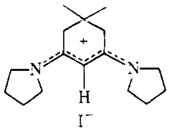
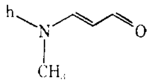
(10) The vinyl proton of



appears at 5.28 ppm and the compound has $\lambda_{max}^{95\%\ EtOH}$ 328 (ϵ 48,700): N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).

(11) K. H. Dudley, A. Ehrenberg, P. Hemmerich, and F. Müller, *Helv. Chim. Acta*, **47**, 1354 (1964).

(12) Prepared by the methods of H. Bredereck, F. Effenberger, D. Zeyfang, and K.-A. Hirsch, *Chem. Ber.*, **101**, 4036 (1968), and Z. Arnold and A. Holý, *Collect. Czech. Chem. Commun.*, **28**, 2040 (1963), by treating



(see ref 13) with dimethyl sulfate in benzene, replacing the solvent with $CHCl_3$, treating the solution at −60° with dimethylamine, precipitating the product from water with 70% perchloric acid, and recrystallizing it from H_2O.

(13) Prepared by the method of S. M. Makin, A. A. Ishmael, V. V. Yastrebov, and K. I. Petrov, *Zh. Org. Khim.*, **7**, 2201 (1971), by the oxidation of propargyl alcohol with MnO_2 in the presence of *N*-methylaniline.

(14) This tenative structure, previously suggested by Zeller et al. (ref 1), was based on analogy to the chemistry of IV. It is of note that at their respective λ_{max}, $\epsilon_{IV}/\epsilon_{V} = \epsilon_{X}/\epsilon_{VI}$.

(15) Cleavage of the C-ring leading to decomposition of IV might occur more rapidly than hydrolysis of the side chain at high pH's. See S. B. Smith and T. C. Bruice, *J. Am. Chem. Soc.*, in press.

(16) Small samples were ozonized to less than completion (by uv spectra), and DMF was detected in the mixtures by NMR. Selective enhancement of the proper peaks occurred when authentic DMF was added to the mixtures.

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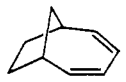
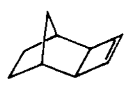
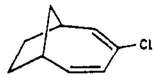
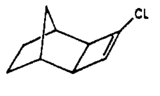
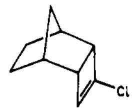
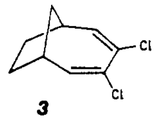
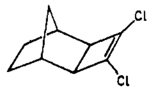
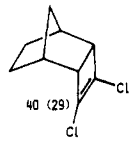
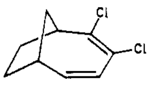
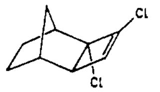
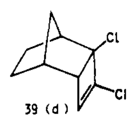
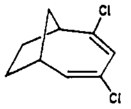
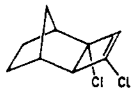
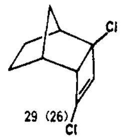
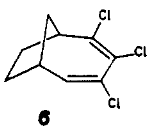
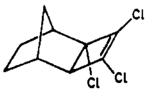
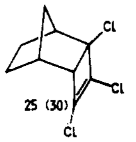
Electrocyclic Closure of Bicyclo[4.2.1]nona-2,4-dienes. Photochemical Steering by a Heavy Atom Effect[1]

Sir:

We previously reported that the light-induced isomerization of bicyclo[4.2.1]nona-2,4-diene to the *exo*- and *endo*-tricyclo[4.2.1.0^{2,5}]non-3-enes is sensitive to the presence of chlorine substituents.[2] On direct irradiation increasing amounts of the exo isomer are formed when more substituent chlorine is present. We attributed these small, but regular differences to the operation of nonbonded interactions arising between the methylene bridge and the polarizable chlorine atom. However, subsequent experiments revealed that far more subtle factors are at work. We now wish to report that the choice of disrotatory mode followed by the electrocyclic reaction is controlled by the multiplicity of the photoexcited states of the diene and that chlorine, where present, affects the multiplicity by acting as a heavy atom.[3]

Bicyclo[4.2.1]nona-2,4-diene (**1**) and a series of chloro derivatives, viz., 3-chloro- (**2**), 3,4-dichloro- (**3**), 2,3-dichloro- (**4**), 2,4-dichloro- (**5**), and 2,3,4-trichlorobicyclo[4.2.1]nona-2,4-diene (**6**) were prepared from norbornene by the carbene route.[4,5] These dienes were submitted to direct and sensitized irradiation and, in all cases save one, the electrocyclization occurred to give both the exo and endo tricyclo[4.2.1.0^{2,5}]non-3-ene derivatives (Table I).[6]

Table I. Direct[a] and Sensitized[b] Irradiation of Bicyclo[4.2.1]nona-2,4-dienes[c]

		Exo	Endo
 **1**	$\xrightarrow{h\nu}$	 30 (68)%	 70 (32)%
 **2**	→	 53 (70)	 47 (30)
 **3**	→	 60 (71)	 40 (29)
 **4**	→	 61 (d)	 39 (d)
 **5**	→	 71 (74)	 29 (26)
 **6**	→	 75 (70)	 25 (30)

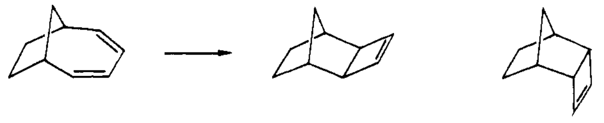
[a] Irradiation performed in hexane as solvent, through quartz, with medium pressure mercury lamp, 254 nm, at 25°. [b] Acetophenone or acetone as solvent and sensitizer, irradiation with medium-pressure mercury lamp through Pyrex glass at 25°. [c] Figures in parentheses are the product ratios obtained in the sensitized irradiation experiments, error ±5%. [d] Products decomposed.

For direct irradiation, it is seen that the exo-endo ratio depends upon the degree of substitution; the percentage of the exo isomer obtained rises sharply and then gradually with increasing chlorine substitution. The effect is most marked on introduction of the first chlorine atom (cf. **1** with **2**). The influence of a second chlorine substituent is less, but nevertheless reinforces the effect of the first, but more so when placed in a 1,3- rather than a 1,2-disubstituted arrangement (cf. **3** and **4** with **5**). The insertion of a third chlorine atom brings about a correspondingly smaller increase in the amount of exo isomer.

Sensitized irradiation produces a dramatic leveling of the exo-endo ratios. All the bicyclo[4.2.1]nonadienes, the parent hydrocarbon as well as the chloro derivatives, now behave similarly in isomerizing to predominantly the exo isomer. In other words, the macroscopic result is that sensitization is tantamount to chlorine substitution or more precisely disubstitution.

The immediate conclusion which can be drawn is that the sensitized process is a triplet reaction which, regardless of substitution, uniformly proceeds to give a consistent ratio of cyclobutene isomers, but dominated by the exo component.

Table II. External Heavy Atom Effect by Solvent on Bicyclo[4.2.1]nona-2,4-diene



	solvent : diene (v:v)	exo	endo
hexane	90 : 10 %	28 %	72 %
CH_2Br_2	50 : 50	29	71
CH_2Br_2	90 : 10	27	73
CH_3CH_2I	50 : 50	37	63
CH_3CH_2I	90 : 10	50	50

On the other hand, direct irradiation is undoubtedly a singlet process, especially since intersystem crossing is notoriously inefficient for conjugated dienes.[7] The parent diene **1** typifies the singlet reaction in giving chiefly the endo cyclobutene isomer. However, substitution on the diene system by a moderably heavy atom, chlorine, facilitates intersystem crossing by spin-orbit coupling and as a result the product composition shifts toward that characteristic of the externally sensitized process.[8,9]

This interpretation, a first example of an intramolecular heavy atom effect steering an electrocyclic reaction toward a particular stereochemical outcome, is confirmed by the direct irradiation of **1** in heavy-atom solvent (Table II).[10,11] Surprisingly, the exo-endo ratio is not visibly disturbed in methylene bromide; however, the desired effect is seen to good advantage in ethyl iodide with a significant increase of exo isomer being observed at higher dilution.

For the pair of tricyclo[4.2.1.$0^{2,5}$]non-3-enes, preliminary calculations indicate that the endo is less stable than the exo isomer by a few kilocalories.[13] Thus the less stable isomer is produced preferentially from the more energetic singlet manifold. It appears that this stability order is reversed for tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dienes with the result that the endo isomer is favored in the sensitized and heavy atom reactions.[12,14] These matters are being investigated.

Acknowledgments. We are indebted to P. S. Skell for a practical suggestion and K. Schaffner for useful advice. We also appreciate the courteous gesture of R. C. Hahn and R. P. Johnson of informing us of their results prior to publication. Lastly we thank U. Burger and B. May for carrying out impeccable NMR spectral and mass spectroscopic measurements.

References and Notes

(1) Part of this research has been submitted as a doctoral dissertation, Thesis No 1638, Faculty of Sciences, University of Geneva, Jan 25, 1974.

(2) C. W. Jefford and F. Delay, *J. Am. Chem. Soc.*, **94**, 4794 (1972).

(3) Most theoretical treatments of light-induced electrocyclic reactions usually neglect the multiplicity of the photoexcited states, the energetics of the process, and in general the problem of how the excited reactant passes to ground state product (However, cf. W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, **88**, 2742 (1966); W. T. A. M. van der Lugt and L. J. Oosterhoff, *ibid.*, **91**, 6042 (1969); K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971); J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972); H. Nohira, *Tetrahedron Lett.*, 2573 (1974)).

(4) C. W. Jefford, U. Burger, and F. Delay, *Helv. Chim. Acta*, **56**, 1083 (1973).

(5) The dichloro derivative **4** was obtained by chlorinating compound **2** and eliminating a molecule of hydrogen chloride from the trichloro adduct with potassium *tert*-butoxide in dimethylformamide. The trichloro derivative **6** was obtained by similar base treatment of 2,3,4,5-tetrachlorobicyclo[4.2.1]non-3-ene (ref 4).

(6) Only reaction to partial conversion (10–50%; 2–4 hr duration) was allowed in order to minimize decomposition by C–Cl bond cleavage and polymerization. The exo–endo isomer ratio was invariant with the reaction time. The cyclobutene isomers were characterized by their NMR spectra and GLC retention times.

(7) E. Havinga, R. J. deKock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960); E. Havinga and J. L. M. A. Schlatmann, *ibid.*, **16**, 146 (1961); R. S. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 4936 (1967); J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

(8) Theoretical and spectroscopic studies of heavy atom effects are plentiful, cf. S. K. Lower and M. A. El-Sayed, *Chem. Rev.* **66**, 208 (1966); S. P. McGlynn, C. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, pp 40, 183, 261, 307, and 371; G. G. Giachino and D. R. Kearns, *J. Chem. Phys.*, **52**, 2964 (1970); G. Kavarnos, T. Cole, P. Scribe, J. C. Dalton, and N. J. Turro, *J. Am. Chem. Soc.*, **93**, 1032 (1971), and references therein.

(9) In an attempt to exploit a greater heavy atom effect, some bromobicyclo[4.2.1]nona-2,4-dienes were irradiated in trial experiments. Unfortunately, extensive decomposition to inseparable complex mixtures occurred, presumably as a result of easy C–Br bond cleavage.

(10) Chemical examples of heavy atom effects are not numerous: (a) conversion of singlet to triplet carbene, A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966); P. S. Skell, S. J. Valenty, and P. W. Humer, *ibid.*, **95**, 5041 (1973); (b) dimerization of acenaphthylene, D. O. Cowan and R. L. E. Drisko, *ibid.*, **92**, 6281, 6286 (1970); (c) addition of acenaphthylene to acrylonitrile (B. F. Plummer and R. A. Hall, *Chem. Commun.*, **44** (1970)), to maleic anhydride (W. Hartmann and H. G. Heine, *Angew. Chem.*, **83**, 291 (1971)), and to cyclopentadiene (W. I. Ferree and B. F. Plummer, *J. Am. Chem. Soc.*, **95**, 6709 (1973)); (d) isomerization of bromostilbene: J. Saltiel, D. W. L. Chang, and E. D. Megarity, *J. Am. Chem. Soc.*, **96**, 6521 (1974).

(11) Other examples, in which di-π-methane rearrangements are potentially competitive, but suppressed when a heavy atom is present, are provided by benzo[7,8]bicyclo[4.2.1]nona-2,4,6-triene and its derivatives (ref 12).

(12) R. C. Hahn and R. P. Johnson, *J. Am. Chem. Soc.*, **97**, 212 (1975).

(13) P. Gund and J. C. Perlberger, unpublished observations.

(14) L. G. Cannell, *Tetrahedron Lett.*, 5967 (1966); H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970).

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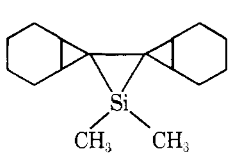
Received December 23, 1974

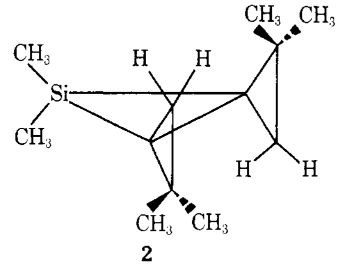
Hexamethylsilirane. A Simple, Isolable Silacyclopropane

Sir:

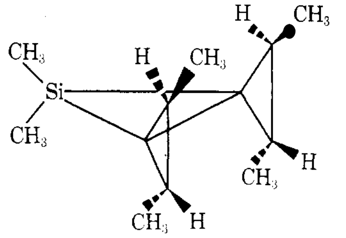
Recently, we have prepared the first silacyclopropanes, **1**, **2**, and **3**.[1] All were found to be quite stable thermally but exceptionally reactive. Thus **2**, whose chemistry has been studied in some detail, reacts exothermally at room temperature with reagents which do not attack the Si-C bonds of larger silacycloalkanes, such as atmospheric oxygen, water, alcohols, ammonia, hydrogen sulfide, and carbon tetrachloride.[1,2] This high reactivity of the Si-C bonds of the silacyclopropane rings of **1**, **2**, and **3** no doubt is a result of the great angle strain in the SiC_2 ring.[3]



1



2



3

The various attempts to prepare silacyclopropanes (siliranes) previous to our synthesis of **1**, **2**, and **3**, in retrospect, do not provide useful information concerning the stability of this ring system since the reaction and work-up conditions used did not anticipate the high reactivity of the silirane