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DIRECT IR-SPECTROSCOPIC OBSERVATION OF (1+2)-CYCLOADDITION OF CYCLOPENTADIENYLIDENE TO ETHYLENE IN ARGON MATRIX

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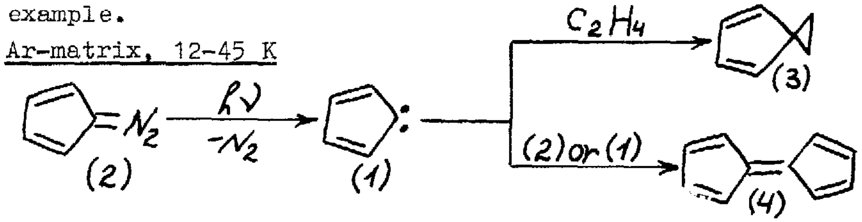
Summary: Cyclopentadienylidene was generated in argon matrix doped with 2% C_2H_4 and the direct reaction of the carbene with C_2H_4 in matrix, when it was annealing from 12 to 40-45 K, was observed.

(1+2)-cycloaddition to olefins is one of the most typical reactions of carbenes. Attempts of the direct spectroscopic study of this reaction, when diazomethane was irradiated with UV-light in inert matrices containing ethylene, have been reported but free methylene hasn't been detected in spite of the observed formation of cyclopropane.[1,2] We succeded in the first direct IR-spectroscopic observation of this reaction in argon matrix using cyclopentadienylidene (1)[3] generated by UV-photolysis of 1-diazocyclopentadiene-2,4 (2)[3] as an example.



When photolysis was carried out in an Ar-matrix doped with 2% C_2H_4, new IR-bands at 828 w., 733 m., 560 w. and 528 v.w. cm^{-1} due to spiro/2,4/heptadiene-4,6 (3)[4] were observed together with IR-bands of (1) and (4) (Fig. 1b). No residual (2) were detected (compare with Fig. 1a). Gradual warming from 12 to 40-45 K caused the increasing of product (3) IR-bands with the simultaneous decreasing of carbene (1) bands to their complete disappearance (Fig. 1b-d). The data obtained clearly show that the formation of (3) during matrix annealing was the result of carbene (1) addition to ethylene on account of its thermal diffusion in the matrix. Thus, carbene (1) interacted with ethylene at 40-45 K in its ground (triplet) state[5], because in the absence of irradiation all molecules in low-temperature matrices are in ground state. Observed cycloaddition of carbene (1) to ethylene either in excited (during UV-irradiation) or in ground (during matrix annealing without irradiation) states is the first successful example of direct spectroscopic observation of carbene reaction with an olefinic substrate in a low-temperature inert matrix.

REFERENCES AND NOTES

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5). When diazocompound (2) was irradiated in solutions of various olefins, practically stereospecific addition of carbene (1) to C=C bond was observed, which showed that it reacted in the excited (singlet) state.[6,7] All attempts to observe addition of triplet carbene (1) to olefins by carrying out the photolysis in large excesses of inert diluents or by decreasing the temperature of reaction mixture to 77 K failed[6,7], which showed that rate of singlet carbene (1) addition to olefins is much higher, than the rate of its singlet-triplet conversion.

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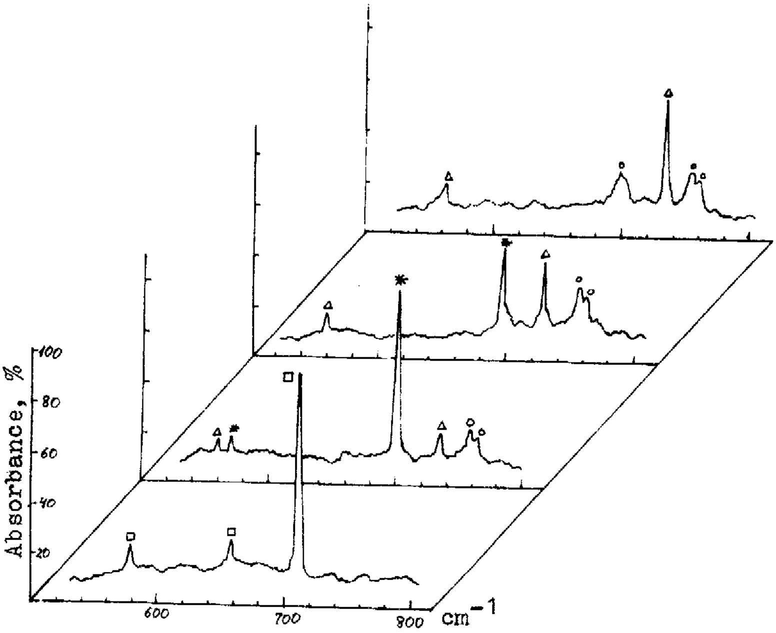

Figure 1. IR-spectra in (Ar + 2% C_2H_4) matrix at 12 K: a - diazocyclopentadiene (2) before photolysis, b - after UV-photolysis (λ >300 nm), c and d - after two successive cycles (matrix annealing from 12 to 40-45 K for 10 min with freezing back to 12 K afterwards).

□ - diazocyclopentadiene (2), ✱- cyclopentadienylidene (1),

Δ- spiro/2,4/heptadiene-4,6 (3), o- fulvalene (4).

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