ArF Excimer Laser-induced Selective Coupling of Cycloalkanes: Photochemical Reaction at the Absorption Edge

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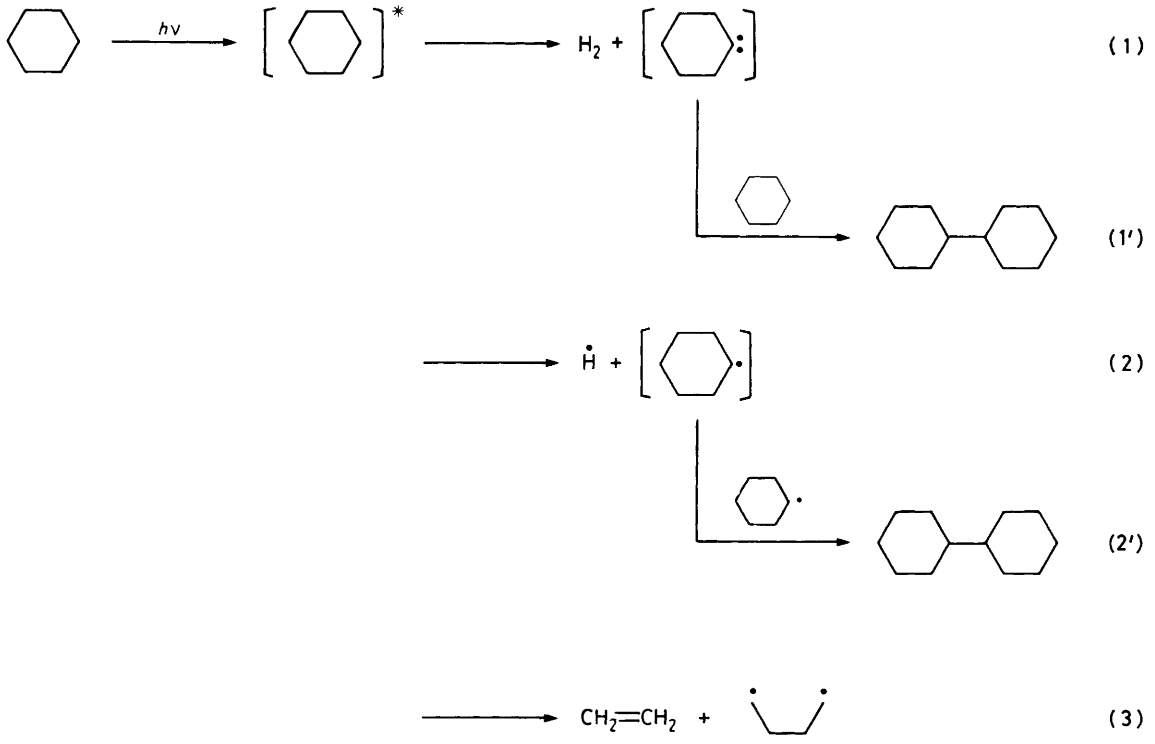
Bicycloalkyls were selectively produced from the corresponding liquid phase cycloalkanes by irradiation at their absorption edge with an ArF excimer laser; the photoreaction proceeded by a radical mechanism and showed a dependence of the dimerization rate on ring size.

Alkanes are highly stable and therefore have been widely used as solvents for various organic reactions without any special precautions. Recently, direct reactions of alkanes were reported using homogeneous transition metal catalysts[1] and mercury vapour sensitized photoreactions.[2] Direct photochemical transformations of alkanes have been reported using high-energy radiation in the vacuum UV[3,4] but unfortunately these photochemical reactions were less selective, probably because of non-selective excitation to several excited states, which independently afford different products. Such reactions



with cycloalkanes have been reported for cyclohexane in the liquid[5] and vapour phases.[6] In our research on the application of lasers to organic reactions, in contrast to the preceding reports, we found a highly selective transformation of liquid phase cycloalkanes into the corresponding bicycloalkyls by ArF excimer laser (193 nm) irradiation at the absorption edge.

The irradiation of nitrogen purged cyclohexane was conducted with an ArF excimer laser (110 mJ/cm^2 per pulse; 10 Hz), the wavelength corresponding to the absorption edge of cyclohexane.[7]† Bicyclohexyl was obtained without production of significant amounts of by-products. In particular, no trace of cyclohexene,‡ butadiene, or ethylene was detected, which were the major products on irradiation at shorter wavelengths.[5] Other possible products, hexenes and butenes, were also not detected; however, a faint colouring of the solution and slight polymerization on the surface of the cell were observed with prolonged irradiations. The yield of bicyclohexyl as a function of irradiation time is shown in Figure 1.

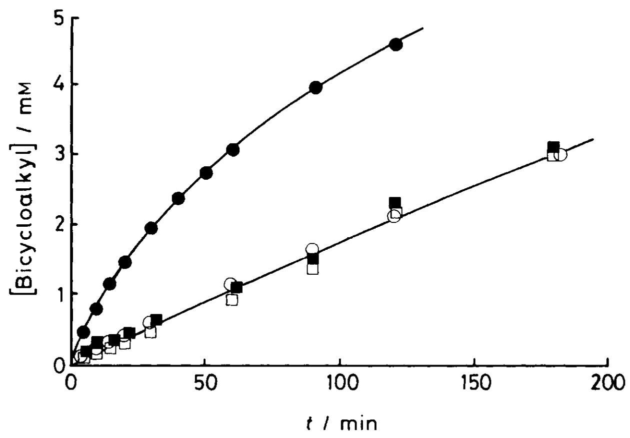


Figure 1. Formation of bicycloalkyls as a function of reaction time: ■ bicyclopentyl; ● bicyclohexyl; ○ bicycloheptyl; □ bicyclo-octyl.

We then conducted the photoreaction at 185 nm, with a 30 W low-pressure mercury lamp fitted with an Acton F185-HR-2S bandpass filter, in order to examine the occurrence of a two-photon process, which often appears in the laser reactions. The reaction proceeded similarly but extremely slowly. This result is rationalized by a one-photon process which depends only on the wavelength, and the large acceleration with the laser is ascribed to the generation of the intermediate in high concentration, which facilitates the intermolecular coupling reactions.

Yang and Servedio have proposed three major primary reactions: (1), (2), and (3), on irradiation of liquid phase cyclohexane with Xe (147.0 nm) and Kr (123.6 nm) resonance lamps.[5] They stated that bicyclohexyl was produced by the coupling of two cyclohexyl radicals, reaction (2′). However,

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† Each bicycloalkyl was identified by comparison of capillary GLC retention times (25 m, PEG 20M; 25 m, OV-1) and GC/MS fragmentation patterns with authentic samples. Bicyclohexyl was isolated from the photolysate by silica gel column chromatography and its ^{1}H NMR, ^{13}C NMR, MS, and IR spectra were found to be identical with those of an authentic sample. Cyclohexene, hexenes, butenes, butadiene, and ethylene were identified with the capillary columns and a packed GLC column [3 m, TCP (5%) + Tween 60 (1%), C-22] by comparison with authentic samples.

‡ Formation of cyclohexene has been reported, *via* disproportionation, in the reaction of cyclohexyl radicals which were generated by hydrogen abstraction of cyclohexane with phenyl radicals: W. A. Cramer, *J. Phys. Chem.*, 1967, **71**, 1171. The absence of cyclohexene in our reactions may be attributed to the different state of the cyclohexyl radicals involved.

carbene insertion into a C–H bond, reaction (1′), was also expected, especially in the liquid phase because Doepker and Ausloos had reported the overwhelming predominance of a carbene formation, reaction (1), with the resonance lamps.[6] Reaction (3) seems to be absent in our reactions, no traces of ethylene or butadiene being found in the products.

The mechanism was determined by conducting the reaction with a 1:1 mixture of cyclohexane (C_6H_{12}) and [$^2H_{12}$]cyclohexane (C_6D_{12}), and subsequent analysis of bicyclohexyls by GC/mass spectrometry. Besides formation of $C_{12}H_{22}$ (*m/z* 166) and $C_{12}D_{22}$ (*m/z* 188) as the common products, $C_{12}D_{12}H_{10}$ (*m/z* 178) and $C_{12}D_{10}H_{12}$ (*m/z* 176) would be obtained by the carbene route, reactions (1)–(1′), while $C_{12}D_{11}H_{11}$ (*m/z* 177) would be produced by the radical route, reactions (2)–(2′). The observed parent peaks were *m/z* 166 (relative intensity 65.0), 177 (39.0), and 188 (8.4). It is concluded, therefore, that reaction (2) is the only major primary reaction participating in the bicyclohexyl formation. The selective production of bicyclohexyl may be attributed to the selective one-photon transition to the lowest excited singlet state of cyclohexane, which is responsible for the homolytic C–H bond cleavage, being the single primary process for the reaction. Upper excited states may be involved in reactions (1) and (3), which may be high-energy processes.

The selective production of other bicycloalkyls was also achieved similarly with ArF laser irradiation of cyclopentane, cycloheptane, and cyclo-octane. The formation of a polymer was not observed for these compounds even after prolonged irradiations. The results are also shown in Figure 1. It is interesting that cyclohexane showed a higher rate of formation than the other cycloalkanes under the same conditions. The reactivity does not parallel the absorption intensity at 193 nm because our measurements showed that % transmittances of C_5—C_8 cycloalkanes were 1.3, 48.0, 0.6, and 0.3% respectively. The origin of the high reactivity for cyclohexane is not clear at present; however, it may be related to structural effects on the lifetime and reactivity of the excited cyclohexane, or to the excitation of specific bands[7] which may exist in the broad absorption of the compound.

Received, 23rd June 1989; Com. 9/02661D

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