoesters **4–6** were prepared in yields of 70–73%, as described for **3**.[4] Their hydrolysis rate constants (Table I) are even slower than those of **3**.

These results may be attributable to a very early transition state, with very little C–O bond breaking and consequently very little strain release. Work is underway, particularly to determine whether the hydrolysis is specific or general-acid catalyzed, to explore the problem further.

Table I. Rates of Hydrolysis of Bicyclic Orthoesters[a]

| Compound | $10^4k_1$, sec$^{-1}$ | Compound | $10^4k_1$, sec$^{-1}$ |
|---|---|---|---|
| $(CH_3O)_3CH$ | 19 | 6 | 4.3 |
| $(C_2H_5O)_3CH$ | 15 | 4 | 4.1 |
| 3 | 10 | 5 | 3.2 |

[a] Conditions: temperature 35°; 0.084 *M* acetic acid catalyst; solutions are initially 1.4 *M* in orthoester in solvent 0.6 ml of acetone-$d_6$ and 0.2 ml of $D_2O$; rates were followed by monitoring $O_3CH$ NMR absorption intensity as a function of time. Good pseudo-first-order plots were obtained.

Recent studies of orthoester hydrolysis[5-7] as models for the behavior of the tetrahedral intermediates in enzyme-catalyzed hydrolysis, and studies of the stereoelectronic preferences in these intermediates,[8-10] have focused attention on the need for models with rigidly defined geometry. Crank and Eastwood[3] had earlier suggested that experimental information could be provided by the synthesis and determination of the properties of rigid bicyclic orthoesters. The ready availability of bicyclic orthoesters means that the suggestion of Crank and Eastwood can now be pursued. Moreover, these compounds will be useful new monomers for studies of ring-opening polymerization to polysaccharide analogs.[11,12]

**Acknowledgment.** We are deeply indebted to the National Institutes of Health Grant GM 18595 for support of this work and to a referee for helpful comments.

### References and Notes

(1) H. K. Hall, Jr., and Fr. DeBlauwe, *J. Am. Chem. Soc.*, **97**, 655 (1975).

(2) F. Pauer, *Monatsh. Chem.*, **58**, 1 (1931), had reported compound **1** as displaying bp 126° (12 mm). However, R. H. de Wolfe, "Carboxylic Ortho Acid Derivatives", Academic Press, New York, N.Y., 1974, p 8, noted that this is much higher than expected and is probably that of a dimer. Our authentic compound **1** boils at 80° (37 mm).

(3) G. Crank and F. W. Eastwood, *Aust. J. Chem.*, **17**, 1385 (1964).

(4) Compounds **4–6** had previously been reported by Crank and Eastwood (ref 3), although in low yields (2, 3, and 39%, respectively). Our NMR spectra agreed with their reported values.

(5) T. H. Fife, *Acc. Chem. Res.*, **5**, 264 (1972).

(6) J. Hine and A. W. Klueppal, *J. Am. Chem. Soc.*, **96**, 2924 (1974).

(7) Y. Chiang, A. J. Kresge, P. Salomaa, and C. I. Young, *J. Am. Chem. Soc.*, **96**, 4494 (1974).

(8) J. P. Guthrie, *J. Am. Chem. Soc.*, **95**, 6999 (1973).

(9) J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **96**, 4048 (1974).

(10) (a) P. Deslongchamps, C. Moreau, D. Fréhel, and P. Atlani, *Can. J. Chem.*, **50**, 3402 (1972); (b) P. Deslongchamps, P. Atlani, D. Fréhel, and A. Malaval, *ibid.*, **50**, 3405 (1972); (c) P. Deslongchamps, C. Lebreux, and R. Taillefer, *ibid.*, **51**, 1665 (1973).

(11) Review: C. Schuerch, *Acc. Chem. Res.*, **6**, 184 (1973).

(12) N. K. Kochetkov and A. F. Bochkov, *Carbohydr. Res.*, **9**, 61 (1969).

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## Simple Alkyl Methylenecyclopropenes via Addition of Unsaturated Carbenes to Alkynes[1]

*Sir:*

Strained small ring systems have long fascinated chemists, and the methylenecyclopropene system, **1**, in particular has been of special interest to theoreticians[2] as well as being a synthetic challenge.[3] The first successful synthesis of a methylenecyclopropene was a diphenylquinocyclopropene reported by Kende[4] in 1963, and, although numerous other stable methylenecyclopropenes have been prepared since, they all have strongly electron stabilizing substituents, such