conformational change of a single lysozyme structure than a redistribution of a population of multiple forms of lysozyme. For example, small temperature dependences of the tryptophan NH protons and the histidine C-2 proton reflect changes in hydrogen bonding of these side chains.

Communications to the Editor

$\Delta^{1,4}$-Bicyclo[2.2.0]hexene[1]

Sir:

$\Delta^{1,4}$-Bicyclo[2.2.0]hexene (I) is one of the more interesting of the unknown small ring alkenes. It is a possible precursor for the theoretically interesting tricyclo[2.2.1.0^{1,4}]heptane and tricyclo[2.2.2.0^{1,4}]-octane,[2] and for a trans-fused bicyclo[2.2.0]hexane. A knowledge of its strain energy, reactivity, and mode of reaction should contribute to a number of currently important theoretical problems.

The alkene, I, has been elusive. Attempts at dehalogenating 1-bromo-4-chlorobicyclo[2.2.0]hexane (II)[3] with metals have failed, and thus the dehalide is similar to 1,2-dibromocyclopropane.[4] The reaction of II in cyclooctane with sodium–potassium alloy, for example, gives bicyclo[2.2.0]hexane,[5] as well as coupling products of cyclooctane with the bicyclo[2.2.0]-hexane ring system. This is probably a free-radical reaction involving, in one step, a hydrogen transfer from cyclooctane to a bridgehead bicyclo[2.2.0]hexyl radical. The reaction of II with sodium in diglyme as solvent also gave bicyclo[2.2.0]hexane. Finally, the reaction of II with the sodium phenanthrene radical anion[6] gave no low molecular weight products, but rather gave a product containing both the cycloalkane and phenanthrene rings.

As we have previously reported,[2] the photolysis of the sodium salt III of spiro[2.3]hexanone-4 tosylhydrazone gave the azine IV when diglyme was used as the sol-

III   IV
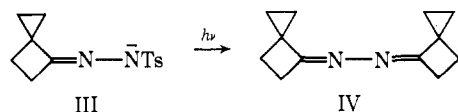
vent. Under these conditions, the reaction was heterogeneous. Dimethyl sulfoxide rendered the reaction homogeneous, but bicyclohexene was not found as a product. The formation of $\Delta^{1,5}$-bicyclo[3.2.0]-heptene from spiro[2.4]heptanone-4 *via* the above reaction, using diglyme as the solvent, has been reported by Kirmse,[7] and this reaction also occurs when dimethyl sulfoxide is used as the solvent.

Although the thermolysis of the sodium salt of spiro-[2.4]heptanone-4 tosylhydrazone has been reported to give a mixture of bicyclo[3.2.0]heptene and 1,2-dimethylenecyclopentane,[7] we have now observed that the reaction, when carried out under high vacuum (in the absence of solvent), leads to a good yield of bicyclo-[3.2.0]heptene and very little of its ring-opened product.
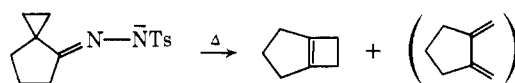
This reaction was applied to III, and the volatile products were collected in a liquid nitrogen cooled trap. As the contents were warmed to room temperature, an exothermic reaction occurred. The products were 1,2-dimethylenecyclobutane and a compound (V) which analyzed by mass spectra and elementary analysis as a dimer. The dimer had a symmetrically tetrasubstituted double bond as shown by the lack of ir absorption in the C=C region, the presence of a band at 1680 cm^{-1} in the Raman spectrum,[8] and the absence of vinyl proton bands in the nmr spectrum. The nmr spectrum had bands at τ 7.58 (4 H),[9] 7.65–7.95 (8 H), and 8.16 (4 H).

Thermolysis of the dimer V was accomplished in the gas phase at low pressure by passing it through a section of glass tubing heated to about 350°. The product of the thermolysis, VI, had four olefinic protons (τ 4.65, 5.27) and four allylic protons (τ 7.27) in an nmr pattern resembling that of 1,2-dimethylenecyclohexane,[10] as well as an nmr band at τ 7.92 (8 H) which strongly resembled that for the cyclobutane ring protons of tricyclo[3.2.0.0^{1,5}]nonane.[11] These data indicate the structures to be those shown below. Therefore, we conclude that the dimer V corresponds to the Diels–Alder adduct of bicyclo[2.2.0]hexene and dimethylenecyclobutane.

The presence of bicyclo[2.2.0]hexene (I) in the reaction mixture was demonstrated by adding cyclopentadiene to the liquid nitrogen cooled reaction product before warming it to room temperature. No dimer V was found under these conditions, but rather, a new

(1) This investigation was supported by the U. S. Army Research Office.

(2) K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, *Tetrahedron Lett.*, 5855 (1968).

(3) K. V. Scherer, Jr., and T. J. Meyers, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P 180.

(4) K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, **82**, 6375 (1960).

(5) We wish to thank Dr. R. Srinivasan for supplying the nmr spectrum of bicyclo[2.2.0]hexane.

(6) This reagent has been used for the dehalogenation of vicinal dihalides: E. Vogel, H. Kiefer, and W. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964); R. Ubersax, Ph.D. Thesis, Yale University, 1969.

(7) W. Kirmse and K. H. Pook, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966).

(8) The Raman band is at about the same position (1677 cm^{-1}) observed for $\Delta^{1,5}$-bicyclo[3.2.0]heptene (see ref 7). The Raman spectrum was kindly run by Kirkwood Cunningham.

(9) Cyclobutene allylic protons lead to nmr bands at τ 7.4–7.5 (*cf.* K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1226 (1961)).

(10) P. D. Bartlett, A. S. Wingrove, and R. Owyang, *ibid.*, **90**, 6067 (1968).

(11) We wish to thank Professor Philip Eaton for supplying the nmr spectrum for this hydrocarbon. It has the corresponding band at τ 8.05.

III → 15%

V, 50%

VI
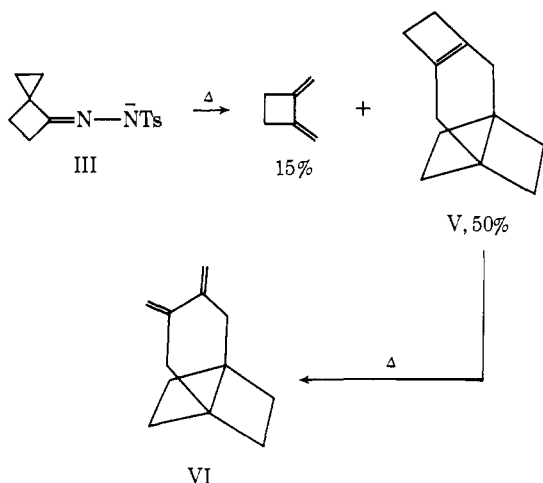
hydrocarbon, VII, was isolated. Its mass spectrum and elementary analysis corresponded to a 1:1 adduct between I and cyclopentadiene. The nmr spectrum indicated two olefinic protons (τ 3.8) coupled to two allylic protons (τ 7.4) and a complex multiplet of ten protons (τ 7.55–8.75). The ir spectrum had no C=C band suggesting a symmetrically substituted double bond.[12] These data strongly suggest that hydrocarbon VII is the Diels–Alder adduct of cyclopentadiene with bicyclo[2.2.0]hexene.

III → I → VII
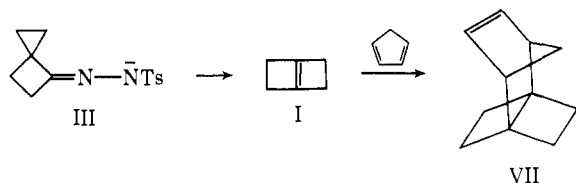
Finally, the product derived by heating III was distilled at low pressure and low temperature into an nmr tube containing deuteriomethylene chloride. The nmr spectrum at *ca.* −52°[13] showed the presence of 1,2-dimethylenecyclobutane (τ 4.86 (2 H), 5.30 (2 H), and 7.43 (4 H)) and a sharp singlet at τ 6.76. The latter, as well as the dimethylenecyclobutane peaks, slowly disappeared at −20° giving the spectrum of the dimer. The singlet must then correspond to $\Delta^{1,4}$-bicyclo[2.2.0]hexene (I). It is now easily prepared, and has at least moderate thermal stability.

(12) Dicyclopentadiene has two C=C bands at 1640 and 1620 cm^{-1} and therefore the two possible Diels–Alder adducts between cyclopentadiene and dimethylenecyclobutane should have an infrared band. The latter adducts also could not account for the observed nmr spectrum.
(13) CDHCl$_2$ (τ 4.70) was used as an internal standard. The chemical shifts of dimethylenecyclobutane appear to vary somewhat with temperature.
(14) National Institutes of Health Predoctoral Fellow (1968–1970).
(15) National Science Foundation Postdoctoral Fellow (1970–1971).
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Organocopper Cluster Compounds. I.
m-(Trifluoromethyl)phenylcopper Octamer and Its Pyrolysis Product, [*m*-(CF$_3$)C$_6$H$_4$]$_6$Cu$_8$

Sir:

Since the first organocopper was prepared by Reich[1] in 1923, very little structural work has been reported.

(1) R. Reich, *C. R. Acad. Sci.*, 177, 322 (1923).

Most workers have assumed polymeric structures (RCu)$_n$ based on the low solubility of many organocoppers. Camus and Marsich find arylcoppers to be low molecular weight[2] and Costa, *et al.*, find they form a bewildering array of complexes, some containing more than one copper by elemental analysis.[3] An X-ray study shows (C$_6$H$_5$)$_3$PCuC$_5$H$_5$ to be a monomer.[4]

We have found that fluorinated arylcoppers exist as discrete stable tetramers and octamers[5] and report here on the determination of the structure of *m*-(trifluoromethyl)phenylcopper as an octamer **1** and its novel pyrolysis to [*m*-(CF$_3$)C$_6$H$_4$]$_6$Cu$_8$, **2**, a stable Cu(0)–Cu(I) cluster compound.

Compound **1** was prepared by the metathetical reaction of *m*-(trifluoromethyl)phenylmagnesium bromide or iodide and cuprous bromide or iodide. The brown solid analyzes for C$_7$H$_4$F$_3$Cu, melts and decomposes at 158°, and has an ir spectrum typical of meta-substituted benzotrifluorides and uv $\lambda_{max}^{benzene}$ 565 nm (ϵ 146), which does not obey Beer's law. It is soluble in ethereal solvents and less soluble in benzene. Its ^{19}F nmr spectrum at room temperature in ether is a sharp singlet. Like most organocoppers it oxidizes in air and hydrolyzes with water.

We first became suspicious of its structure while studying its thermal decomposition. When **1** is heated in benzene, it quickly forms a deep green solution and up to 50% yield of 3,3'-bis(trifluoromethyl)biphenyl (**3**) *before copper metal appears*. The formation and stability of the green color and the rate of formation of biaryl **3** are not altered by added copper powder, ruling out colloidal copper as the green species. Instead, we believe the green color is due to the formation of the stable Cu(0)–Cu(I) cluster compound **2**.

The aggregation of **1** was determined cryoscopically in benzene under a nitrogen atmosphere to be 7.7–10.7 and by vapor pressure osmometry as 9.0–10.6.[6] No copper-containing fragments were detected by mass spectrometry at 100–200° under conditions where (C$_6$F$_5$Cu)$_4$ was easily detected.[5c] This probably rules out the presence of monomer, dimer, and trimer.

Studies of the thermal decomposition of **1** by cryoscopic molecular weight in benzene, assay both for biaryl **3** and hydrolyzable benzotrifluoride groups, and direct nmr observation in dioxane show that decomposition slows drastically when 25% biaryl **3** has formed (*i.e.*, **2** is more stable than **1**), the decomposition is unimolecular, and the average size of the copper aggregate stays about the same during the pyrolysis. The kinetic data were plotted for several large aggregates but only fit the following scheme (see Figure 1).

$$R_8Cu_8 \xrightarrow{k_1} R_2 + R_6Cu_8 \xrightarrow{k_2} R_2 + R_4Cu_8$$
$$\quad\ \mathbf{1} \qquad\quad \mathbf{3} \qquad \mathbf{2}$$
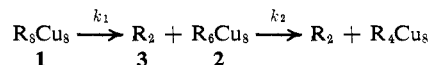
(2) A. Camus and N. Marsich, *J. Organometal. Chem.*, 14, 441 (1968).
(3) G. Costa, A. Camus, N. Marsich, and L. Gatti, *ibid.*, 8, 339 (1967).
(4) F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, 92, 2353 (1970).
(5) (a) A. Cairncross and W. A. Sheppard, *ibid.*, 90, 2186 (1968); (b) for preliminary accounts of this, see A. Cairncross and W. A. Sheppard, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN 118; Abstracts, 4th International Conference on Organometallic Chemistry, Bristol, England, July 1969, No. E1; (c) A. Cairncross, H. Omura, and W. A. Sheppard, *J. Amer. Chem. Soc.*, 93, 248 (1971).
(6) The molecular weights were hard to determine because 1 reacts with traces of oxygen and water. Unfortunately, 1 is not very soluble in benzene. These problems caused us to erroneously report 1 as a trimer.[5a]