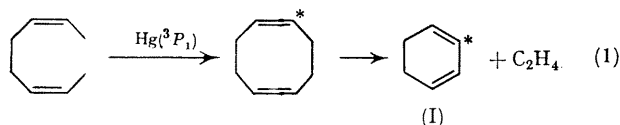


Photochemical Elimination of Ethylene from 1,5-Dienes. Mercury-photosensitized Decomposition of Hexa-1,5-diene Vapour

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IN the mercury-photosensitized decomposition of cyclo-octa-1,5-diene, ethylene is eliminated by a molecular process:¹ other photochemical reactions, including isomerizations² and dissociation into two buta-1,3-diene molecules, also occur.



The vibrationally activated molecule (I) produced by the elimination of ethylene may either decompose to benzene and hydrogen or be collisionally stabilized to cyclohexa-1,3-diene or hexa-1,3,5-triene. Our preliminary results with hexadiene-1,5-diene clarify the C₂H₄ elimination process.

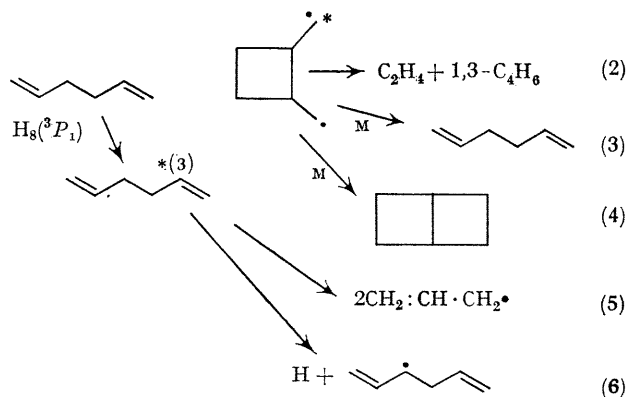
Mercury-photosensitized decomposition of hexa-1,5-diene during 3 min.

Pressure (mm.)	Product (μmole)				[C ₂ H ₄]
	H ₂	C ₂ H ₄	C ₃ H ₆	1,3-C ₄ H ₆	[1,3-C ₄ H ₆]
4.0	0.22	0.56	0.68	0.55	1.04
4.5	0.15	0.52	0.91	0.51	1.02
9.5	0.11	0.35	0.56	0.35	1.00
14.0	0.15	0.31	0.41	0.32	0.97
18.0	0.15	0.36	0.47	0.35	1.03
32.0	0.11	0.31	0.23	0.29	1.07
40.0	0.11	0.28	0.27	0.28	1.00
49.0	0.07	0.24	0.22	0.25	0.96

Hexa-1,5-diene (99.9%, g.l.c.) was irradiated [low-pressure mercury lamp, cylindrical quartz cell, room temp. in the

presence of mercury (*ca.* 0.5 g.)]. Product analysis was carried out by a conventional greaseless vacuum line and gas chromatography (silica gel, 100° for gaseous products: squalane, 80° for higher products). Hydrogen, ethylene, propene, and buta-1,3-diene were observed as decomposition products as well as other photoisomers³ (Table).

The following primary dissociations are possible for the mercury-photosensitized decomposition,

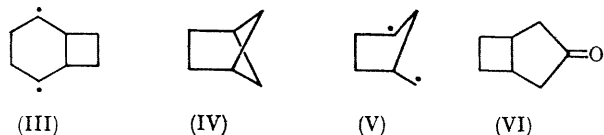


Ethylene and buta-1,3-diene are formed in equal amounts ([C₂H₄]/[1,3-C₄H₆] = 1.01 ± 0.06) under a wide variety of conditions; the ratio is unaffected by the addition of nitric oxide. This suggests a molecular dissociation such as (2), *via* diradical (II). Formation of buta-1,3-diene by recombination of two vinyl radicals is less probable since acetylene formation, expected by the disproportionation of

the vinyl radical, was not observed. This type of intermediate (III) is also consistent with the results for cyclo-octa-1,5-diene.

Diradical (V) is an intermediate in the mercury-photo-sensitized isomerization of hexa-1,5-diene to bicyclo[2,1,1]-hexane (IV).⁴ Present results clearly demonstrate that an alternate diradical (II) was also produced, though in small amounts, leading to the molecular elimination of ethylene. Further, bicyclo[2,2,0]hexane⁵ is produced.

It has been shown that the diradical (II), produced by



photochemical decarbonylation of bicyclo[3,2,0]hepta-3-one (VI) (vapour) gives bicyclo[2,2,0]hexane and hexa-1,5-diene, (1:0.05).⁶ When carbon dioxide (150 mm.) was added to the ketone (VI) (15 mm.), and a Pyrex filter was used (II) seemed to be less energetic and hardly dissociate to ethylene and buta-1,3-diene. These dissociations are subject to collisional quenching (Table). The Stern-Volmer plots ($1/\phi$ vs pressure) with ethylene and buta-1,3-diene are linear and both sets of points fit the same straight line. The quantum yields† of ethylene and buta-1,3-diene extrapolated to zero pressure were both 0.09, indicating that 9% of excited molecules follow this pathway if they are not quenched by collisions. Since the Stern-Volmer plots with propene gave a straight line with a different slope, the precursors of the processes (2) and (5) appear to differ.

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† Quantum yields were determined by comparison with the decomposition of propane at 300 nm. The hydrogen yield from propane was assumed to be unity at low conversion (0.06%).

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