Table I. Reaction of (+)-R_3Si^*H with Carbon Tetrachloride in the Presence of Dibenzoyl Peroxide at 80.0°

	Reactant used, mmoles				R_3Si^*Cl			R_3Si^*H after redn	
Run	(+)-R_3Si^*H	BPO	CCl_4	Reaction time, hr	Mole %	$[\alpha]_D$, deg	Opt purity, %	$[\alpha]_D$, deg	Opt purity, %
1	6.76	0.47	105.7	14	93.2	−5.34	85.5		
2	11.52	0.85	120.2	11	94.9	−5.20	83.2	−31.7	93.9
3	7.44	0.27	59.8	12	64.6	−3.57	57.1		
4	(0.981 g)[a]	0.14	*Ca.* 3 ml	12	92.1	−4.76	76.4	−29.4	87.8

[a] Products of run 3 were used as a mixture.

unpaired electron, the optical activity of the parent compounds is lost and racemic products are formed, except in unusual situations.[2] The loss of optical activity in the products can be ascribed either to planar configurations or to the very rapid inversion of the radicals.[3]

In spite of current interest in silyl radicals, no investigation on the stereochemical course of reactions in which silyl radicals play an important role has been reported to date. The silyl radical derived from an optically active hydrosilane has been presumed to lose its optical activity.[4] However, we now report that the silyl radical produced from an optically active hydrosilane undergoes chlorine-abstraction reaction mostly with *retention of configuration.*

The abstraction of chlorine atoms by silyl radicals was reported by several investigators; the silyl radicals may be produced by photolysis,[5,6] peroxide-catalyzed reaction,[7-9] and thermolysis[10] of hydrosilanes. The free-radical nature of the reaction has been clearly established, and a chain reaction involving chlorine abstraction by silyl radicals was suggested. In addition, there

$$\gtrdot\mathrm{SiH} \xrightarrow{h\nu\text{, or initiator, In}\cdot} \gtrdot\mathrm{Si}\cdot + \mathrm{H}\cdot \text{ (or InH)} \tag{1}$$

$$\gtrdot\mathrm{Si}\cdot + \mathrm{RX} \longrightarrow \gtrdot\mathrm{SiX} + \mathrm{R}\cdot \tag{2}$$

$$\gtrdot\mathrm{SiH} + \mathrm{R}\cdot \longrightarrow \gtrdot\mathrm{Si}\cdot + \mathrm{RH} \tag{3}$$

is other good evidence indicative of the formation of free silyl radicals from hydrosilanes in reactions catalyzed by peroxides.[11-13]

When an optically active hydrosilane, (+)-α-naphthylphenylmethylsilane (**1**),[14] $[\alpha]_D$ +33.7° (*c* 10.9, cyclohexane) [lit.[14] $[\alpha]_D$ +34.3° (*c* 10.9, cyclohexane)], was heated with carbon tetrachloride without any catalyst in a sealed tube at 80.0°, no reaction took place even after 117 hr. However, the presence of a small amount of dibenzoyl peroxide resulted in the formation of the corresponding chlorosilane, (−)-α-naphthylphenylmethylchlorosilane (**2**) [lit.[14] $[\alpha]_D$ −6.28° (*c* 10.5 cyclohexane)], in good yield. The product, obtained after evaporation of carbon tetrachloride followed by recrystallization from pentane, contained a small amount of **1** (glpc). Separation of **2** from the mixture was not feasible because of thermal racemization of **2**.[15] Since unreacted **1** can be separated from the mixture by glpc with configuration retention (at least 95% optical purity),[15] it is likely to assume that **1** in the mixture must have the same optical activity as it had originally. Therefore, optical activities of **2** in each run were determined on the basis of proportional allotment. Furthermore, **2** was converted to **1** again by the reduction with lithium aluminum hydride. The results are listed in Table I.

The stereochemical sequence established by Sommer and coworkers[14] indicates clearly that free-radical chlorination of **1** proceeds with retention of configuration.

$$(+)\text{-}R_3Si^*H \xrightarrow[\text{retn}]{} (-)\text{-}R_3Si^*Cl \xrightarrow[\text{invn}]{\text{LiAlH}_4} (-)\text{-}R_3Si^*H$$

The most straightforward explanation of the results may be that the chlorine-abstraction step (reaction 2) is so fast that the optically active silyl radical can be trapped before racemization by inversion. However, several alternative explanations would be possible for such an unexpectedly highly stereospecific free-radical reaction. We will discuss details in a future publication.

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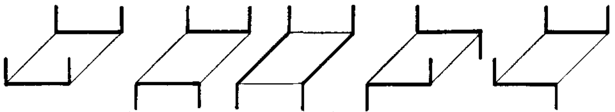
Stereospecific Photochemical Cyclodimerization of 2-Butene in Liquid Phase

Sir:

We wish to report stereospecific photochemical cyclodimerization of liquid 2-butene with retention of geometric configuration in both 2-butene fragments.

The four 1,2,3,4-tetramethylcyclobutane isomers formed can be represented schematically as follows (with the original two 2-butene fragments indicated by heavier lines).



a (cis,cis,cis) b (cis, trans,cis) c (trans,trans,trans) d (cis,cis,trans)

Only two isomers, a and b, can be formed by cyclodimerization of pure *cis*-2-butene with complete retention of configuration. Similarly, only b and c can be formed from pure *trans*-2-butene while the fourth isomer, d, can be formed only from one *cis*- and one *trans*-2-butene molecule. We indeed find that pure *cis*-2-butene gives only a and b, pure *trans*-2-butene gives b and c, while mixtures of *cis*- and *trans*-2- butene give besides a, b, and c, also the fourth isomer, d. These results therefore show that the electronically excited 2-butene molecules, present either free or as excimers, retain their geometric configuration from the time of photon absorption until completion of cyclodimerization, which itself is stereospecific. The greater part of the excited 2-butene molecules are degraded to *cis*- and *trans*-2-butene and (to a small extent) to butene-1. However, free rotation around the original CC double bond does not take place in those excited molecules which cyclodimerize. An alternative explanation in terms of simple steric effects operative in the course of cyclodimerization must be ruled out since it would not predict distinct products, respectively, from *cis*-2-butene, *trans*-2-butene, and the mixture of the two.

Liquid 2-butene was irradiated (usually for about 24 hr) with a Phillips 93107E cadmium lamp or a 93106 E zinc lamp. The former provided the intense cadmium resonance line at 2288 Å and much weaker lines at 2265 and 2144 Å; the latter provided the 2139-Å zinc resonance line. The longer wavelengths from both lamps were not absorbed. Several different types of flat quartz reaction vessels were used either at room temperature (25 ± 2°) or at about −60°. The results were approximately the same at the two temperatures and were also little dependent on whether the cadmium or the zinc lamp was used as the source of radiation.

Three main types of products were observed: (1) cyclodimerization, (2) isomerization, and (3) fragmentation products. Very small amounts of several additional C_8 products were also formed. In an analysis, kindly performed by Mr. M. Bednas using a 150-ft Ucon 550 (polypropylene glycol) column programmed from 40 to 100° at 4°/min, no or only trace amounts of products heavier than butene dimer were found. A typical composition of the products from irradiated *cis*-2-butene, for example, was *trans*-2-butene, 1.000 (taken as unity); 1-butene, 0.040; dimer a, 0.022; dimer b, 0.017; fragmentation products, 0.024. Assuming that the yield of *trans*-2-butene provides an approximate measure of a half of the quanta absorbed, the quantum yield of cyclodimerization is about 0.02–0.03 and of fragmentation about 0.01.

On a squalane capillary column the adjusted retention times ($t - t_0$, with the retention time of CH_4 taken as t_0) relative to *n*-hexane were a, 8.92; b, 4.24; c, 1.67; and d, 3.97. From an empirical relationship between log ($t - t_0$) and the normal boiling points of normal paraffins, the approximate normal boiling points were a, 128°; b, 109°; c, 83°; and d, 107°. The reported[1] boiling points of a and d are 122–122.5 and 106–107°, respectively. The agreement is as good as may be expected since the boiling point–retention time correlation on squalane columns is somewhat dependent on molecular structure.

Mass spectrometric analyses at ionization voltages of 70 eV showed very similar spectra for the four isomers, with the parent ion peak at m/e 112. The most prominent peak is at mass 56, suggesting cyclobutane ring structure readily undergoing symmetrical rupture to give fragment ions of mass equal to half the parent ion.

Nmr measurements in CCl_4 solution with TMS (tetramethylsilane) as reference showed two groups of protons, the methyl group protons at higher field and the protons bound to the ring at lower field and with smaller (approximately one-third) peak area. In the symmetrical a, b, and c isomers, double resonance shows single methyl group and ring proton peaks. The chemical shifts (in parts per million from TMS, with $\delta(CH_3)$ given in each case first) are a, 0.87, 2.4; b, 0.94, 1.9; c, 0.99 (~1.05). In c the ring proton peak is largely overlapped by the larger CH_3 peak and the value in parentheses is approximate. The chemical shifts appear to depend on the number of the vicinal *cis*-oriented CH_3 groups. As this number increases from zero to two, $\delta(CH_3)$ decreases from 0.99 to 0.87 and δ(ring C–H) decreases from 2.4 to about 1. In isomer d, double resonance shows, as expected, three types of CH_3 (δ 0.83, 0.90, and 0.98 ppm) and of ring protons (δ 2.3, 1.8, and, presumably, around 1). The chemical shifts and peak shapes of a and d are quite similar to those of the *cis,cis,cis*- and *cis,cis,trans*-1,2,3,4-tetramethylcyclobutane.[2a]

Infrared spectra of the products a and b were determined in CCl_4 solution. Product a showed absorption bands at 2978 (s), 2925 (s), 2880 (s), 1470 (m), 1455 (m), 1392 (m), 1376 (m), 1335 (w), 1316 (w), 1173 (w), 1141 (w), 1016 (mw), and 1000 (mw) cm^{-1}, in agreement with the reported ir spectrum of *cis,cis,cis*-1,2,3,4-tetramethylcyclobutane.[2] Product b showed bands at 2965 (s), 2920 (s), 2875 (s), 1465 (m), 1457 (m), 1382 (m), and 916 (mw) cm^{-1}, and the spectrum was very similar to the spectrum of *cis,trans,cis*-1,2,3,4-tetramethylcyclobutane communicated by Professor G. W. Griffin.

On the basis of the foregoing evidence, the products a, b, c, and d are identified with *cis,cis,cis*-, *cis,trans,cis*-, *trans,trans,trans*-, and *cis,cis,trans*-1,2,3,4-tetramethylcyclobutane. The isomer c is formed from *trans*-2-butene alone and has the lowest boiling point, as would be expected in view of its very symmetrical structure.

Close proximity of the 2-butene molecules in the liquid phase appears to be an essential prerequisite for the photochemical cyclodimerization. When *cis*-2-butene is diluted by neopentane in a 1:1 ratio, the yield of the dimers is decreased and at a 1:4 ratio it is almost completely suppressed.

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The effect of experimental variables, such as dilution, wavelength, temperature, state of aggregation, etc., is being further investigated and a more detailed discussion of the results will be delayed until this additional information is obtained. It may be mentioned at this time that the observation of the stereospecific photochemical cyclodimerization of 2-butene in the liquid phase may be of considerable interest in connection with the recent spectroscopic and theoretical discussions concerning the low-lying electronic states of olefins.[3] It may also be of importance as the simplest model of photochemical cyclodimerization and in general cycloaddition with cyclobutane ring formation. Cyclobutane ring formation in more complex systems is observed, for example, in the photochemistry of nuclei acids[4] and in the photochemical cycloadditions to steroids.[5] Detailed studies of numerous other photochemical cycloadditions of this type have been made.[6,7] The noteworthy feature of the present case is the retention of the original geometric configuration of both fragments in the cycloadduct although energies in excess of 5 eV are absorbed.

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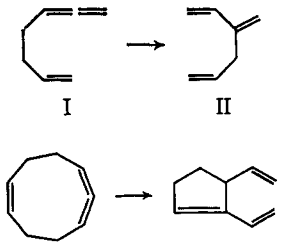
Photosensitized Cope Rearrangements of 1,2,6-Trienes[1]

Sir:

The Cope rearrangement[2] of 1,5-dienes is one of the better known examples of valence isomerization. The unimolecular reaction is relatively insensitive to changes in solvent or to catalysis and consequently occurs with facility in both gas phase and solution. Although the Cope rearrangement is predicted to proceed with thermal and with photochemical activation, only the thermal mode has been thoroughly documented by experiment.[3] Two specific examples of the thermal Cope rearrangement are the isomerizations of 1,2,6-heptatriene (I) and 1,2,6-cyclononatriene (III).[4]


I II

III IV

We have observed that the benzene-sensitized photolysis (2537 Å) of I in the vapor phase[5] gives 3-methylene-1,5-hexadiene (II),[6] identical with the products of pyrolysis. At low intensity and very short irradiation time, II is the only product formed, and a plot of per cent conversion *vs.* time gives a straight line with zero intercept. The quantum yield for the formation of II is 0.24 based on a benzene–*cis*-butene actinometer.[7,8] When II is irradiated under identical conditions several isomeric products are formed; these same compounds appear when the triene I is photolyzed to higher conversion (>0.2%).[9] The photorearrangement is not reversible; the photolysis of II does not yield I. Compound II is formed as a major photoproduct of the direct vacuum ultraviolet photolysis[10] of I along with

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(1) This research was supported by the National Aeronautics and Space Administration.

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(5) All 2537-Å photolyses were done in a cylindrical Vycor cell at ambient temperature (21–23°), with triene/benzene $\approx$ 7, and total pressures of 10–20 torr.

(6) Identification of the photoproducts was made on the basis of retention times and mass spectra, which are identical with those of authentic materials (obtained by the thermal rearrangement of I and III). Retention times relative to benzene: 10% Ucon 50H (50°), 0.87; 15% TCEP (50°), 0.53; 15% squalane (50°), 1.4. The pyrolysis products were identified by their nmr and ir spectra.[4]

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(9) Direct photolysis of II in solution gives a single product, 1-(prop-2-enyl)cyclobut-1-ene: J. L. Charlton, P. deMayo, and L. Skattebøl, *Tetrahedron Letters*, 4679 (1965).

(10) The vacuum ultraviolet lamp and wavelength distribution are described in J. S. Wishnok, Ph.D. Thesis, Brown University, 1968.