of the trans-fused products. Although sufficient evidence is not available as yet to define the charge distribution or mechanism for these cycloadditions, the results presented here add some support to the proposal that the widely studied α,β-unsaturated ketone cycloadditions[8] are reasonable models for related reactions of the uracils, and presumably thymines.[5,9]

In contrast to the photoadducts of cyclic α,β-unsaturated ketones, the cycloadducts from uracil possess a hydrolyzable urea function. The high yields of cycloadducts and potential degradation of the urea portion of the molecule open a new and versatile method for the synthesis of four-membered rings (cyclobutanes, cyclobutenes, and perhaps cyclobutadienes). Aspects of this chemistry are currently under study.[10]

Acknowledgment. We wish to thank Dr. M. Logue and Dr. N. Leonard for helpful comments.

[8] O. L. Chapman and G. Lenz, *Org. Photochem.*, **1**, 294 (1967).

[9] (a) A. A. Lamola, *Photochem. Photobiol.*, **7**, 619 (1968); (b) P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **92**, 181 (1970).

[10] All compounds noted gave acceptable combustion analyses, and, except for **9**, were obtained as crystalline solids. All yields reported are isolated yields. All structures were consistent with 100-MHz nmr spectra. Due to space limitations and the complexity of these spectra they have not been described in the text. The spectra as well as decoupling studies will be discussed thoroughly in our full paper.

[11] Alfred P. Sloan Fellow (1970–1972); Camille and Henry Dreyfus Teacher-Scholar Awardee (1971–1976).

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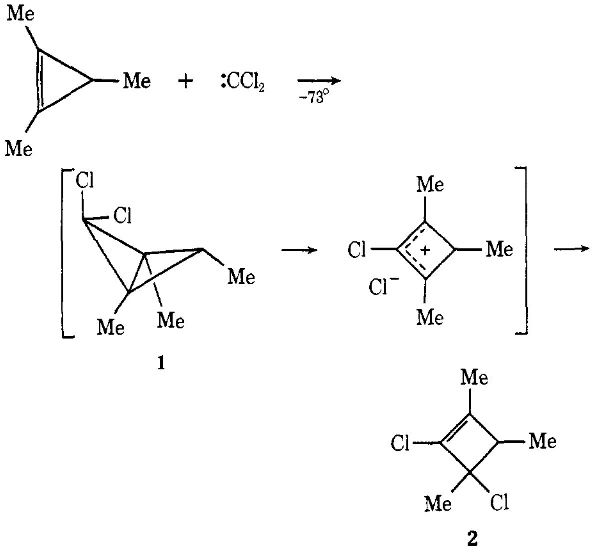
Spontaneous Generation of a Bridgehead Double Bond in a Seven-Membered Ring

Sir:

As is well known, addition of dihalocarbene (or its equivalent) to the double bond of small cyclic olefins can result in ring opening of the initial adduct[1] to yield a vinyl, allylic dihalide, *via* the intermediate haloallylic cation (*e.g.*, eq 1[2] and 2[1]). However, when the olefin is internal to two rings, the initial cyclopropane adduct is stable (*e.g.*, eq 3[3] and 4[4]).

We wish to report that when dichlorocarbene (generated *via* the $CHCl_3$ + KO-*t*-Bu in pentane route) is added to 3,6-dihydrobenzcyclobutene (**7**),[5] the initial adduct **8**[6] is thermally labile when neat or when dissolved in a dipolar aprotic solvent (*e.g.*, DMSO, DMF, acetone, acetonitrile). Thus when the neat liquid **8** was allowed to warm to room temperature, an exothermic reaction occurred, whereupon crystals were deposited in the reaction flask. The crystals could be isolated in 50–60% yield, and melted sharply (mp 228° dec). Both mass spectrometry and elemental analysis indicated a formula of $C_{18}H_{20}Cl_4$, *i.e.*, a dimer of **8**. The remainder of the material in the reaction flask (*i.e.*, that which did not crystallize) proved isomeric with the crystalline dimer **9**.



1

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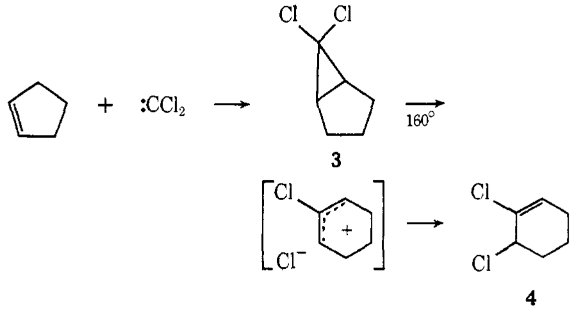
(1)



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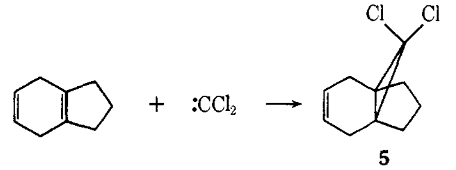
(2)



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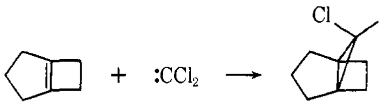
(3)



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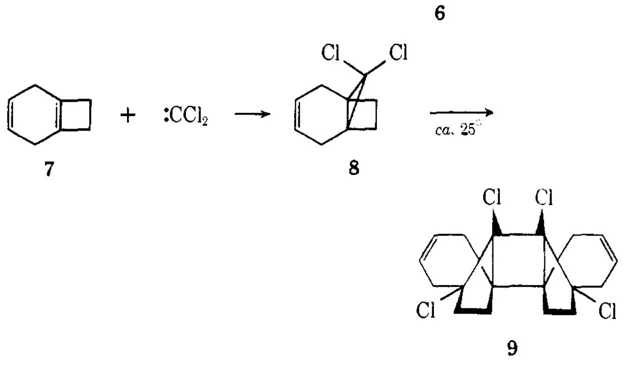

7

8

9

Since the nmr (τ 4.53, 4 H, olefinics; τ 6.68–8.21, 16 H, aliphatics) was relatively uninformative, an X-ray analysis of the crystalline dimer was undertaken. Single crystals of **9** were grown by slow evaporation of a CH_2Cl_2 solution. Preliminary photographs displayed $2/m$ Laue symmetry and systematic extinctions for $h0l$ ($h + l = 2n + 1$ missing) and $0k0$ ($k = 2n + 1$ missing) required the monoclinic space group $P2_1/n$ (C_{2h}^5 alternate setting). Diffractometer measured cell constants were $a = 7.484$ (3), $b = 16.787$ (4), and $c =$

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[1] For a general review, see R. Barlet and Y. Vo-Quang, *Bull. Soc. Chim. Fr.*, 3729 (1969).

[2] B. M. Trost and R. C. Atkins, *Chem. Commun.*, 1254 (1971).

[3] The addition of dichlorocarbene to 4,7-dihydroindene was carried out and gave results analogously to the dibromocarbene addition already described [E. Vogel, W. Wiedemann, H. Kiefer, and W. Harrison, *Tetrahedron Lett.*, 673 (1963)].

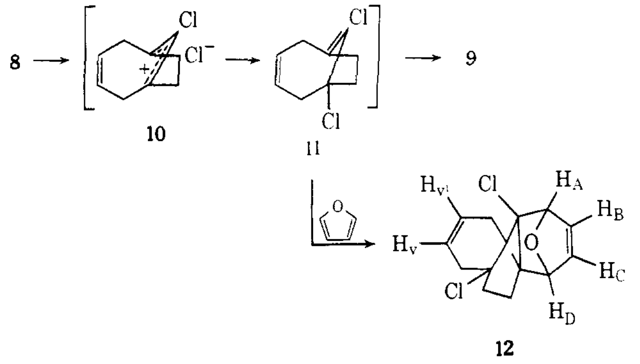
[4] K. B. Wiberg and G. J. Burgmaier, *ibid.*, 317 (1969).

[5] J. M. Garrett and G. J. Fonken, *ibid.*, 191 (1969).

[6] P. Warner and R. LaRose, *ibid.*, 2141 (1972).

13.100 (3) Å, and $\beta = 91.05(3)°$. A calculated density of 1.53 g/cm^3 for $Z = 4$ was interpreted to mean one molecule of $C_{18}H_{20}Cl_4$ (**9**) per asymmetric unit. All reflections (2897) in a 2θ sphere of 50° were measured for the hkl and $\bar{h}kl$ octants. After correction for Lorentz and polarization effects, 1630 reflections had $I \geqslant 3\sigma(I)$ and were judged observed. Normalized structure factors were computed and phases were assigned to all 363 E values with magnitudes greater than 1.5.[7] The four chlorine atoms were located in the subsequent three-dimensional E synthesis.[8] The 18 carbon atoms were easily located on the chlorine phased electron density synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for all atoms smoothly converged to the present minimum of 0.09 for the conventional crystallographic discrepancy index $[\Sigma_o(||F_o| - |F_c||/|F_o|)]$ for the observed data.[9] Bond distances and angles generally agree with accepted values within the estimated standard deviations (0.01 Å and 1°, respectively).[10] Figure 1 is a computer generated drawing of the final X-ray model of **9**. The dihedral angle between the five- and four-membered rings is 118° while that between the five-and seven-membered rings is approximately 130°.

The only rational pathway for the formation of **9** is the ring opening of **8**, *via* **10**, to the transient species **11**, which has a bridgehead double bond in a seven-membered ring.[11] This is, to our knowledge, the first example of a bridgehead double bond in a one-carbon bridge in this small a ring.[12] It is noteworthy that the preponderant dimer (of the eight possible) is the most symmetrical one. Inasmuch as **11** may exist in either a *d* or *l* form, **9** had to be formed *via* a combination of one *d*-**11** and one *l*-**11**. Furthermore, **9** is a $({}_{\pi}2_s + {}_{\pi}2_s)$-type dimer, although the concertedness or nonconcertedness of the dimerization is unestablished.[13]



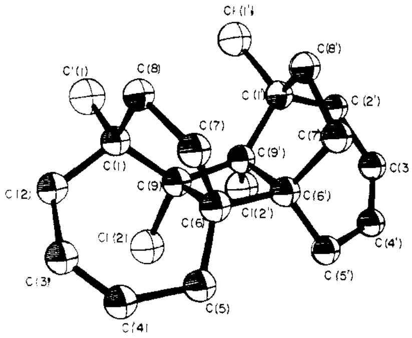


Figure 1. A computer generated perspective drawing of **9**.

In order to provide further evidence for the formation of **11**, we sought to trap **11** with a diene. Thus, when 1 equiv of furan was added to cold, neat **8**, and the mixture warmed to room temperature, a mixture of 1:1 adducts (**12**) was formed[14] (as shown by mass spectrometry and elemental analysis). From the nmr spectrum we concluded that the mixture (we could not achieve separation *via* tlc or glpc) consisted of *ca.* 90% of one (of four possible) adduct.[15] Both the chemical shifts and coupling constants [τ 4.74, H_A; 3.37, H_B; 3.59, H_C; 5.34, H_D; 4.56, center of H_V and $H_{V'}$; 7.0–8.5, all other protons; $J_{AB} = 1.5$ Hz, $J_{BC} = 6$ Hz, $J_{CD} = 1.5$ Hz (decoupling experiments)] confirm the gross features of structure **12**.

Some comment on the unexpectedly and unprecedentedly facile thermal generation of **11** seems warranted. The ΔH for the conversion of **1** to **2** is *ca.* −15 kcal/mol,[16] while that for **3** to **4** is *ca.* −10 kcal/mol. Since **3** requires much higher temperatures to react than **8**, the **8** to **11** conversion must be exothermic by >10 kcal/mol (roughly 14 kcal/mol based on temperature differences), *assuming no effect of the different cyclopropane substitution patterns* in **3** and **8**.[20] However,

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(7) (a) J. Karle and I. Karle, *Acta Crystallogr.*, 23, 494 (1967); (b) R. E. Long, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1965.

(8) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT and FRIEDEL," Ames Laboratory, U. S. Atomic Energy Commission, Iowa State University, Ames, Iowa, 1971.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(10) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," U. S. Atomic Energy Commission Report No. ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(11) For a discussion of bridgehead double bonds and Bredt's rule, see (a) J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, **92**, 956 (1970), and references therein; see also (b) M. Toda, H. Niwa, K. Ienaga, and Y. Hirata, *Tetrahedron Lett.*, 335 (1972), and (c) G. Köbrich and M. Baumann, *Angew. Chem. Int. Ed. Engl.*, **11**, 52 (1972). For an example of a bridgehead double bond in (d) a seven-membered ring, see J. R. Wiseman and J. A. Chong, *J. Amer. Chem. Soc.*, **91**, 7775 (1969); (e) a six-membered ring, see R. Keese and E. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971).

(12) However, Wiseman[11a] has presented evidence for enolate formation in bicyclo[4.2.1]nonane systems with the carbonyl function in the 1 bridge.

(13) Analogous dimerizations with reliable stereochemical structure determination are extremely rare. In the dimerization of the hydrocarbon derived from the norbiphenylene anion [M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, **91**, 2378 (1969)], one of the two dimers formed contains a mirror plane, and is therefore analogous to **9** (the other dimer's structure was not reported).

(14) However, **11** failed to form an adduct with benzene, but instead dimerized.

(15) While we could see small peaks corresponding to at least one other isomer of the major adduct (**12**), we cannot exclude accidental chemical-shift equivalence of two isomers of comparable concentration. However, we feel this is unlikely, since the equivalence would have to hold for the six *different* protons, H_A, H_B, H_C, H_D, H_V, $H_{V'}$. Notably, Keese and Krebs[11e] found two furan adducts in an 80:20 ratio.

(16) This was calculated by assuming a strain energy of 63.6 kcal/mol for **1**,[17] a 28.5 kcal/mol strain energy for **2**,[18] and $\Delta H = -7.8$ kcal/mol for the cyclopropane to propylene interconversion.[19] It was tacitly assumed, then, that the effects of the methyl groups would largely cancel (in the overall strain energy difference).

(17) This is the value for bicyclobutane itself [K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965)]. Herein we assume, as seems reasonable,[19] that the geminal chlorine atoms have little or no *net* effect.

(18) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968).

(19) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(20) Here we make the reasonable assumption that, for these similar reactions, changes in activation energies will be linearly reflected in changes in ground-state energies. This seems to be borne out by the reactivity of **1**.[21]

it is known that each additional alkyl substituent lowers the activation energy for rearrangement by *ca.* 2.5–3 kcal/mol.[21] Therefore, the **8** to **11** conversion need be exothermic by only *ca.* 8–9 kcal/mol.[22] The calculated exothermicity for the **8** to **11** reaction is, neglecting any strain on the bridgehead double bond, *ca.* −29 to −30 kcal/mol. Therefore, we estimate the strain of the bridgehead double bond in **11** to be 20–22 kcal/mol.[22,23] It now becomes clear why **5** is stable: comparable ring opening in that system would be endothermic by some 10–12 kcal/mol.[22,24] Similar considerations about the stability of **6** indicate that a bridgehead double bond in a six-membered ring has at least 30 kcal/mol strain energy.

We are continuing to investigate other facets of the chemistry of **8**, including what, if any, role is played by the 3,4 double bond.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Atomic Energy Commission for partial support of this work.

[21] H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966). This effect is, of course, operative in the **1** to **2** conversion.

[22] This estimate of the bridgehead double bond strain in **11** would seem to be an upper limit, since the presumed intermediate **10** (and related transition states) must be relatively less stable than the corresponding one(s) for the **3** to **4** conversion. This serves to counteract the assumption of ref 20, and would require a greater exothermicity for the **8** to **11** conversion (which means a lower value for the bridgehead double bond strain energy).

[23] Compare this to the *ca.* 12 kcal/mol strain energy found for the bridgehead double bond of bicyclo[3.3.1]non-1-ene, which is a bridgehead double bond in an eight-membered ring [P. M. Lesko and R. B. Turner, *J. Amer. Chem. Soc.*, 90, 6888 (1968)].

[24] We note that 11,11-dibromotricyclo[4.4.1.$0^{1,6}$]undecane does not undergo ring opening even when ionized; rather a 1,2-alkyl shift is observed [D. B. Ledlie, *J. Org. Chem.*, 37, 1439 (1972)].

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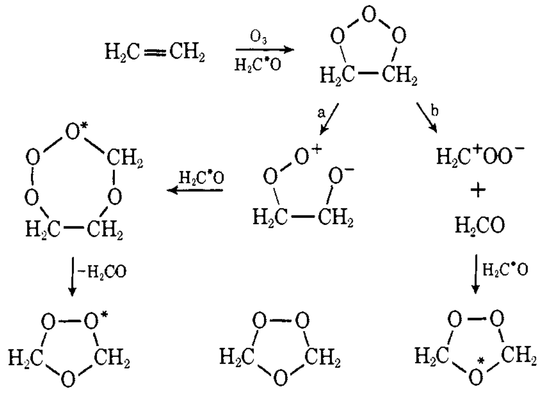
Oxygen-18 Formaldehyde Insertion in the Ozonolysis of Ethylene and the Microwave Spectrum of Oxygen-18 Ethylene Ozonide[1]

Sir:

We have recently determined the structure of ethylene ozonide (1,2,4-trioxacyclopentane) and shown that it has C_2 symmetry (half-chair conformation).[2] This result and the related finding that the ozonolysis of $HDC{=}CH_2$ produced the normal isotopic species, two singly deuterated species, and three doubly deuterated species were related to three mechanistic proposals. One proposal, the modified Criegee mechanism,[3] did not correlate with our results because it postulates a preferred conformation of the final ozonide which differs from that of ethylene ozonide. Two proposals, the Criegee[4] and the aldehyde interchange mechanisms,[5] were consistent with the results. This report discusses our initial experiments which distinguish between these two mechanisms in the ozonolysis of ethylene.

Fliszar, *et al.*,[6] and Story, *et al.*,[7] first utilized the fact that the two mechanisms predict a different site of incorporation of an aldehydic oxygen into the final ozonide. As shown below, the ozonolysis of ethylene in the presence of oxygen-18 formaldehyde should yield ozonides I, II, and III *via* the aldehyde interchange mechanism (paths a and b) but only II and III *via* the Criegee mechanism (path b). We have found only II and III when mixtures of ethylene and oxygen-18 formaldehyde were ozonized.



I II III

Mixtures of 0.19 *M* ethylene and 0.36 *M* formaldehyde (27 ± 1.4% oxygen-18 enriched) in methyl chloride were ozonized at −78°. The ozonide was separated from the solvent by low temperature vacuum distillation[2] employing fast warm-up procedures.[8]

The site and quantity of oxygen-18 enrichment in ethylene ozonide was determined by microwave spectroscopy. This technique could be used because the complete structure of ethylene ozonide was known;[2] hence the regions for the rotational transitions of the two different oxygen-18 species could be predicted. The spectrum of only one species enriched in oxygen-18 has been found as well as the spectrum of II. The transitions of the oxygen-18 enriched species were close to those predicted for III. Moreover, an intensity alternation arising from nuclear spin statistics was observed demonstrating that the C_2 symmetry axis was retained upon enrichment. This is only consistent with oxygen-18 enrichment at the ether position (ozonide III). Seven transitions arising from this species were assigned on the basis of their frequency fit and Stark effects. The rotational constants (megahertz) which fit the spectrum are $A = 8094.14 \pm 0.16$, $B = 7877.01 \pm 0.03$, and $C = 4469.11 \pm 0.02$. These can be compared with those calculated for III and I from the structure:[2] III, 8095, 7869, 4467; I, 8144, 7832, 4481.

A systematic search was conducted to identify spectra from I. Several frequency regions were investigated

[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

[2] C. W. Gillies and R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **94**, 6337 (1972).

[3] N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).

[4] R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

[5] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **89**, 2429 (1967).

[6] S. Fliszar and J. Carles, *ibid.*, **91**, 2637 (1969); S. Fliszar, J. Carles, and J. Renard, *ibid.*, **90**, 1364 (1968).

[7] P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, 90, 1907 (1968).

[8] R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1098 (1971).