Suhadolnik and Dr. M. Anchel for valuable discussions and help with some aspects of the experimental work.

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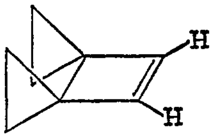
Dispiro[2.0.2.2]oct-7-ene

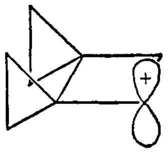
Sir:

There have been reported in the literature no examples of the highly interesting dispiro[2.0.2.2]oct-7-ene system (**1**). This molecule is ideally conducive to various studies of the interaction of cyclopropyl groups with conjugated π systems since it possesses the minimum-energy bisected geometry[1] in which the planes of both cyclopropane rings are normal to the nodal plane of the adjacent double bond. This should allow maximum delocalization between the π system and the p-character bonds of the cyclopropane rings.



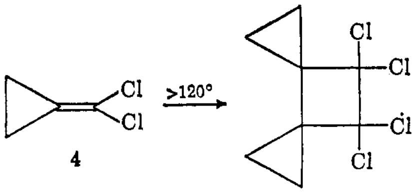
1

Among various possible probes into the chemical nature of this system, the thermal and photochemical reorganizational reactions as well as the study of the carbonium ion chemistry of the dispiro[2.0.2.2]oct-7-ene system should prove of significant theoretical value to organic chemists. The molecule should prove rather resistant to thermal rearrangement since all of the modes of decomposition that have previous analogy are unfavorable here. Indeed the cyclobutene → butadiene, vinylcyclopropane → cyclopentene, and bicyclopropyl → cyclohexene conversions each have obvious drawbacks when applied to this system. Generation of the carbonium ion **2** should also bring about intriguing results, since **2** has the ideal geometry for maximum overlap between the vacant p orbital and the π-like orbitals of the cyclopropane ring.[2] A symmetrical homoallylic structure would be predicted for the species, and one would expect a great resistance to skeletal rearrangement such as that observed by Winstein in a similar system.[3]



2

The first synthesis of this system was accomplished *via* our observation of the heretofore unknown thermal dimerization reaction of dichloromethylenecyclopropane (**4**).



5

Decomposition of sodium trichloroacetate in the presence of allene provided 2,2-dichloromethylenecyclopropane (**3**), in ~20% yield.[4] **3**, on heating in the gas phase at 215° for 1 hr, was converted quantitatively to dichloromethylenecyclopropane (**4**);[5] the nmr spectrum showed a singlet at 1.51 ppm and the mass spectrum, a parent peak at m/e 122. Longer heating or direct heating of **3** in the liquid phase results in quantitative conversion to 7,7,8,8-tetrachlorodispiro[2.0.2.2]octane (**5**) which had two symmetrical multiplets in the nmr centered at 0.64 and 1.13 ppm and a mass spectrum with a parent peak at m/e 244. Treatment of **5** with zinc in ethanol leads, in 85% yield, to 7,8-dichlorodispiro[2.0.2.2]-oct-7-ene (**6**), which showed two symmetrical multiplets in the nmr centered at 0.50 and 0.85 ppm; a mass spectrum with a parent peak at m/e 174; $\lambda_{\max}$ (hexane) 203 mμ (ϵ 1.0×10^3). Reduction of **6** with sodium–tetrahydrofuran–t-butyl alcohol results in the formation, in 80% yield, of the desired dispiro[2.0.2.2]-oct-7-ene, which showed two symmetrical multiplets in the nmr centered at 0.47 (4 H) and 0.73 (4 H) ppm and a singlet at 6.13 (2 H) ppm; bands, *inter alia*, in the ir (12 mm, gas phase) at 3080, 3010, 1014, 933, 876, and 737 cm^{-1}; $\lambda_{\max}$ (ethanol) 203 mμ (ϵ 5.72×10^3); a mass spectrum with a parent peak at m/e 106. Ozonolysis of **1** followed by treatment with performic acid results in >80% yield of bicyclopropyl-1,1′-dicarboxylic acid,[6] displaying two symmetrical multiplets in the nmr at 0.62 (4 H) and 1.01 (4 H) ppm and a broad singlet at 12.7 (2 H) ppm.

As might be expected, dispiro[2.0.2.2]oct-7-ene is thermally stable at temperatures up to 300°. We will report results from our investigation of its thermal rearrangement and other aspects of its chemistry.

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[1] See S. W. Staley, *J. Am. Chem. Soc.*, **89**, 1532 (1967), and references therein.

[2] R. Hoffmann, *Tetrahedron Letters*, 3819 (1965); *J. Chem. Phys.*, **40**, 2480 (1964).

[3] L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966).

[4] H. G. Peer and A. Schors, *Rec. Trav. Chim.*, **161**, 86 (1967).

[5] All new compounds gave satisfactory elemental analyses.

[6] L. Eberson, *Acta Chem. Scand.*, **13**, 40 (1959).

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Ion-Pair Return in Racemization and Isomerization of Sulfinate Esters

Sir:

Sulfinate esters of aliphatic alcohols are known to undergo isomerization to sulfones when the nature of the alkyl moiety is such as to give rise to a comparatively stable carbonium ion.[1,2] Structure and solvent effects indicate that the isomerization is likely to occur by an ionization process, which appears to involve an ion-pair intermediate.[2] Since the sulfinate anion is

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[1] A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, 3603 (1958).

[2] D. Darwish and R. A. McLaren, *Tetrahedron Letters*, 1231 (1962).