(12) Diene **5**: NMR (220 MHz, CCl_4) δ 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) λ_{max} 240 nm (ϵ 6940). Diene **6**: NMR (220 MHz, CCl_4) δ 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).

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(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**.

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Stuart W. Staley,* Alan S. Heyn

Department of Chemistry, University of Maryland
College Park, Maryland 20742

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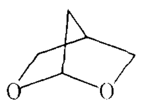
2,6,7-Trioxabicyclo[2.2.1]heptane

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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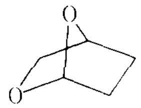

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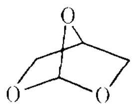

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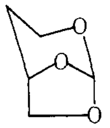
We now report the synthesis of 2,6,7-trioxabicyclo[2.2.1]heptane[2] and note that, despite expected high ring strain, it undergoes acetic acid catalyzed hydrolysis at a rate slightly *less* than those of acyclic model compounds.

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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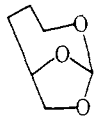

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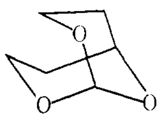

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To extend this finding, orthoesters **4–6** were prepared in yields of 70–73%, as described for **3**.[4] Their hydrolysis rate constants (Table I) are even slower than those of **3**.

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.

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H. K. Hall, Jr.,* Fr. DeBlauwe, T. Pyriadi

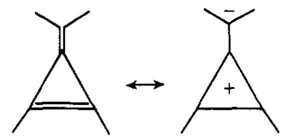
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received March 21, 1975

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



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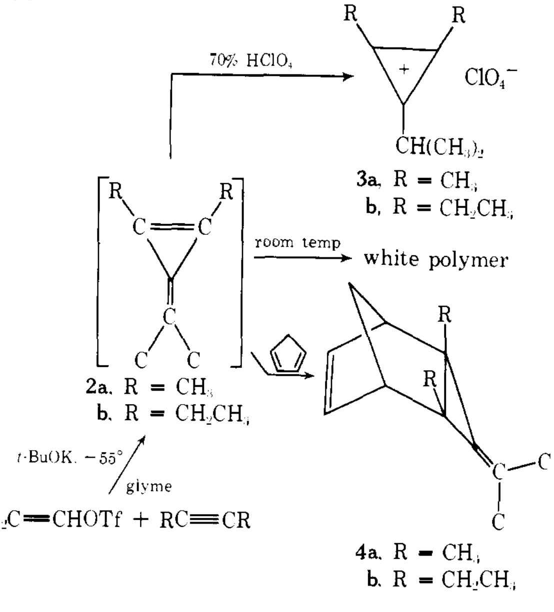
as CN,[5] CF_3,[6] CO_2R,[7] and O═CR,[8] on the exocyclic double bond and with one exception[5a] aryl groups on the ring. Although attempts have been made[3,9] to prepare simpler alkyl substituted methylenecyclopropenes and even the parent compound,[10] they have so far not been successful. This has probably been due as much to the stringent reaction conditions employed as to the instability due to the strain energy of the desired product. Hence in this communication we wish to report the ready in situ preparation under mild conditions of simple alkyl methylenecyclopropenes, **2.**

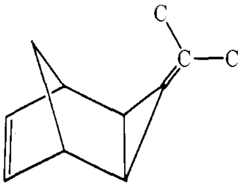
Addition of $(CH_3)_2C{=}CHOTf$[11] to an equal molar amount of *t*-BuOK in a 20-fold excess of 50:50 glyme and alkyne at −55° results in a light yellow solution that yields a white polymer if allowed to warm to room temperature. NMR monitoring of the reaction with 2-butyne shows the disappearance of the starting triflate (absence of olefinic H at 6.4 ppm) within 10–15 min and formation of two new singlets[12] at 1.89 and 2.17 ppm (relative to TMS) that in turn disappear over a period of several hours. Addition of 70% $HClO_4$ to this solution after being maintained at −20° up to 12–24 hr and work-up gives the corresponding crystalline cyclopropenium perchlorate salts, **3,** and addition of cyclopentadiene the corresponding Diels–Alder adducts, **4,** as summarized in Scheme I.

As best we can determine the indicated methylenecyclopropenes, **2,** are the sole products formed in these reactions and the two derivatives, **3,** and **4,** were obtained in excellent yields for small scale (5 mmol) preparations. Adducts **3** and **4** were fully characterized by spectral means as follows: **3a** mp 111–113 dec (recrystallized from ethyl acetate); ir 7.15 and 9.2 μ; NMR ($CDCl_3$) δ 1.45 (d, J = 7 Hz, 6 H), 2.81 (s, 6 H), 3.42 (sept, J = 7 Hz, 1 H); for **3b** mp 176–177 (recrystallized from ethyl acetate); ir 7.2 and 9.1 μ; NMR ($CDCl_3$) δ 1.45 (d, J = 6.9 Hz, 6 H) 1.46 (t, J = 7 Hz, 6 H), 3.17 (quart, J = 7 Hz, 4 H) 3.40 (sept, J = 6.9 Hz, 1 H), consistent with the known[13] spectral properties of similar cyclopropenyl cations. For **4a,** MS 174 (M^+, 13), 159 (65), 131 (16), 105 (15), 93 (100), 92 (31), 91 (40), 82 (21), 77 (35), 67 (41), 66 (29); ir 1380, 1240, 1192, 1045, and 738 cm^{-1}; NMR (CCl_4) δ 1.20 (s, 6 H), 1.53 (s, 6 H), 1.70–2.01 (m, 2 H) 2.63 (m, 2 H) 5.75 (t, J = 1 Hz, 2 H); for **4b,** MS 202 (M^+, 10) 173 (53), 155 (40), 153 (19), 131 (20), 107 (91), 91 (37), 81 (51), 79 (100), ir 1370, 1330, 1242, 1190, 890, and 785 cm^{-1}; NMR (CCl_4 δ 0.9–1.3 (m, 6 H) 1.56 (s, 6 H) 1.4–1.9 (m, 6 H) 2.75 (m, 2 H) 5.76 (t, J = 1.1 Hz, 2 H). The Diels–Alder adducts, **4,** are clearly endo as indicated by the spectral data in comparison to the known adduct[14] of cyclopropene itself and in contrast to the exo adduct, **5,** resulting from the addition of $(CH_3)_2C{=}C$: to norbornadiene.[15] So far we have been unable to characterize the polymers due to their complete insolubility but in analogy to the behavior of cyclopropene[14a] assume it to be substituted polymethylenecyclopropane.

Scheme I



Formation of **2** undoubtedly proceeds via the addition of the unsaturated carbene,[16] $(CH_3)_2C{=}C$: to the alkyne, which has not heretofore been explored.[17] In order to examine the generality of this procedure we also investigated the reaction of $(CH_3)_2C{=}CHOTf$ with diphenylacetylene and 1-phenylpropyne. In the former case the sole product was the *tert*-butyl vinyl ether **6** indicating that the carbene preferentially inserts[11] into the O–H of *tert*-butyl alcohol over addition to the triple bond. In the latter case the sole product isolated was the dimethylenecyclopropane, **7.** Product **7** could arise from either addition of the carbene to phenylallene, formed by base catalyzed isomerization of the acetylene,[18] or by migration of the double bond to the exocyclic position from the ring[19] in the corresponding methylenecyclopropene.



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$(CH_3)_2C{=}CHO\text{-}t\text{-}Bu$

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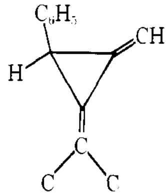

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In summary, addition of unsaturated carbenes generated from the appropriate vinyl triflate and *t*-BuOK to dialkylacetylenes in glyme at low temperatures gives the corresponding methylenecyclopropenes. Triafulvenes, **2a** and **2b,** represent the simplest known methylenecyclopropenes to date.[20] We believe this procedure to be general for the preparation of any fully substituted alkyl triafulvene but not applicable to aryl methylenecyclopropenes. These alkyl methylenecyclopropenes are remarkably stable in solution at −20° but polymerize at room temperature and in the absence of solvent. Possible low temperature isolation and full characterization are presently under way.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. 1-RO-CA16903-01 from the National Cancer Institute.

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Peter J. Stang,* Michael G. Mangum
Chemistry Department, The University of Utah
Salt Lake City, Utah 84112

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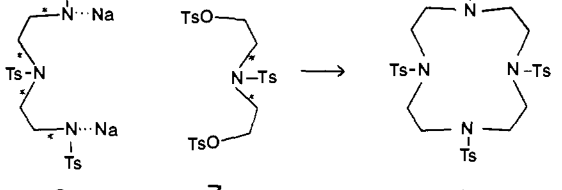
Formation of Large Rings, Internal Metalation Reactions, and Internal Entropy Effects

Sir:

In order to induce long open-chains with α- and ω-functional groups to condense internally into large rings it is generally necessary to use either (1) a dilution technique or (2) a template effect, otherwise long open-chain structures are formed.[1,2] However, there are a few instances where large rings are preferentially formed in the absence of either (1) or (2) and which have not been explained hitherto. Three examples, (a), (b), and (c), where this occurs are as follows. (a) The 12-membered ring derivative of 1,4,7,10-tetraazacyclododecane (**1,** Ts = *p*-toluenesulfonyl) is formed in 80% yield from **2** and **3.** Many analogs were similarly synthesized, no dilution being necessary, and a template effect was ruled out since tetramethylammonium could be used as a cation in place of sodium.[3] (b) Similarly the 14-membered ring (**4**) is formed in high (75%) yield from mesityl oxide and ethylenediamine monoperchlorate.[4] (c) It has been shown that long chain diphosphines, t-$Bu_2P(CH_2)_nP$-t-Bu_2 (n = 9, 10, or 12) give large ring metal chelate compounds (12- to 45-membered rings) in preference to open-chain polynuclear species even after long reaction times under vigorous conditions (12 hr, 125°). Analogous diphosphines with less bulky end groups (e.g., Ph) preferentially give open-chain polynuclear complexes.[5]



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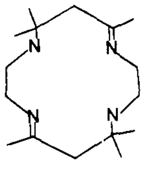
Enthalpy, external entropy, and internal entropy effects will influence whether a large ring is formed or not. In particular internal entropy is lost on cyclization and if the loss is large it will tend to favor the formation of open-chain products. It is suggested that the factor which distinguishes examples (a), (b), or (c) from the great majority of cases where cyclization is not preferred is the unusually small internal entropy of the open-chain intermediates and therefore the unusually small loss on cyclization.[6] Thus in (a) the bulky *p*-toluenesulphonyl groups in **2** and **3** restrict rotation about the six bonds marked with an asterisk and therefore the loss in internal entropy on cyclization to **1** is small. Similarly one would expect the *gem*-dimethyl and methyl substituents and the C═N double bonds to restrict rotation in the open-chain intermediates involved in the formation of **4.**[7] A small loss in internal entropy could also be an important factor in the conversion of α,ω-diacetylenes to macrocycles by oxidative coupling since the internal entropy of the linear C⋮CC or -CC⋮C-C⋮CC- systems is low.[8]



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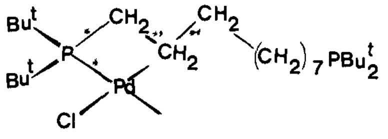

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There is abundant ^{31}P and ^{1}H NMR evidence for restricted rotation about P–metal bonds in P-t-Bu_2R–metal complexes.[9,10] Space filling molecular models show that on complexing one end of a diphosphine such as t-$Bu_2P(CH_2)_{10}P$-t-Bu_2 to a metal halide such as $PdCl_2$ there will be severely restricted rotation around the bonds marked with an asterisk (**5**) and that the preferred orientation around the bonds marked with a double asterisk or asterisk (**5**) is the same as that found for the structures of *trans*-$[IrCl(CO)\{t\text{-}Bu_2P(CH_2)_{10}P\text{-}t\text{-}Bu_2\}]$[11] or *trans*-$[PdCl_2\{t\text{-}Bu_2P(CH_2)_{10}P\text{-}t\text{-}Bu_2\}]_2$[12] and *trans*-$[RhCl(CO)\text{-}t\text{-}Bu_2P(CH_2)_{10}P\text{-}t\text{-}Bu_2]_2$[11] by X-ray diffraction. Similar restrictions would occur at the other end of a CH_2CH_2P-t-Bu_2–metal system. These effects would favor cyclization. In the formation of very large ring binuclear (or trinuclear) species, similar arguments would apply.

The above arguments are in part extensions of some which have been put forward,[13,14] to explain the so-called "Thorpe–Ingold" or "*gem*-dimethyl" effect for small (≤seven-membered) rings.[15,16] It is now well-established that *gem*-dimethyl or similar groups cause remarkable stabilization of small rings and also increase the rate at which small rings are formed.[15,16] For similar steric effects to operate with an atom much larger than carbon, such as phosphorus, one would expect more bulky groups such as *tert*-butyl to be necessary; i.e., for phosphorus we would have "a *gem*-*tert*-butyl" effect.

We have also demonstrated that steric effects are important in internal metalation reactions of tertiary phosphines or tertiary arsines;[17] e.g., -P-t-Bu_2- or -As-t-Bu_2- derivatives are readily metalated under conditions where the corresponding -PMe_2- or -$AsMe_2$- derivatives are not—another example of a "*gem*-di-*tert*-butyl" effect. Similarly