November, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3101—3106 (1975) 3101

Vapor-Phase Photolysis of *cis*- and *trans*-4,5-Dimethylcyclohexenes

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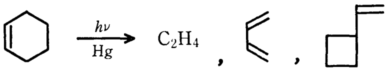
(Received April 12, 1975)

Direct and sensitized photolyses of 4,5-dimethylcyclohexene vapor were investigated using a stereochemical approach at room temperature over the pressure range from 1 to 9 Torr. In the direct photolysis, decomposition of the retro-Diels-Alder type was the main course of the reaction, leading to the formation of 2-butene and 1,3-butadiene with the retention of the original configuration; 3,4-dimethyl-1-methylenecyclopentane was also formed as a minor product from a pressure-independent process. Mercury sensitization, on the other hand, produced *cis*- and *trans*-2-butenes, butadiene, 2,3-dimethyl-1-vinylcyclobutane, and *cis-trans* isomers of the substrate together with radical-induced products, *i.e.*, hydrogen, 1,2-dimethylcyclohexane, and dimeric products. The intermediacy of a "*hot*," "*triplet*" *biradical* was suggested from the pressure-dependence of the *trans*- to *cis*-2-butene ratio in the mercury sensitization. The differences in the results between the direct and sensitized photolyses are interpreted in terms of spin correlation effects.

Few studies have been reported on the direct photolysis of cycloalkenes, although there is some literature on the mercury-sensitized photolysis of this species.[1] Regarding the cyclohexene derivatives dealt with in the present report, Gunning *et al.* have investigated in detail the kinetics of the mercury-sensitized photolysis of cyclohexene itself.[1a] They proposed a biradical



mechanism for the formation of ethylene, butadiene and vinylcyclobutane, which involves an alkyl-allyl biradical produced by the familiar allylic C–C bond cleavage, and the kinetics seem to support this mechanism. De Maré has reported on the mercury-sensitized photolysis of 3-methylcyclohexene vapor *via* a similar reaction mechanism.[2] However, little evidence has been obtained regarding the nature of the intermediate species and the mechanism involved. We have elucidated the reaction mechanism of the vapor-phase photolysis of cycloalkene using a stereochemical approach.

Recently it has been shown that the spin multiplicity of the intermediate 1,4-biradical drastically affects the stereochemistry of the reaction in Norrish type-II photocleavage,[3] as well as in other systems.[4] A study of the direct and sensitized photolyses of *cis*- and *trans*-4,5-dimethylcyclohexenes (**1c** and **1t**) is of interest since the results are expected to provide insight into both the reaction mechanism and the spin correlation effects.

Experimental

Materials. *cis*- and *trans*-4,5-Dimethylcyclohexenes were prepared according to procedures similar to those described by Peter *et al.*[5] *cis*-4,5-Dihydroxymethylcyclohexene, prepared by the reduction of *cis*-cyclohexene-4,5-dicarboxylic anhydride with $LiAlH_4$ in ether, was converted into ditosylate by a reaction with *p*-toluenesulfonyl chloride in dry pyridine. The *cis*-ditosylate was reduced in turn to *cis*-4,5-dimethylcyclohexene by $LiAlH_4$ in ether. The dimethyl ester of *trans*-cyclohexene-4,5-dicarboxylic acid, prepared by a Diels-Alder reaction of dimethyl fumarate with 1,3-butadiene at 200 °C for 3 hr in an autoclave,[6] was reduced to *trans*-4,5-dimethylcyclohexene by similar successive treatments with $LiAlH_4$, *p*-toluenesulfonyl chloride, and again $LiAlH_4$. All the compounds prepared were identifield by means of infrated and NMR spectrometry. *cis*- and *trans*-Dimethylcyclohexenes thus obtained were purified by preparative gas chromatography (gc) on a 6 m polyethylene glycol-6000 column. Quantitative analysis by gc indicated that the purities of **1c** and **1t** are at least 99.9 and 98.0%, respectively. Samples of **1t** contained a small amount (1%) of **1c** as an impurity. A correction was applied to all of the data for the presence of the impurity. The samples of **1c** and **1t** were admitted to a vacuum line, dried over evaporated sodium, and degassed at liquid nitrogen temperature before use.

The NMR spectra of **1c** and **1t** were in good agreement with those reported by Peter *et al.*[5] Their steric configurations were confirmed by the gc comparison of commercially available *cis*- and *trans*-1,2-dimethylcyclohexanes with the saturated compounds obtained from the hydrogenation of **1c** and **1t** on 5% Pd–charcoal.

Apparatus and Procedure. All the experiments were carried out at room temperature and under static conditions. A cylindrical cell, 5 cm long and 5 cm in diameter, made of Suprasil and a mercury-free vacuum system were available for the vapor-phase direct photolysis. The direct irradiation was run using a 30 W low-pressure mercury lamp fitted with a Suprasil envelope, the light path being flushed with nitrogen gas. The mercury-sensitized photolysis was carried out using a quartz cell of similar size, a conventional vacuum system, and the same mercury lamp fitted with a Toshiba UV-25 filter which removes the 1849-Å resonance line of mercury. The lamp was allowed to warm up for at least 30 min before each run in order to reach stable operating conditions. The quantum yields in mercury-sensitization were determined by ethylene (100 Torr) actinometry.[7] The absorption of the incident radiation was incomplete in the cell and appropriate corrections were made in the determination of the quantum yields.

After each run, materials were trapped in a capillary at liquid nitrogen temperature. The noncondensable products were analyzed and measured by a combination of Toepler pump, gas burette, and Pd-chamber. The condensable material was analyzed by gc on a 6 m column of 20% β,β'-oxydipropionitril (ODPN) on 60/80 Celite 545 at 50—70 °C. The stereoisomers of 2-butene were clearly separated from one another under these conditions, while a trace amount of the stereoisomers of **1** could not be separated from one another enough for quantitative analysis, especially in the higher pressure (>3 Torr) experiments. The analyses of the dimeric products from the mercury-sensitization were conducted by gc on a 3 m column of polyethylene glycol-6000 on Celite at 150 °C and a 1.5 m column of FFAP on Celite at 150 °C. The molecular weights of the dimers were confirmed using a Hitachi RMS-4 gc-mass spectrometer.

Identification of 2,3-Dimethyl-1-vinylcyclobutane (3). Mercury sensitization of **1c** was carried out on a prepatative scale using the mercury lamp and an apparatus composed of a 5 l Pyrex vessel, two 100 ml quartz cells for irradiation, and a thermosiphon for circulation of the gas. The irradiation of **1c** with 10% nitric oxide in the presence of mercury was run at 1 Torr for 15 hr. The photolyzed sample was trapped at liquid nitrogen temperature and then subjected to preparative gc in order to isolate **3**. The NMR spectrum of **3** was obtained with TMS as an internal standard in CCl_4 and showed three vinyl protons at δ 5.5—6.0(m), 4.9(d), and 4.95(d), six methyl protons at 1.0(d), and five cyclobutyl protons at 1.2—2.2(m). The mass spectrum indicated the following relative intensities: *m/e*, 110(2.1), 95(28.3), 81(40.5), 69(45.5), 68(67.8), 67(70.7), 56(35.1), 55(100), and 54(6.4). These spectral data indicate a 2,3-dimethylvinylcyclobutane structure of **3**, but its steric configuration is not known. The mercury sensitization of **1t** also produced a compound which has the same retention time on the gc and an identical mass spectrum with that of **3**. Consequently, it is considered that the mercury sensitization of both **1c** and **1t** produced dimethylvinylcyclobutane **3** with an identical steric configuration.

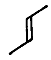
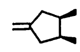
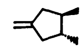
Identification of 3,4-Dimethyl-1-methylenecyclopentane (2). Eighty mg of **1c** in a sealed Suprasil tube, 2 mm in diameter, was photolyzed in the liquid phase without a solvent using a 30 W low-pressure mercury lamp. The irradiation was continued for 350 hr resulting in a conversion of *ca.* 10% and the photolyzed sample was subjected to preparative gc to isolate **2c**. The NMR spectrum of **2c** was obtained with TMS in CCl_4, and showed two olefinic protons at δ 3.5(s), six methyl protons at 0.86(d), and six other protons at 1.8—2.4(m). The mass spectrum of **2c** indicated the following relative intensities: *m/e*, 110(26.9), 95(100), 81(32.6), 69(20.0), 68(32.3), 67(60.0), 55(47.7), and 54(26.2). The gc analysis on an ODPN column indicated that the isolated C_8H_{14} isomer has a shorter retention time relative to those of the authentic samples of *cis*-3,4-*trans*-4,5-, *cis*-4,5-, 2,3-, 1,2-dimethylcyclohexenes and 2-methyl-1-methylenecyclohexane, and that the retention time of the saturated compound, prepared by hydrogenation of **2c** on Pd–charcoal, is different from that of *trans*- or *cis*-1,2-dimethylcyclohexane. All the data described above suggest a 3,4-dimethyl-1-methylenecyclopentane structure for **2c**, the steric configuration of which is deduced to be *cis* from that of the starting material(**1c**).

Vapor-phase direct photolysis of **1c** produced the same C_8H_{14} compound (**2c**), the mass spectrometric, gas chromatographic, and chemical (hydrogenation) features of which were identical with those of the **2c** obtained in the liquid-phase photolysis of **1c**. Vapor-phase photolysis of **1t** afforded another C_8H_{14} isomer (**2t**), which has a shorter retention time on ODPN relative to that of **2c**. The mass spectrum of **2t** indicated: *m/e*, 110(33.0), 95(100), 81(41.7), 69(33.0), 68 (46.1), 67(60.0), and 55(54.8). The structure of **2t** was identified to be *trans*-3,4-dimethyl-1-methylenecyclopentane on the basis of resemblance of the mass spectra.

Results

Direct Photolysis. As major decomposition products, 2-butene and 1,3-butadiene were obtained together with a minor isomeric product, 3,4-dimethyl-1-methylenecyclopentane (**2**), in the direct photolysis of **1c** and **1t** at a substrate pressure of 5 Torr, as shown in Table 1. Dimeric products and a vinylcycloalkane derivative, which are usually produced in the mercury-sensitized photolysis of cycloalkenes,[1] were not detected in significant yields. The total yield of 2-butenes was equal to that of butadiene. The photolysis of **1c** and **1t** at 5 Torr gave almost selectively *cis*- and *trans*-2-butenes at *cis-trans* ratios of 16: 1 and 1: 20, respectively. Irradiation of **1** through a UV-25 filter did not result in any products under comparable conditions.

Table 1. Products of direct photolysis of **1**

Compd	Press, Torr	Exposure time, min	Products, μmol × 10^3				
							
1c	5.0	1.0	53.8	3.4	61.7	5.1	a)
1t	5.0	1.0	2.8	57.0	61.7	a)	6.1

a) Not detected.

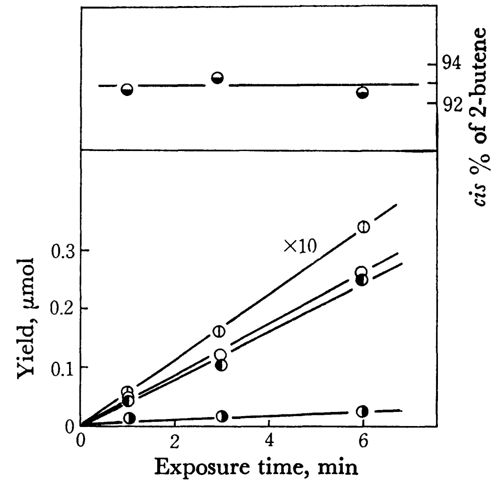


Fig. 1. Product yields as a function of exposure time in direct photolysis of **1c** (8 Torr). ◐, *cis*-2-butene; ◑, *trans*-2-butene; ○, 1,3-butadiene; ⦶, *cis*-3,4-dimethyl-1-methylenecyclopentane (×10); ⊖, *cis* % of 2-butene.

The effects of exposure time on the product yields were examined in the photolysis of **1c** at a pressure of 8 Torr, since the further irradiation of initially formed 2-butene could produce isomeric 2-butene.[8] According to the data appearing in Fig. 1, all the yields increase linearly with exposure time, which indicates that these are the products from the primary process. The percentage of *cis*-2-butene, on the other hand was constant over the range of 1—6 min, and therefore, the isomeric 2-butene cannot result from the further photoisomerization. Direct photolysis of **1c** was performed over the pressure range of 1—8 Torr. The results are shown in Fig. 2. Although the pressure range was limited by the low vapor pressure of the substrate, the suppressing effect of pressure on the formation of butene and butadiene is evident from the data. The percentage of *cis*-2-butene was independent of the pressure, in spite of the decrease in the yields with increasing pressure. The yield of **2c** remained constant over the entire pressure range.

Mercury-sensitized Photolysis. The products of the mercury sensitization were hydrogen, 2-butene,

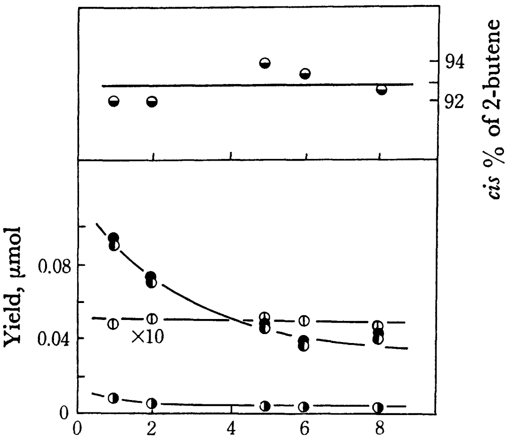


Fig. 2. Product yields as a function of initial substrate pressure in direct photolysis of **1c**. Exposure time is 1 min. ◐, *cis*-2-butene; ◑, *trans*-2-butene; ●, 1,3-butadiene; ⦶, *cis*-3,4-dimethyl-1-methylenecyclopentane (×10); ⊖, *cis* % of 2-butene.

1,3-butadiene, 2,3-dimethylvinylcyclobutane (**3**), 1,2-dimethylcyclohexanes, and some dimeric products. The gas chromatographic and mass spectrometric analyses of the dimeric products showed that the dimeric fraction is composed of at least five compounds, the molecular weights of which are in the range of 218—222. The mass spectra of the dimers appears to suggest the absence of cyclodimers of **1**. On the basis of these results and observations in other systems,[1] the dimeric products were assumed to have a bicyclohexyl, cyclohexylcyclohexene, or bicyclohexenyl skeleton. The quantum yields of all products except the dimers are shown in Table 2. The distribution of the products from shorter exposure time (1 min) experiments is in good agreement with this result. The total yield of the 2-butenes equals that of butadiene. The 2-butene resulting from the mercury sensitization was predominantly *trans* even when **1c** was used. In addition, the photolysis of both **1c** and **1t** produced dimethylvinylcyclobutane having the same steric configuration as the major product.

A pressure-dependent study was also carried out for the mercury sensitization of **1c** and **1t**. In order to further examine the pressure effects, a higher pressure experiment was also performed above vapor pressure limit of the substrate using **1c** (3 Torr) with xenon added (112 Torr). The results are plotted in Figs. 3 and 4. While the suppressing effect of the pressure on the yields of 2-butene, butadiene, and **3** is evident, the 1,2-dimethylcyclohexane yields show no pressure dependence above *ca.* 5 Torr in the photolysis of both **1c** and **1t**.

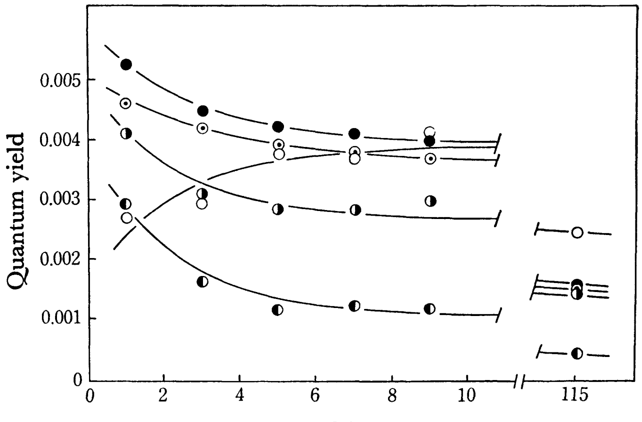


Fig. 3. Product yields as a function of pressure in mercury-sensitized photolysis of **1c**. Exposure time is 3 min. Plots at a pressure of 115 Torr were obtained by adding xenon (112 Torr) to **1c** (3 Torr). ◐, *cis*-2-butene; ◑, *trans*-2-butene; ●, 1,3-butadiene; ⊙, 2,3-dimethyl-1-vinylcyclobutane; ○, *cis*-1,2-dimethyl cyclohexane.

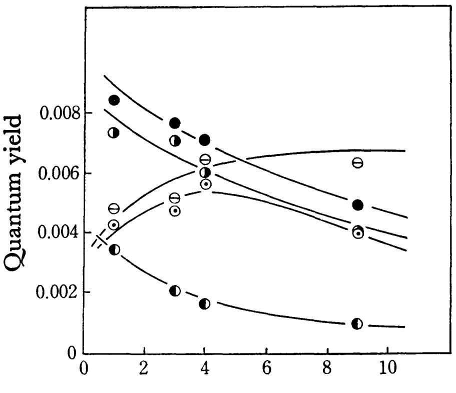
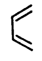
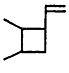
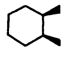
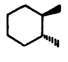


Fig. 4. Product yields as a function of substrate pressure in mercury-sensitized photolysis of **1t**. Exposure time is 3 min. ◐, *cis*-2-butene; ◑, *trans*-2-butene; ●, 1,3-butadiene; ⊙, 2,3-dimethyl-1-vinylcyclobutane; ⊖, *trans*-1,2-dimethylcyclohexane.

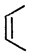
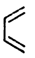
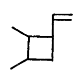
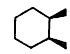
An inhibiting experiment was performed with a small amount of nitric oxide added since radical-initiated reactions caused by excited mercury atoms are well-known in the mercury sensitization of hydrocarbons.[9] As can be seen from Table 3, the formation of 1,2-dimethylcyclohexane and the dimeric products were completely suppressed by the addition of nitric oxide which acts as a radical scavenger, while the yields of the other products merely decreased to a small extent.

Table 2. Products of mercury-sensitized photolysis of 1

Compd	Press, Torr	Exposure time, min	Products, $\Phi \times 10^3$						
									H_2
1c	9.0	3.0	1.2	3.0	4.0	3.7	3.7	a)	27.2
1t	9.0	3.0	0.6	3.0	3.7	3.0	a)	4.8	b)

a) Not detected. b) Not determined.

TABLE 3. EFFECTS OF NITRIC OXIDE ON MERCURY-SENSITIZED PHOTOLYSIS OF **1**

Press, Torr		Exposure time, min	Products, μmol × 10^3					
1c	NO							Dimers
5.0	0	3.0	4.0	9.7	14.4	13.4	12.9	138
5.0	0.5	3.0	5.5	7.5	9.0	10.0	a)	a)

a) Not detected.

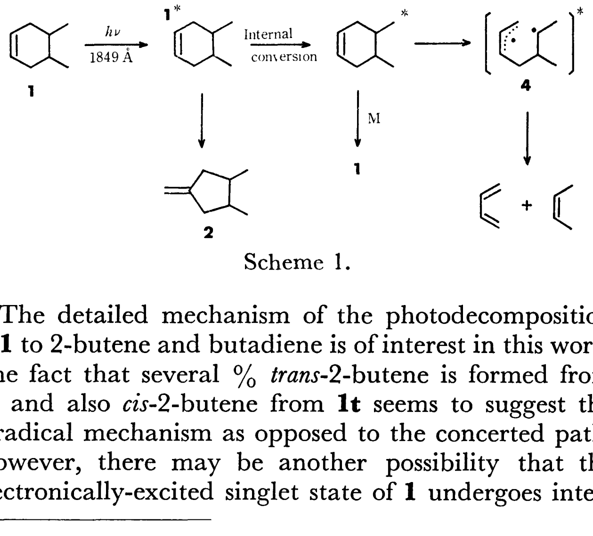
In other experiments, it was observed qualitatively that (i) the sensitized decomposition of **1c** (5 Torr) at 2537 Å in the vapor phase with benzene vapor (5 Torr) as a sensitizer did not produce detectable amounts of any products and (ii) irradiation at 1849 Å of **1c** in the liquid phase with no solvent produced no detectable yields of 2-butene, butadiene, or **3**. The only detectable products were saturated *cis*-1,2-dimethylcyclohexane and isomerized *cis*-3,4-dimethyl-1-methylenecyclopentane (**2c**).

Over the temperature range of 400—700 °C, pyrolyses of **1c** and **1t** were conducted using a Shimadzu PYR-2A pyrolyzer-gas chromatograph. The products of the pyrolysis were merely decomposition products of lower molecular weight, and no 2-butene, butadiene or isomeric product was detected in significant amounts.

Discussion

Decomposition of the retro-Diels-Alder type appears to be the main course of the direct photolysis of **1** in the vapor phase, which results in the stereospecific formation of 2-butene together with an equimolar amount of butadiene. No detectable amounts of 2-butene and butadiene were formed in the direct photolysis of **1** in the liquid phase. Irradiation through a UV-25 filter produced no products in the direct photolysis of **1** in the vapor phase. From these results and the stereospecificity of the reaction, it is inferred that **1** is promoted to an electronically excited singlet state principally by the 1849 Å resonance line of mercury and then decomposes directly or *via* a short-lived biradical produced by an allylic C–C bond cleavage into 2-butene and butadiene with the retention of its original configuration. It is, however, difficult to determine if these are direct products from the electronically-excited states or if significant amounts are formed as a result of decomposition after internal conversion to a vibrationally-excited ground state.

The most significant observation in the direct photolysis of **1c** is the effect of pressure, resulting in a decrease in the yields of the decomposition products with increasing pressure, whereas the yield of *cis*-3,4-dimethyl-1-methylenecyclopentane (**2c**) remains constant. The **2c** observed is, therefore, considered to be formed in a pressure-independent process,* probably from an electronically-excited singlet state which has a lifetime short compared to the effective time between deactivating collisions even at higher pressures. On the other hand, the high pressure dependence of the yields of the other decomposition products suggests that these are the products from a vibrationally-excited ground state, since with molecules of this size, the lifetimes should be long enough to permit collisional deactivation of any energetic ground-state species which might be formed *via* an internal conversion process. This elucidation is also supported by the observation that only **2c** is formed in the liquid-phase photolysis of **1c**, in which vibrational energy is quickly removed. Although 2-butene and butadiene were not detected in the attempted pyrolysis of **1** at 400—700 °C, the vibrationally-excited ground state species as the intermediate in direct photolysis cannot be eliminated from this result since raising the temperature from room temperature to 700 °C is considered to involve very little energy difference relative to the large energy input of the direct photolysis.



Scheme 1.

The detailed mechanism of the photodecomposition of **1** to 2-butene and butadiene is of interest in this work. The fact that several % *trans*-2-butene is formed from **1c** and also *cis*-2-butene from **1t** seems to suggest the biradical mechanism as opposed to the concerted path. However, there may be another possibility that the electronically-excited singlet state of **1** undergoes inter-

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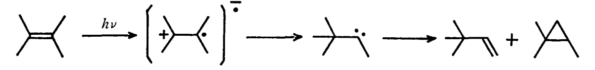
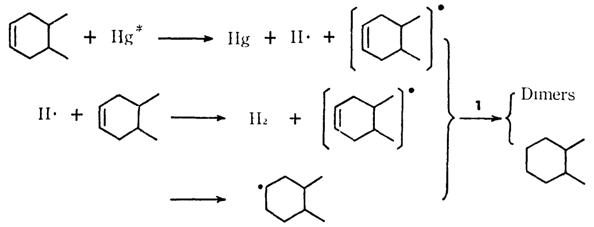
* The formation mechanism of **2** is of interest. Fields and Kropp have reported that only tetrasubstituted alkenes undergo photorearrangement of the alkyl group *via* π,R(3*s*) Rydberg excited states on direct irradiation in a pentane solution; T. R. Fields and P. J. Kropp, *J. Amer. Chem. Soc.*, **96**, 7759 (1974).



In the present system, although the nature of the electronically-excited state involved is uncertain, the disubstituted alkene **1** seems to undergo a similar photorearrangement producing **2** upon direct irradiation in both the liquid and vapor phases. We have also observed photoisomerization of cycloheptene to carbene-derived products, *i.e.*, methylenecyclohexane and norcarane, on direct photolysis in the liquid phase. The detailed mechanism and the nature of the intermediate of these rearrangements are under investigation and will be the subject of a separate report.

system crossing in part to a triplet species, which would give nonstereospecific 2-butene in a manner similar to the sensitized photolysis described below. Although such a process is important in the photolysis of aromatic and carbonyl compounds,[10)] it is believed that the large difference in energy causes singlet-triplet intersystem crossing to be very slow in such a monoolefin. The absence of the vinylcyclobutane **3** in the direct photolysis of **1** also indicates the low efficiency of the intersystem crossing since photoisomerization to **3** is characteristic of triplet species as shown in the mercury sensitization of **1**. It is therefore concluded that the photodecomposition of **1** proceeds *via* the short-lived singlet biradical **4**.

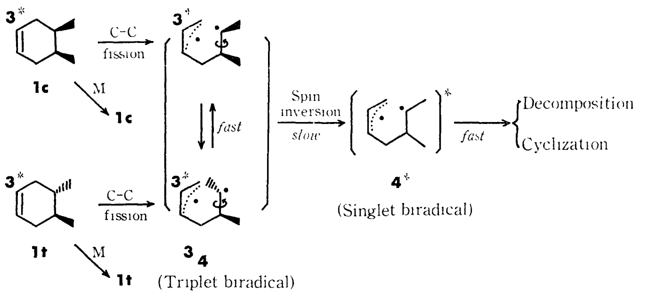
In mercury sensitization, 2,3-dimethyl-1-vinylcyclobutane **3**, the *cis-trans* isomers of **1**, and the radical-induced products were obtained in addition to the decomposition products, as shown in Table 2. Since the formation of 1,2-dimethylcyclohexane and the dimeric products was completely suppressed by the radical scavenger NO, these products, and probably hydrogen, are considered to be formed from the well-known hydrogen abstraction reaction initiated by the excited mercury atom.[1a,9)] The mechanism for the formation of hydrogen, 1,2-dimethylcyclohexane and the dimers is deduced to be as follows:



Scheme 2.

In contrast to direct photolysis, the 2-butene resulting from the mercury sensitization of **1** is predominantly *trans* even when **1c** was used. Furthermore, the mercury sensitizations of both **1c** and **1t** produced 2,3-dimethylvinylcyclobutane having the same steric configuration as a major product, and in addition the isomerization of **1c** to **1t** was confirmed at low pressure. On the basis of these results and the generally accepted view of mercury photosensitization of olefins,[1,9,11)] it is suggested that the vibrationally-excited triplet state of **1**, produced by energy transfer from the excited mercury atom, undergoes the usual allylic C–C bond fission resulting in an allylic triplet biradical **4**, where rotation about the C–C bond adjacent to the alkyl radical site is possible. Then the biradical ^{3}**4** decomposes into *cis*- and *trans*-2-butenes with an equimolar amount of butadiene, and/or combines to **1** or **3**.

Spin inversion is required in order for the triplet biradical ^{3}**4** to undergo decomposition and/or ring closure. Although the present intermediate is an alkyl-allyl biradical, ring closure of the photolytically derived singlet 1,4-biradical has been shown to be fast relative to the time required for free rotation about the C–C bonds.[12)] If the same is true in this system, equilibrium will be established among triplet, not singlet, biradical rotamers. The rate-determining step in the sensitized photolysis may, therefore, be the spin inversion of the triplet biradical.



Scheme 3.

As for benzene photosensitization in the vapor phase, it has been shown by Schmidt and Lee[13)] that energy transfer from the benzene triplet to olefins is fast enough to produce olefin triplets in most cases. It is therefore noted that the triplet state of **1** produced in benzene sensitization resulted in no photoproducts. The difference between the benzene- and mercury-sensitizations can be attributed to the triplet energy of the sensitizers, 84 and 113 kcal/mol, respectively. The triplet state of **1** produced by mercury sensitization is considered to have a larger vibrational energy by *ca.* 30 kcal/mol than that produced by benzene sensitization. Consequently, the excess vibrational energy is suggested to play a singificant role in the triplet reaction.

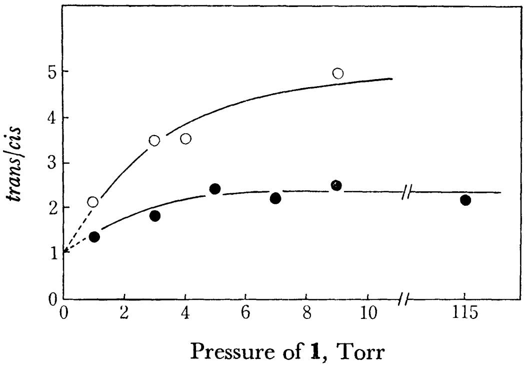
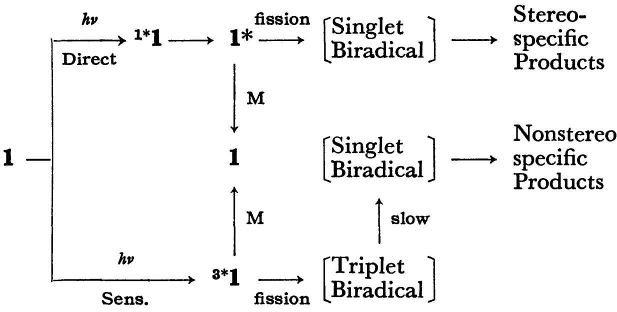


Fig. 5. Pressure dependence of *trans-cis* ratio of 2-butene in mercury-sensitized photolysis of **1c** (●) and **1t** (○). Plot at a pressure of 115 Torr was obtained by adding xenon (112 Torr) to **1c** (3 Torr).

The *trans-cis* ratio of 2-butene in the mercury sensitization of **1** was found to depend on the substrate pressure as shown in Fig. 5. Regardless of which isomer is used, the value of the *trans-cis* ratio seems to approach unity at 0 Torr, while it increases with increasing pressure. The higher pressure experiment with xenon added showed that, although the *trans-cis* ratio decreases considerably at lower pressure (<3 Torr), the ratio is constant from 5 to 115 Torr in the mercury sensitization of **1c**. An explanation of the results may be found in the vibrational energy of the triplet biradical **4**, this alkyl-allyl biradical being a novel instance of a "hot," "triplet" biradical produced in the vapor phase, although a hot, triplet biradical of the alkyl-thiyl type has recently been reported by Dice and Steer.[14)] The biradical **4** formed from **1t** is considered to have a lower vibrational energy than that formed from **1c** by an amount equal to the difference in the stabilities ($\triangle H_f$) of the two isomers, **1t** and **1c**. In the absence of deactivating collisions, the hot, triplet biradical **4** has a large amount of excess vibrational energy, which renders insignificant the slight differences in stabilities, and therefore, the *trans-cis* ratio approaches unity in the sensitized photolysis of both **1c** and **1t**. At higher pressures, the difference between the energies of **4** resulting from **1c** and **1t** has a considerable influence on the value of the *trans-cis* ratio. Because of the lower vibrational energy, the biradical formed from **1t** produces much more *trans*-2-butene than that from **1c** at a comparable pressure. These estimations appear to explain the present results reasonably well, and also suggest that the lifetime of the biradical **4** is not long enough to be deactivated by collisions because the *trans-cis* ratio from **4** is different at higher pressures.



Scheme 4.

The excess energy in the direct photolysis is larger by *ca.* 40 kcal/mol than that in the mercury sensitization, which in itself may account for the different reactivities between the direct and sensitized photolyses, since with increasing excess energy the lifetime of the intermediates should decrease favoring decomposition over rearrangement. If this is the case, it is expected that the stereospecificity of butene-formation in direct photolysis must decrease with increasing pressure, since collisional deactivations diminish the excess energy of the intermediates to give nonstereospecific 2-butene. However, the *trans-cis* ratio of 2-butene in the direct photolysis is not affected by increasing the pressure in spite of the considerable decreases in yield (see Fig. 2). The rate-determining step of the direct photolysis may be the allylic C–C bond cleavage. The different results for the direct and sensitized photolyses are, therefore, attributed to the difference in the spin states of the intermediates.

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