Excited State and Cyclobutadiene Intermediates in the Radiation Chemistry of Alkynes. γ Radiolysis of 2-Butyne

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Abstract: γ radiolysis of liquid 2-butyne gives rise to 3-methyl-2-hepten-5-yne, 2,6-octadiyne, *cis*- and *trans*-2-butene, hexamethylbenzene, and *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene as major products. These products account for approximately 72% of the reacted alkyne. The first four products arise from radicals; scavenging experiments suggest that either ions or excited states (or both) could be immediate precursors to the "radical products." These four products are formed also in the photolysis of 2-butyne with a low-pressure mercury lamp. The latter two products of radiolysis, hexamethylbenzene and the tricyclooctadiene, appear to arise from a cyclobutadiene precursor. Formation of the cyclobutadiene precursor can be suppressed by scavengers only at very high scavenger concentration.

Recent evidence indicates that excited states are frequently important intermediates in the radiation chemistry of organic liquids possessing bound excited states.[2-12] Correlations between photochemistry and high-energy radiation chemistry have been observed for aromatic hydrocarbons[2-6] and carbonyl compounds[7-9] as well as for olefins and dienes.[10-12] In at least two important respects the use of γ radiolysis as a means of producing excited states offers conceivable advantages over ultraviolet irradiation. First, most of the initial excitation is delivered to the solvent so that even molecules with very weak transitions can be activated in the presence of strongly absorbing solutes. Secondly, energy from ionizing radiation is deposited in spurs or tracks where reactive intermediates are formed close enough together so that there is some probability that the intermediates will react with each other.[13,14] These advantages are offset to some extent by the fact that radiolysis produces several reactive species, including positive and negative ions as well as radicals in addition to electronically excited states. The relative importance of the different intermediates has been determined for relatively few systems and paths for interconversion of reactive intermediates are the subject of much investigation.

A particularly attractive class of compounds for investigation appeared to be the simple dialkylacetylenes. These compounds absorb light at *ca.* 2300 Å[15] near the edge of the readily accessible ultraviolet. An extended photochemical study of these compounds is complicated by the fact that any unsaturated products would absorb strongly; further reaction of the products and attenuation of the primary process would then hinder systematic investigation. Relatively little is known about excited states of simple alkynes. Acetylene itself and methylacetylene undergo polymerization and formation of benzene upon either photolysis or radiolysis.[15-18] Perfluoro-2-butyne has recently been reported to add to benzene and other aromatic hydrocarbons photochemically.[19] It has been suggested[17,18] that the acetylene triplet is involved in the radiation-induced formation of benzene. Spectroscopic studies[20] in the gas phase indicate that the lowest excited states of acetylene and related derivatives are nonlinear and can exist in one of two bent forms in which each acetylenic carbon is sp^2 hybridized. That such a bent excited state might be a favored relaxed form in solution seems reasonable since the energy input required for rehybridization is offset by relief of antibonding interactions present in the linear form.[21] Higher excited states of acetylene such as the first Rydberg transition at 1520 Å appear to be linear.[22] Diradical species could be implicated in the photoreduction of conjugated diacetylenes in the presence of saturated hydrocarbons[23] or in the photocyclization of 2,2′-di(phenethynyl)biphenyl.[24]

Conjugated acetylenes such as phenylacetylene and diphenylacetylene absorb in the accessible ultraviolet. Their photolysis leads to the formation of adducts with aromatic compounds as well as to dimerization to naphthalenes and azulenes.[25-27] Although diradical

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intermediates could be involved, it has been suggested[27] that substituted cyclobutadienes may be the initial photoproducts.

In the present paper we report a study of the γ radiolysis of 2-butyne, the simplest dialkylacetylene, in the liquid phase. We have identified the major products of the radiolysis and attempted to identify their precursors by scavenging experiments. Comparison of the photochemical behavior of 2-butyne with its radiolysis suggest that several of the radiolysis products may arise, at least in part, from excited states.

Experimental Section

Materials. 2-Butyne (Farchan Research Laboratory, Willoughby, Ohio) was 99% pure and was used as received. Benzene (B and A Reagent Grade) was stirred over concentrated acid for several days, washed with sodium bicarbonate and then several times with water, dried over anhydrous magnesium sulfate, and then distilled through a column. The middle cut was retained. Carbon tetrachloride and 2-propanol (Matheson Coleman and Bell, 99%) were used as received. Hexamethyl(Dewar benzene) was prepared by the method of Schäfer.[28]

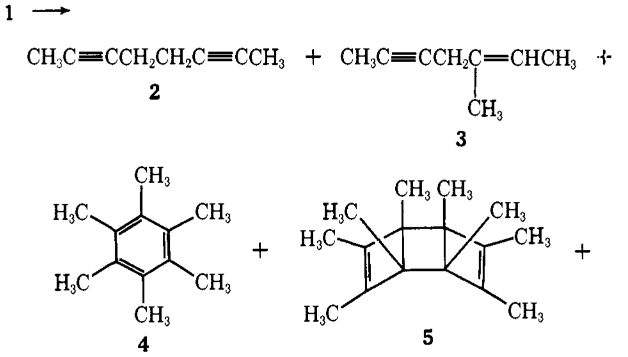
Preparation and Irradiation of Samples. Samples for radiolysis were degassed by three freeze–pump–thaw cycles and sealed in 13-mm diameter Pyrex ampoules. A ^{137}Cs source was used for the radiolysis studies. The γ radiation absorbed dose rate was *ca.* 1.1×10^{19} eV ml^{-1} hr^{-1} corrected for the electron density of 2-butyne. The water-cooled irradiation cavity temperature was 28 ± 2°. The Fricke dosimeter was used to calibrate the source. Photochemical reactions were carried out in similarly degassed samples sealed in quartz tubes. A Hanovia low-pressure mercury lamp was used without external filters. The samples were maintained at 25 ± 2° throughout the irradiation.

Product Identification. Up to 12 tubes of 2-butyne (4 ml each) were irradiated for 160 hr as previously described. The yellow oil remaining after evaporation of the 2-butyne was separated into its components by preparative gas chromatography on a $^1/_4$ in. × 10 ft Chromasorb G column coated with 10% SE-30. 2,6-Octadiyne (**2**) was identified by its nmr spectrum (complex multiplet at τ 7.67 (2 H) and 8.20 (3 H) in $CDCl_3$), its mass spectrum (*m/e* 106), and its mp, 27° (lit.[29] 27°). 3-Methyl-2-hepten-5-yne (isomer not determined) (**3**) was identified by its nmr spectrum (quartet at τ 5.2 (1 H, J = 3 cps), quartet at 7.1 (2 H, J = 2.5 cps), and complex multiplet at 8.2 (9, H, in $CDCl_3$)), and its mass spectrum (*m/e* 108). Hexamethylbenzene (**4**) could be recovered by recrystallization from the crude product mixture or by preparative vpc. Its identity was established by comparison with an authentic sample. *syn*-Octamethyltricyclo[4.2.0.0^{2,5}]octadiene (**5**) was identified by its nmr spectrum (τ 8.6 (12 H) and 9.0 (12 H) in CCl_4), the characteristic C=C valence frequency at 5.94 μ in the ir (CCl_4), and its mass spectrum (*m/e* 216) in agreement with reported values.[30,31]

Analysis. After irradiation, the sample tube was opened, the butyne was evaporated, and the residue was mixed with a benzene solution of an internal standard (tetralin). The sample was analyzed by vpc on a $^1/_8$ in. × 8 ft stainless steel column packed with 5% SE-30 on Chromasorb G. A flame-ionization type detector was used to analyze the products which were separated by temperature programming over a range 60–180°. To avoid isomerization of hexamethyl(Dewar benzene), the injection port temperature was kept at 190°.

Results

γ radiolysis of degassed solutions of pure 2-butyne (**1**) leads to the production of several monomeric, dimeric, trimeric, and tetrameric products as well as to very small amounts of polymer. The dimeric through tetrameric products are conveniently separated by vpc; analysis reveals that four products comprise over 64% of the 42 products detected by chromatography over the temperature range 60–250°. The four products were isolated by preparative vpc and identified by spectral techniques. The major products of γ radiolysis of **1** are summarized in eq 1.[32,33] G values for the prod-



$$1 \longrightarrow \underset{2}{CH_3C\equiv CCH_2CH_2C\equiv CCH_3} + \underset{3}{CH_3C\equiv CCH_2\underset{CH_3}{\underset{|}{C}}=CHCH_3} +$$

cis- and trans-2-butene (**6**) (1)

ucts analyzed in this study are: 2,6-octadiyne (**2**), G = 0.63 ± 0.09; 3-methyl-2-hepten-5-yne (**3**), G = 0.23;[34] hexamethylbenzene (**4**), G = 0.23 ± 0.04; and *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene (**5**), G = 0.22 ± 0.04. The G value for disappearance of 2-butyne is approximately 7, including the small amount of polymeric material ($G_{-C_4H_6} \sim 0.34$) but not including decomposition to very light gases (H_2, CH_4, etc.), so that products **2–6** account for approximately 72% of the reacted alkyne. The yields of **2**, **4**, and **5** were independent of dose over the range $2\text{–}13 \times 10^{20}$ eV/ml and therefore appear to be initial products of radiolysis of **1**.[35]

Effects of Additives. Table I summarizes the effects of several additives on the yields of **2**, **4**, and **5**. Although product **3** is not included in the table, its yield was always directly proportional to the yield of **2**, except for the studies with 2-propanol where the 3:2 ratio increased with increasing 2-propanol concentration. 2-Propanol, which has been used in previous studies as a cation quencher,[10,12,36] had little effect on the yield of products **4** and **5** at moderate concentrations. At very high concentrations of 2-propanol (1–3 M) some quenching of **5** and enhancement of **4** were observed. The yields of **2** and **3** increased slightly in the presence of 2-propanol; this can probably be attributed to the ease of hydrogen atom abstraction from 2-propanol.[36] Carbon tetrachloride, which has been frequently used to scavenge electrons in radiolysis studies,[10,12,37] did not quench production of **2** and **3**. Low concentrations of CCl_4 produced little changes in the yield of any of the products. At higher CCl_4 concentrations the yield of the tricyclooctadiene **5** decreased while the yield of **4** increased.

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(31) H. M. Rosenberg and E. C. Eimutis, *Can. J. Chem.*, 45, 2263 (1967).

(32) We did not analyze for monomeric products. A previous investigation[33] reports G_{butenes} = 1.75 and $G_{1,2\text{-butadiene}}$ = 0.23.

(33) R. E. Rondeau, L. A. Harrah, T. D. Nevitt, H. H. Barber, Jr., and R. Schaffer, Air Force Technical Report AFML-TR-64-353, 1964.

(34) Inclusion of a minor component, very likely a geometric isomer of **3**, would raise this value to 0.29.

(35) Although quantitative analysis of shorter irradiated samples was not possible, product ratios appeared to be the same and no additional products were detected.

(36) J. W. Buchman and F. Williams, *J. Chem. Phys.*, **44**, 437 (1966). These authors indicate that quenching involves proton transfer to alcohols. Such reaction would yield the precursor to **2** so it is difficult to predict the effect of alcohols on G_2 and G_3.

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Table I. Summary of the Effect of Additives on the Yield of Selected Products of γ Radiolysis of 2-Butyne

Additive	IP,[a] eV	M	**2**	**4**	**5**
None			0.63	0.23	0.22
CCl_4	11.48	0.5	0.73	0.39	0.10
2-Propanol	10.15–10.41	0.6	0.76	0.21	0.21
Oxygen	12.07	1.04 atm	0.64	0.41	0.04
1,3-Cyclohexadiene	8.4	0.5	0.06	0.17	0.17
		1.0	0.08	0.11	0.12
Benzophenone	9.35–9.46	0.5	0.36	0.47	0.6
		1.0	0.16	0.49	0.9
Acetone	9.68	1.0	0.62	0.32	0.27
Iodine		0.12	0.02	0.57	0.01
Benzene	9.24	0.3	0.73	0.23	0.22
Hexamethyl(Dewar benzene)[b]		0.24	Not anal.	22.31	0.19
trans-Stilbene		0.03	0.66	0.39	0.23
Azulene	7.4	0.003	0.58	0.22	0.16
		0.025	0.13	0.34	0.19
		0.25	0.03	0.10	0.03

[a] Ionization potentials from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **26** (1969). [b] Hexamethyl(Dewar benzene) could not be detected as a product of radiolysis of 2-butyne. Our limit of detection would be a G value 0.01–0.02.

Hexamethyl(Dewar benzene) (**7**), which had been anticipated as a possible product of 2-butyne radiolysis, was found to decompose rapidly under radiolysis in dilute 2-butyne solution (Table I). Conversion of **7** exclusively and quantitatively to **4** was observed; G_7 was found sufficiently high (18–22) at low concentrations of **7** to ensure that any **7** produced in radiolysis of **1** could not be detected but would be isolated as **4**.

Moderate concentrations of additives possessing low-lying bound excited states such as azulene, 1,3-cyclohexadiene, biacetyl, benzophenone, and *trans*-stilbene generally quenched products **2** and **3** to a considerable extent (Table I). A plot of G_0/G for **2** *vs.* [azulene] is linear with a slope of 200 l. M^{-1}. Acetone did not quench formation of **2**; however, ultraviolet irradiation of acetone ($\lambda > 2800$ Å) (*vide infra*) in the presence of 2-butyne leads to formation of **2** and **3**. Surprisingly, benzene appeared to produce little effect on any of the radiolysis products up to 0.3 M benzene. In general, these scavengers affected the yield of products **4** and **5** relatively little at low concentrations. At higher quencher concentrations diverse results were obtained. High concentrations of azulene quenched all products; **4** was the least quenched under these conditions. High concentrations of 1,3-cyclohexadiene quenched all products but the ratio $G_4:G_5$ remained approximately the same. Benzophenone and acetone increased both G_4 and G_5; for benzophenone there was a substantial increase in the ratio $G_5:G_4$. Biacetyl appeared to quench **5** and increase the yield of **4** but several new products were observed, even on short-term irradiation, so that the primary effect of biacetyl could not be assessed with certainty.

Iodine quenched products **2** and **5** but increased the yield of **4**. Irradiation of **1** in an atmosphere of oxygen led to an increase in G_4 and a decrease in G_5.

Sensitization of Stilbene Isomerization. In previous work, sensitized isomerization of olefins such as stilbene has been used to assess the importance of scavengeable excited states of the solvent in radiolysis.[2,4,6,7] Since singlet and triplet energies of alkynes (*ca.* 130 and 105[38] kcal/mol, respectively) are considerably above those of stilbene (*ca.* 88 and 50–57[40] kcal/mol, respectively), energy transfer from excited alkyne to stilbene would be expected to be a favored process. Irradiation of dilute solutions of *cis*- and *trans*-stilbene in **1** did lead to isomerization of the stilbenes. Table II compares G_{t-c} for stilbene in **1**, pentane, and benzene. G_{t-c} was much lower in **1** than in benzene[4] or naphthalene,[2] where isomerization proceeds *via* energy transfer from solvent-excited states, or in cyclohexane[6] or pentane where charge neutralization presumably leads to excited states. The trans-rich radiostationary state suggests that considerable isomerization occurs by paths not involving excited states. The low value of G_{t-c} indicates that the yield of long-lived scavengeable excited states of **1** is small.

Table II. γ Radiation Induced Isomerization of *trans*-Stilbene in Hydrocarbons[a]

Solvent	G_{t-c}	% cis, stationary state
2-Butyne	0.65	*Ca.* 25
Pentane	1.15	57
Benzene[b]	1.83	59

[a] Initial concentration of *trans*-stilbene = 0.03 M in each case. [b] Data from ref 4.

Photochemical Experiments. Irradiation of liquid **1** with a low-pressure mercury lamp leads to the production of **2** and **3** in a ratio of approximately 3:1. **2** and **3** are initial products of ultraviolet irradiation of **1**; only very slight amounts of other products (unidentified) can be detected. No formation of **4** and **5** could be detected on either very short- or long-term irradiation of **1**.

Photochemical experiments with sensitizers such as benzene, acetone, and benzophenone failed to yield any evidence of production of excited states of **1**. Products **2**–**5** could not be detected when benzene or benzophenone was irradiated in 2-butyne. When 2-butyne solutions of acetone were irradiated, some **2** and **3** were formed in addition to other unidentified products;

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(38) S. Trajmar, J. K. Rice, P. S. P. Wei, and A. Kupperman (*Chem. Phys. Lett.*, **1**, 703 (1968)) obtained a value of 5.2 eV for the lowest singlet → triplet transitions in acetylene with an onset of 4.5 eV. Similar values were obtained for propyne and acetylene in an earlier study by the same method.[39]

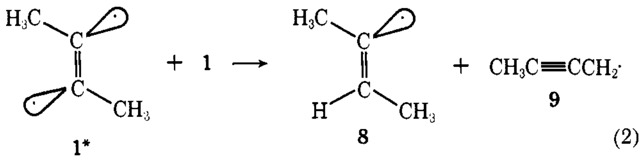
(39) P. S. P. Wei, *Nucl. Sci. Abstr.*, **22**, 11, 193 (1968).

(40) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

as mentioned previously it is likely that these arise from hydrogen abstraction from **1** by excited acetone.

Discussion

The major products of radiolysis of 2-butyne can be separated conveniently into two groups. The first group includes 2,6-octadiyne (**2**), 3-methyl-2-hepten-5-yne (**3**), the 2-butenes **6**, and possibly other "radical products" having carbon–hydrogen ratios different from **1**. The second group of products consists of **4** and **5**, the "molecular products" which have the same carbon–hydrogen ratio as **1**. The "radical products" **2**, **3**, and **6** are produced in both photolysis and radiolysis of 2-butyne.[41,42] A bound excited state of 2-butyne is the likely precursor to these products in the photolysis since the gas-phase ionization potential of **1** is 9.9 eV;[43] even allowing for substantial lowering of the ionization potential in the condensed phase it appears unlikely that the *ca.* 5.5-eV photon delivered to 2-butyne by uv irradiation could promote formation of free ions. Although there is no available evidence as to the configuration of the lowest excited state of 2-butyne, formation of **2**, **3**, and **6** can be envisioned as occurring from a bent, rehybridized excited state[20–22] as illustrated in eq 2–5.



(2)

$$9 + 9 \longrightarrow 2 \qquad (3)$$

$$8 + 9 \longrightarrow 3 \qquad (4)$$

$$8 + 1 \longrightarrow 6 + 9 \qquad (5)$$

The importance of excited state participation in the radiation-induced formation of **2**, **3**, and **6** is less easily determined. The fact that **2** and **3** are obtained in the same ratio in both photolysis and radiolysis indicates that they *could* arise from a common precursor. All of the additives found effective in quenching formation of **2** and **3** possess low-lying excited states; however, they also have ionization potentials lower than that of 2-butyne (Table I). Therefore, these should quench cations as well as singlet or triplet excited states of **1**. Quenching rates are not the same for all quenchers; azulene is a considerably better quencher than *trans*-stilbene, biacetyl, or benzophenone. Therefore, a diffusion-controlled collisional process such as triplet energy transfer cannot be solely responsible for these reactions.

A question which cannot be answered at this time is whether ions or excited states of **1** (or both) are the immediate precursors of the "radical products." Ion recombination is well known to lead to excited state production;[44] however, proton transfer from a positive ion of **1** could lead to **8** and subsequent reactions of **9** could yield **2** and **3**. Although our photochemical experiments demonstrate that excited states of **1** yield the "radical products," the stilbene isomerization results (Table II) suggest that excited states of **1**, if formed in radiolysis, have extremely short lifetimes. The finding that CCl_4 (which should impede ion recombination by electron scavenging) does not suppress, but very slightly enhances, formation of **2** and **3** could be taken as evidence that both ions and excited states are involved as precursors to the radicals.

The second set of products (**4** and **5**) evidently arises through a common intermediate but *via* different immediate precursors. The structure of *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene (**5**) clearly suggests a cyclobutadiene precursor. Syn dimers having this basic structure are frequently the major products obtained when cyclobutadienes are liberated from their metal complexes.[45,46] **5** itself is formed by dehalogenation of *cis*-3,4-dichloro-1,2,3,4,-tetramethylcyclobutene under various conditions.[30,47,48] It is also reasonable that hexamethylbenzene (**4**) could arise from addition of a cyclobutadienoid species to 2-butyne to yield hexamethyl(Dewar benzene). Cyclobutadienes and their metal complexes add efficiently to acetylenes to yield both isolable Dewar benzenes[28,45] and benzenes.[49] Our experiments indicate that hexamethyl(Dewar benzene), if formed in the radiolysis of **1**, could not be isolated since it decomposes efficiently to **4**.

The fact that the yields of **4** and **5** are affected differently by various additives (Table I) demands that they arise from different precursors. However, the fact that **5** is often quenched concurrently with the buildup of **4** suggests that one primary product may lead to both products. A scheme which accommodates the observed results includes two cyclobutadiene intermediates, A and B. Reactions involving the intermediates are summarized in eq 6–13. Equations 8 and 12 are included to allow for our finding that the yields of **4** and **5** (within the precision of our experiments) cannot be directly equated.[50] A is assumed to be the higher energy, more reactive species such that quenching by iodine, oxygen, and CCl_4 can accelerate its conversion to B (eq 10). Enhancement of the yield

$$1 \xrightarrow{\gamma} \longrightarrow \mathrm{A} \qquad (6)$$

$$\mathrm{A} \xrightarrow{(\mathrm{A\ or\ B})} 5 \qquad (7)$$

$$\mathrm{A} \longrightarrow 1 \text{ or other products} \qquad (8)$$

$$\mathrm{A} \longrightarrow \mathrm{B} \qquad (9)$$

$$\mathrm{A} + \mathrm{Q} \longrightarrow \mathrm{B} + \mathrm{Q} \qquad (10)$$

$$\mathrm{B} + 1 \longrightarrow 4 \qquad (11)$$

$$\mathrm{B} \longrightarrow 1 \text{ or other products} \qquad (12)$$

$$\mathrm{B} + \mathrm{D}^{3*} \longrightarrow \mathrm{A} + \mathrm{D}^{0} \qquad (13)$$

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(41) The $CH_3C{\equiv}CCH_2\cdot$ radical has been detected by esr from γ irradiation of 2-butyne at low temperatures.[34]

(42) V. I. Smirnova, T. S. Zhuraleva, D. N. Shigorin, E. P. Gracheva, and M. F. Shostakovakii, *Russ. J. Phys. Chem.*, 38, 246 (1964).

(43) F. H. Coats and R. C. Anderson, *J. Amer. Chem. Soc.*, 79, 1340 (1957).

(44) R. Cooper and J. K. Thomas, *J. Chem. Phys.*, 48, 5097 (1968), and references therein.

(45) R. Pettit, *Pure Appl. Chem.*, 17, 253 (1968), and references therein.

(46) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, Chapters 1 and 2.

(47) P. S. Skell and R. J. Petersen, *J. Amer. Chem. Soc.*, **86**, 2530 (1964).

(48) R. Criegee and K. Noll, *Justus Liebigs Ann. Chem.*, **627**, 1 (1959).

(49) J. Font, S. C. Barton, and O. P. Strauz, *Chem. Commun.*, 499 (1970).

(50) At least one example is reported[51] where generation of cyclobutadiene leads to the production of acetylene.

(51) M. Avram, C. D. Nenitzescu, and E. Marica, *Chem. Ber.*, **90**, 1857 (1957).

of **5** by benzophenone and acetone is attributed to eq 13, energy transfer to B to regenerate A. Since eq 13 simply increases the steady-state concentration of A and eq 8 and 12 have been included, operation of eq 13 can enhance the yield of **4** as well as that of **5**.

The observed results can be explained by assuming that A and B are tetramethylcyclobutadienes differing in multiplicity, one a singlet state and the other a triplet. Conversion of A to B, eq 10, could easily be assisted by long-lived radical species (O_2, $\cdot CCl_3$, and other intermediates) or by heavy atoms in the solute. This could also explain the sensitivity of G_5 to impurities present in the additives and those building up during the course of the irradiation. It is tempting to suggest that A is a triplet cyclobutadiene and B is a lower energy singlet. Theoretical calculations[52] suggest that for free cyclobutadiene a "rectangular" singlet should lie 14–21 kcal/mol below a "square" triplet. Recent experimental evidence appears to indicate a rectangular singlet is the ground state of cyclobutadiene.[53] Such an energy difference would explain a lack of quenching of A (and hence **5**) by azulene ($E_T \approx$ 31–39 kcal/mol)[54] and other additives with higher triplet energies. Presumably lack of observed increases in G_5 could be due to short lifetimes for triplets of 1,3-cyclohexadiene and azulene.[55] It is reasonable that singlet tetramethylcyclobutadiene should react rapidly with 2-butyne in an allowed, concerted reaction; it is also conceivable that the triplet might react slowly with 2-butyne, but very rapidly either with another triplet or with the singlet in a Diels–Alder reaction.

Examination of data in Table I reveals that formation of the initial tetramethylcyclobutadiene is very difficult to quench. While an extremely short-lived excited state or ion from **1** (different from the precursor of the radical products) cannot be excluded as the precursor, an attractive alternative possibility is that the tetramethylcyclobutadiene is formed within the region where energy is initially deposited by a process not involving one discrete activated molecule. The fact that radiolysis of liquid alkynes offers a direct route to uncomplexed cyclobutadienes offers interesting possibilities for future investigation.

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[55] Quenching by 1,3-cyclohexadiene might produce an excited singlet. The cyclohexadiene singlet intersystem crosses with very low efficiency.[56,57]

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Homo-Favorskii Rearrangement

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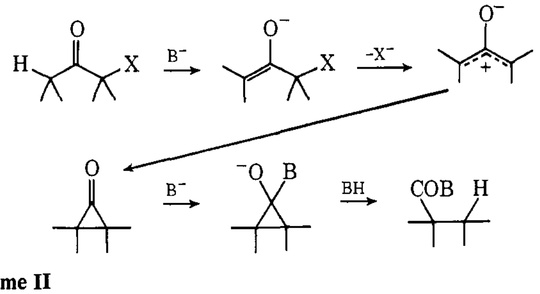
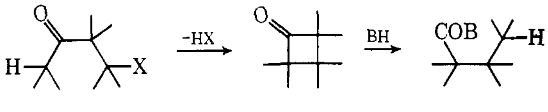
Abstract: The structures of the acidic products of the reaction between 3,6-dimethyl-6-dichloromethyl-2-cyclohexenone and aqueous base have been revised. Full mechanistic and stereochemical analyses of the homo-Favorskii rearrangement (base-induced dehydrochlorination of β-haloketones, followed by scission of the resultant cyclobutanones in analogy with reactions of the Haller–Bauer type) of 6-dichloromethyl-6-methyl-2-cyclohexenone and of the hydrolyses of 2-dichloromethyl-2-methylcyclohexanone, 2-keto-1-methylcyclohexylcarbinyl *p*-toluenesulfonate, and the enol ether of the latter are presented.

In analogy with the Favorskii rearrangement,[1] the base-induced dehydrohalogenative conversion of α-haloketones into carboxylic acids or their derivatives (*cf.* Scheme I), a homo-Favorskii rearrangement can be envisaged to involve a similar transformation of β-haloketones (*cf.* Scheme II). However, two facts mitigate against a frequent occurrence of the latter reaction. Firstly, exposure of β-haloketones to base normally leads to α,β-unsaturated ketones. Hence, the production of cyclobutanone intermediates (Scheme II) can be

Scheme I



Scheme II



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