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THE PHOTOREARRANGEMENT MECHANISM OF α-ALLENIC COMPOUNDS: ITS SPECIFIC CHARACTER

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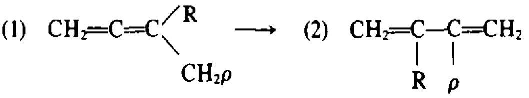
Abstract—The α-allenic compounds liquid-phase rearrangement to 1,3-dienes involves a free-radical, photoinduced rate-determining step. Several inhibiting effects have been observed and interpreted. The bimolecular rearrangement mechanism accounts quantitatively for experimental data, from very dilute to highly concentrated solutions; it rules out the existence of a mesomeric intermediate.

The liquid-phase rearrangement of α-substituted 1,2-dienes to the corresponding 1,3-dienes can be catalysed (Cu dust, Cu^+, Zn^{2+}, etc) or induced either thermally or photochemically[1-6]



$$(1)\ CH_2{=}C{=}C(R)CH_2\rho \longrightarrow (2)\ CH_2{=}C(R){-}C(\rho){=}CH_2$$

(R = alkyl)
(ρ = Cl, Br, OH, OAc)

The rearrangement products are always **2** or their polymers. Mechanisms depend on experimental conditions and competing mechanisms can probably be involved in some cases.[5] The photorearrangement appears to proceed through the least complex mechanism.

It occurs only at wavelengths below 2500 Å, where all α-allenic molecules begin absorbing, the absorption extending until and far into the vacuum ultraviolet.[5,7]

Features of the photorearrangement. The following compounds have been photolysed by steady illuminations (Philips SP 500 high pressure Hg lamp), under a nitrogen stream, of n-pentane solutions: 1-chloro-, 1-bromo-, 1-hydroxy and 1-acetoxy-2-ethyl buta-2,3-diene, 1-bromo-2-n-butylbuta-2,3-diene, 1-bromo-buta-2,3-diene. Their photoisomerisation, studied most extensively on 1-chloro- and 1-bromo 2-ethylbuta-2,3-diene, exhibits the following features:

The reaction kinetics show no definite order.

Bromides react faster than chlorides, showing that the C-ρ bond-splitting is the rate-determining step (Fig. 1).

The rate temperature-coefficient (measured between $-10°$ and $+32°$) is 1.00 ± 0.03. The reaction-rate is therefore photocontrolled.

1,3-dienes inhibit the rearrangement (Fig. 2). UV absorption by the 1,3-diene is not responsible for this inhibition (Fig. 3), which is induced by any compound with a 1,3-dienic skeleton.

The allenic reagent is also an inhibitor of its own rearrangement, as shown by the fact that the amount of rearranged compound goes through a maximum with increasing reagent concentration. Compounds with an allenic skeleton exhibit the same inhibiting efficiency.

The photorearrangement is irreversible. The 1,3-dienic (**2**) compound cannot be photorearranged to **1** and forms only polymers of **2**.

Although many side-reactions have been mentioned for allenic compounds (cyclisation, polymerisation, etc.) the only products ever obtained from haloallenes were 1,3-dienes and their polymers. Duplication or addition products (from alkadienyl- or halogen free-radicals) were never observed in any significant amount under our experimental conditions.[8]

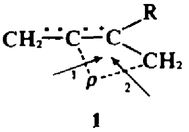
Experience shows that reaction-rates depend very little on R (except the case where R = H) but strongly on the nature of ρ. Besides, the (**1**)→(**2**) reaction is sometimes complicated by side-reactions when ρ = OH or OAc, but the rate-law remains nevertheless the same, although within a narrower concentration-range.

An example of the dependence on ρ is the case of α-allenic esters. While α-haloallenes photorearrange normally from the most dilute to the most concentrated (3M) solutions, the α-allenic acetates follow the (**1**)→(**2**) mechanism in the 10^{-2}–$10^{-3}\,M \cdot l^{-1}$ range. At higher concentrations there is no reaction and with very dilute solutions the acetate-group splitting competes with the normal rearrangement.

Another case is that of the α-allenic alcohols. They do not photoisomerise except at concentrations below $10^{-4}\,M \cdot l^{-1}$, where they give the enol form of an unsaturated ketone. At higher concentrations the OH group inhibits all isomerising effect.

Grignards with the **1** structure (actually they are always mixtures of two forms with the structures of **1** and **2**[9]) can also be rearranged according to the (**1**)→(**2**) scheme.

Role of free-radicals in the photorearrangement. The reaction would normally be expected to proceed through free-radical species. But all reagents absorb in the vicinity of 2000 Å and a number of them have a very high absorptivity. These facts could also be consistent with an excited singlet-state, the rearrangement involving an intramolecular complex such as



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The products would have the **1** or **2** structures depending on the way the complex would split: splitting along $(_1)$ would retain the reagent structure, and the isomeric **2** would be formed by a $(^2)$ splitting.

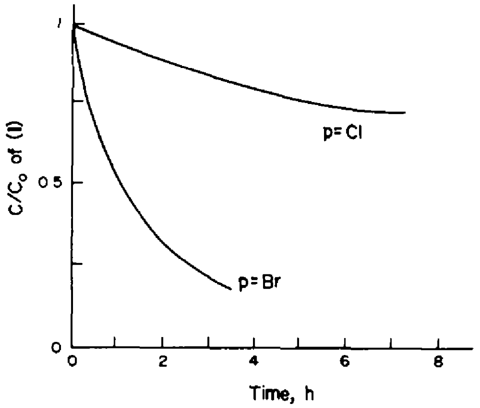


Fig. 1. Photorearrangement kinetics of 1-chloro and 1-bromo 2-ethylbuta-2,3-diene.

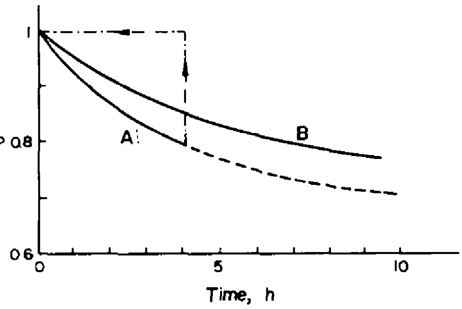


Fig. 2. Influence of 1,3-dienic product on allene rearrangement: A, rearrangement kinetics of a pure allene; B, rearrangement kinetics of the partly rearranged mixture, after restoring the initial allene concentration.

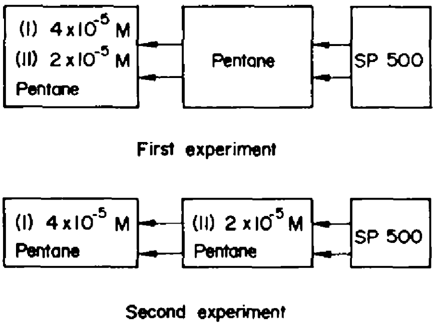
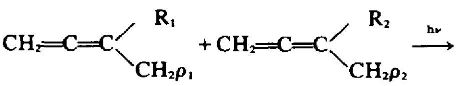
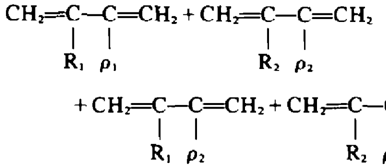


Fig. 3. Two consecutive photolyses of an allene in the presence of equal amounts of 1,3-diene: First experiment: allene and 1,3-diene are mixed; Second experiment: allene and 1,3-diene are in separate cells. No inhibition of rearrangement in this case.

It therefore had to be established whether the mechanism is a free-radical one. This was shown by a competition reaction where a mixture of two **1** halides differing by the nature of both R and ρ, was photolysed. Among the products are molecules with the alkyl group of one reagent and the halogen of the other, a proof there is a free-radical splitting-step.[8]

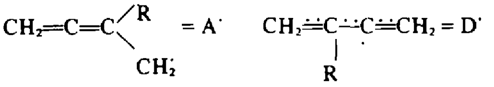


$$CH_2{=}C{=}C(R_1)(CH_2\rho_1) + CH_2{=}C{=}C(R_2)(CH_2\rho_2) \xrightarrow{h\nu}$$



$$CH_2{=}C(R_1){-}C(\rho_1){=}CH_2 + CH_2{=}C(R_2){-}C(\rho_2){=}CH_2 + CH_2{=}C(R_1){-}C(\rho_2){=}CH_2 + CH_2{=}C(R_2){-}C(\rho_1){=}CH_2$$

Not only is the mechanism a free-radical one but it involves two free-radical species, although it could be expected that the reaction would proceed through a common mesomeric intermediate. The photolysis of a **1** compound in a methyl-cyclohexane (MCH) matrix at 77°K is evidence of this fact. The ESR spectrum is of poor quality as MCH is slowly destroyed under the illumination conditions, forming methyl-cyclohexyl free-radicals that react with the other free-radicals in the mixture and thus blur the spectrum. But it is still possible to observe the build-up of one free-radical species which rearranges to another radical species. A reasonable assumption is that the first appearing species is the allenic radical A$^{\cdot}$, the second radical species to appear being its D$^{\cdot}$ rearrangement product.



$$CH_2{=}C{=}C(R)CH_2^{\cdot} = A^{\cdot} \qquad CH_2\dot{=}C(R)\dot{-}C\dot{=}CH_2 = D^{\cdot}$$

This view is supported by flash-photolysis experiments on dilute solutions of **1** or **2**. Both reagents form the same mixture of polymers of **2**. The formation of these polymers from the photolysis of a **1** compound implies that **2** or the corresponding free-radical is an intermediate step in the mechanism. One transient is observed in the photolysis of **1**. Its structure could not be established but its spectrum (absorption max at 2450 Å) and decay kinetics are consistent with a 1,3-dienic structure. It is therefore reasonable to assume that the A$^{\cdot}$ species absorbs too far in the UV to be seen and that the observed transient is D$^{\cdot}$.

The existence of two free-radical species accounts quantitatively for kinetic data, from highly concentrated to very dilute solutions, a fact no other reaction scheme can explain. The accuracy is excellent, as shown by the time-law for the rearrangement. This law is $t = \alpha - \beta C - \gamma \operatorname{Log} C/C_0$ (t = time, C = concentration, C_0 = initial concentration). Curves computed from this law are within 5–15% of experimental figures for rearrangement ratios of up to 75%, although this law is deduced from data covering a much narrower concentration range (Fig. 4).

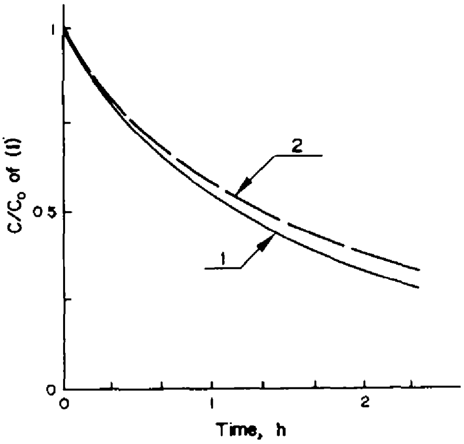


Fig. 4. (1) Experimental rearrangement kinetics. (2) Rearrangement kinetics computed from the time-law.

Mechanism of the photorearrangement. Kinetic data show that the primary step is:

$$A-\rho+h\nu\longrightarrow A^{\cdot}+\rho^{\cdot}$$

The final step has to be:

$$D^{\cdot}+\rho^{\cdot}\longrightarrow D-\rho$$

The inhibiting effects of allenic or 1,3-dienic skeletons or of OH group must express the rearrangement of $D^{\cdot}$ to $A^{\cdot}$. In the liquid-phase these effects cannot be related to any vibrationally excited species, which would have a much too short lifetime to account for experimental data. The rearrangement of a free-radical must occur through one of the following collisions:

$$D^{\cdot}+A-\rho\longrightarrow A^{\cdot}+A-\rho$$
$$D^{\cdot}+D-\rho\longrightarrow A^{\cdot}+D-\rho$$

The isomerisation step can be either mono- or bimolecular, in three possible ways:

(a) $A^{\cdot}+A-\rho\longrightarrow D^{\cdot}+A-\rho$

(b) $A^{\cdot}\longrightarrow D^{\cdot}$

(c) $A^{\cdot}+\rho^{\cdot}\longrightarrow D-\rho$

Such a step as (c) is not consistent with the existence of two free-radical species, but the choice between (a) and (b) is less clear-cut as the reaction-rate is relatively slow, the rate being controlled by the halogen-abstraction primary step. There is no reason to consider the possibility of a rearrangement and recombination in the solvent-cage, as a cage reaction could not account for the various observed inhibiting effects.

If not occurring within the solvent-cage, a reaction such as the collision between $A^{\cdot}$ and $\rho^{\cdot}$ would be highly improbable. It is moreover reasonable, from many known mechanisms, to take as a first assumption that the rearrangement step is bimolecular. The complete mechanism could then be:

(1) $A-\rho+h\nu\longrightarrow A^{\cdot}+\rho^{\cdot}$ (rate-controlling) k_1
(2) $A^{\cdot}+A-\rho\longrightarrow D^{\cdot}+A-\rho$ (rearrangement) k_2
(3) $A^{\cdot}+\rho^{\cdot}\longrightarrow A-\rho$ (recombination) k_3
(4) $D^{\cdot}+\rho^{\cdot}\longrightarrow D-\rho$ (reaction) k_4
(5) $D^{\cdot}+A-\rho\longrightarrow A^{\cdot}+A-\rho$ (inhibition) k_5
(6) $D^{\cdot}+D-\rho\longrightarrow A^{\cdot}+D-\rho$ (inhibition) k_6

The usual steady-state treatment, with the additional equation

$$(\rho^{\cdot})=(A^{\cdot})+(D^{\cdot})$$

gives-neglecting the polymerisation of the 1,3-dienic product- the following expression:

$$-\frac{d(A\rho)}{dt}=\frac{k_1k_2k_4I(A\rho)}{(k_3k_5+k_2k_4-k_3k_6)(A\rho)+k_3k_6G_0+k_3k_4(\rho^{\cdot})}$$

where $G_0=(A\rho)_{t-0}+(D\rho)_{t-0}$ and I = light intensity.

As the variation of $(\rho^{\cdot})$ can be neglected the integration of this equation gives the expression of the reaction-time as:

$$t=\alpha-\beta C-\gamma\ \mathrm{Log}\ C/C_0$$

(γ = positive constant, α, β = constants of same sign, see Table A).

Table A. Coefficients of the time-laws

$$\beta=\alpha/C_0=\frac{k_2k_4+k_3k_5-k_3k_6}{k_1k_2k_4I}$$

$$\gamma=\frac{k_3k_6G_0+k_3k_4(\rho)}{k_1k_2k_4I}$$

$$a_1=\frac{k_2k_4+k_3k_5-k_3k_6}{\eta k_1k_2k_4I}$$

$$a_2=-\frac{k_3k_6G_0}{2k_1k_2k_4I_0}$$

$$a_3=\frac{k_3k_6G_0}{\eta k_1k_2k_4I_0}$$

$$a_4=-\frac{(k_2k_4+k_3k_5-k_3k_6)+(\eta/12)k_3k_6G_0}{k_1k_2k_4I_0}$$

In dilute solutions the absorption is less than total and I, in the rate expression, has to be replaced by $I_0(1-\exp\{-\eta A\rho\})$, with $\eta=2.3\epsilon L$. The integration of the rate-law gives then the following time-law (Table A):

$$t=a_1\ \mathrm{Log}\,(1-\exp\{-\eta C_0\})/(1-\exp\{-\eta C\})+a_2\ \mathrm{Log}\ C/C_0+a_3(1/C_0-1/C)+a_4(C-C_0).$$

Both these time-laws for concentrated and dilute solutions are in good agreement with kinetic data. Mechanisms involving either a monomolecular isomerising step or a single mesomeric free-radical give computed kinetic curves that do not agree at all with experience.

Experimental check on the kinetic laws. In the case of haloallenes the kinetic curves computed from the above formulas agree remarkably well with experimental curves up to very high rearrangement ratios (Fig. 4).

These computations provide an additional check on the values of α and β. Actually these are the same constant as $\beta=\alpha/C_0$, but the α and β values are computed from the curves as if these constants were independent. Both α and β have negative values except in the case of Grignard reagents. As their expressions contain the rate-constants of the inhibition-steps, the difference in sign expresses the fact that inhibiting collisions are much less efficient in the case of a Grignard reagent, where the solvation shell of the Grignard protects the reactive group.

All numerical coefficients (α, β, γ, a_1, a_2, a_3, a_4) are in an inverse ratio to the light intensity I (Table A), the agreement being good.

The values of α, β and γ can be quite different for experiments done at intervals which can be of several months. This is due to the fact that illumination conditions are not very reproducible, as they are influenced by a number of factors: ageing of silica and Suprasil cell-windows, of the lamps (they have a relatively short lifetime), difference in values of the light intensity for two different new lamps, etc. Such experimental factors can hardly be predicted or controlled, and it appears useful to have an expression that does not depend on them. We used

$$-\gamma/\beta G_0=k_3k_6/(k_3k_6-\{k_3k_5+k_2k_4\})$$

which is independent of both the illumination-conditions and the reagent's initial concentration. It was checked that this expression has a constant value for all kinetic curves relating to a given molecule. When comparing the rearrangement kinetics of compounds with differing substituents (Table B), it can be seen that the values are still quite similar. As $-\gamma/\beta G_0$ does not depend on the $C-\rho$ splitting-step this is an additional confirmation of the fact that the efficiency of inhibiting collisions depends more on the skeleton of the inhibiting molecule than on the nature of the ρ substituent. The inhibiting effects of allenic or 1,3-dienic molecules are thus quantitatively accounted for.

Table B. Influence of substituent

Substituent	Concentration range	$-\gamma/\beta G_0$	Estimation method
-Br	3M to 10^{-3}M	1.25±.25	IR,VPC
	$10^{-4}$to 10^{-5}M	1.4	UV
	10^{-4}M	1.6(*)	UV
-Cl	3M to 10^{-3}M	1.20±.15	IR,VPC
-AcO	$10^{-2}$to 10^{-3}M	1.0-1.2	VPC
-OH	5,10^{-4}M	(**)	UV
-MgBr	.1 to 2.5M	-.65	IR(***)

(*)Gas-phase photolysis

(**)Abnormally low value,.probably related to the product being in its enol form

(***) In Et_2O solution, all other experiments being in n-pentane

With dilute solutions the values found for $-\gamma/\beta G_0$ agree very well with those found in concentrated solutions and with a few experiments done in the gas phase (Table B).

Comments on the reaction mechanism. It has been shown how kinetic data lead to the assumption that the rearrangement of α-substituted allenes involves two different free-radical species, one being allenic and the other 1,3-dienic. The kinetic agreement is so good that it could be said to be too good: it is probable, considering that the reagents are seldom perfectly pure, etc. that some errors cancel each other. It remains that no other hypothesis can account for the rearrangement rates of these compounds. The apparently plausible assumption of a mesomeric intermediate gives kinetic curves widely different from experimental figures.

Although the study of the reaction transients is far from complete, the flash-photolysis experiments establish a strong presumption that the seen transient has a 1,3-dienic structure (Fig. 5): the more so as its decay, computed from the time-law for dilute solutions, is in agreement with the experimental curve.

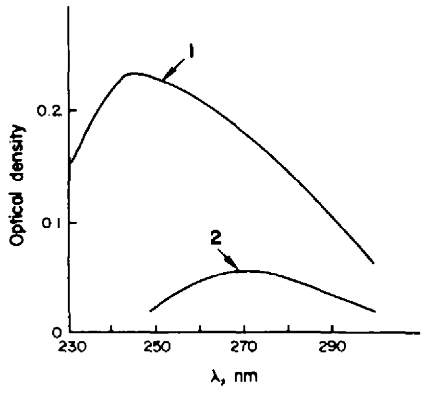


Fig. 5. (1) Absorption spectrum of transient observed in flash-photolysis. (2) Absorption spectrum of 1,3-diene polymer as seen in flash-photolysis experiments.

The matrix experiments in MCH are definite evidence that two different radical species take part in the reaction mechanism, a result supported by a CNDO-INDO computation in which four possible free-radical forms have been considered:

A_1 non-planar allenic A_2 planar allenic
D_1 transoid 1,3-dienic D_2 cisoid 1,3-dienic (Fig. 6).

The total energies for a given structure are as follows:

$A_1 = -30.800$ A.U. $A_2 = -30.739$ A.U.
$D_1 = -30.746$ A.U. $D_2 = -30.743$ A.U.

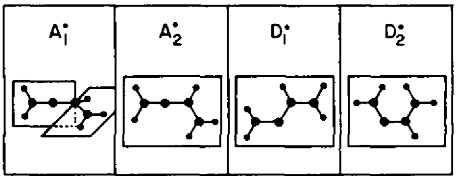
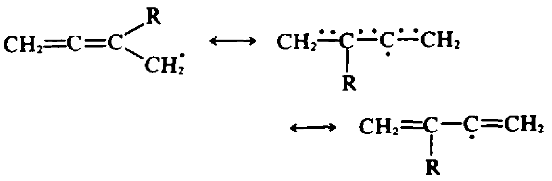


Fig. 6. Free-radical structures for CNDO-INDO computation.

The non-planar allenic free-radical A_1 thus appears as the stablest form by far, which rules out any possibility of a mesomery, where all limiting structures have to be planar. It would also seem that the D_1 transoid form is slightly privileged over the cisoid D_2, but it must be kept in mind that the substituted molecules cannot be used in the computation as they are too flexible. The computing had to be done on unsubstituted allenic or 1,3-dienic structures, and the presence of an alkyl group could change the numerical values which are very close to each other for D structures.

The point is that the rearrangements of unsaturated 3-carbon systems: allylic, acetylenic-allenic, allenic-1,3-dienic, have always been implicitly assumed to involve similar mechanisms, as they occur in series which exhibit many similarities in their chemical behaviour. It has usually been admitted that the reactions proceed through a mesomeric intermediate, which would here be:



Such assumptions are unwarranted. It has already been established that Grignard formation from allenic bromides followed a course different from what occurs with allylic reagents.[10,11] The example of the photorearrangement of allenic compounds is further evidence that the allene-1,3-diene rearrangement has a specific character, and that the idea of a mesomeric structure for the reaction intermediate is not tenable. What has been established in several cases of allylic rearrangements does not apply here.[12]

If the rearrangement of some allenes to 1,3-dienes has certainly a specific character it could be imprudent to assume that this is an absolutely general case. Even in the case of haloallenes, their reactions seem to follow different paths depending on whether the halogen atom is a primary[13] or tertiary[14] one. It can also be imagined that some allylic or acetylene-allene rearrangements do not follow the reaction schemes too often assumed to be universal. As all systems with a low symmetry and a number of π or unshared electrons can give a variety of intermediate structures, we believe that caution should be the rule and that some generalisations have been somewhat hasty.

EXPERIMENTAL

Reagents. Allenic compounds were prepared as described previously.[15,16] All compounds were substantially pure except the **1** bromides, which had usually a 3–10% content in isomeric **2**, due to some thermal rearrangement occurring even at room temperature.

1-chloro-2-ethylbuta-2,3-diene:	n_D^{25}: 1.472	$\epsilon = 87{,}300\ l \cdot M^{-1} \cdot cm^{-1}$
1-bromo-2-ethylbuta-2,3-dient:	n_D^{25}: 1.506	$\epsilon = 8{,}250\ l \cdot M^{-1} \cdot cm^{-1}$
1-bromo-2-n-butylbuta-2,3-diene	n_D^{25}: 1,510	
1-acetoxy-2-ethylbuta-2,3-diene	n_D^{25}: 1.451	$\epsilon = 2{,}000\ l \cdot M^{-1} \cdot cm^{-1}$
1-hydroxy-2-ethyl-buta-2,3-diene	n_D^{25}: 1.473	$\epsilon = 3{,}200\ l \cdot M^{-1} \cdot cm^{-1}$

1-bromo-buta-2,3-diene was prepared from 1-hydroxybuta-2,3-diene according to Bailey and Pfeiffer.[17]

All ϵ are at 2000 Å in n-pentane solution.

Grignard solutions were prepared in Et_2O from 1-bromo-2-ethylbuta-2,3-diene $\epsilon = 40{,}000\ l \cdot M^{-1} \cdot cm^{-1}$.

n-Pentane used as solvent is purified by stirring repeatedly, until colourless, with 20% oleum, then dried and destilled.

Steady illuminations. The source was a Philips SP 500 high-pressure mercury lamp. Suprasil or fused silica vessels. Reaction temp. usually 32° (dry boiling n-pentane solns, 10^{-5} to 3 M, commonly 0.4 M). Continuous bubbling of n-pentane N_2 saturated ensured stirring while maintaining a constant volume. Samples were drawn through a capillary tap.

It was checked with interference filters that no wavelength below 2500 Å induced any photolysis. The reaction progress was followed by measuring the $\nu_{C=C=C}$ 1950 cm^{-1} band-area (conc solns) or by UV spectrometry (dil solns). Sample analysis was done by VPC (10% DEGS on carefully silanized W Chromosorb, temp. 80–110°C). Chromatographic measurements were duplicated in the case of bromides and alcohols, as some α-allenic compounds can rearrange on VPC columns,[17] through a thermal phenomenon (avoided by low-temp. operation) and the effect of active sites in the packing-material (reduced by an alkaline silanizing reagent such as HMDS, at the cost of a slightly diminished column-efficiency). All VPC and spectral data were checked with samples prepared independently. Spectrometric estimations for the integrated band-intensities were restricted to the **1** allenes as the 1,3-dienes partly polymerised.

Flash-photolysis. Photoelectric Porter-type apparatus (rectilinear, fused-silica flashlamp, i.d. 15 mm, overall length 400 mm, W electrodes) operated at 10–15 kV (Bosch KO/MPS condensers, capacitance $2 \times 7{,}71\ \mu F$, self-inductance 27 nH). With energies in the 500–1,800 J range the half-peak duration was 6–8 μs. The continuous analytic source was an Osram XBO 500 W tungsten lamp. The solns (2×10^{-6} to 5×10^{-5} M of allenic bromide or isomeric 1,3-diene in pentane, $R = Et$, $\rho = Br$) were flashed under a thickness of 10 mm in a 400 mm fused-silica cell.

Electron-spin resonance. Jeol ME 1 X apparatus, detection level 10^{11}–10^{12} free-radicals · ml^{-1}.

All experiments were performed at 77°K or slightly above, with 10^{-3} M solns of 1 - bromo - 2 - ethylbuta - 2,3 - diene or 2 - bromo - 3 - ethylbuta - 1,3 - diene in methylcyclohexane, in a quartz Dewar vessel. Illumination by a Philips SP 500 source. MCH (Eastman, spectro grade) was purified by column chromatography on a mixture of activated alumina and silica gel, then carefully degassed by repeatedly freezing and melting under vacuum.

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