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RADIATION - INDUCED AMIDATION OF DIENES

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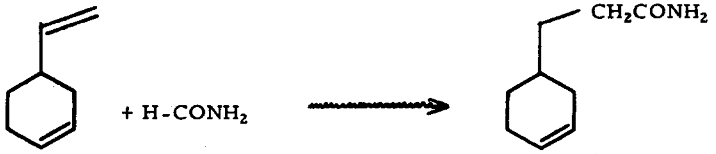
The light-induced amidation of a variety of olefins and the γ-radiation and electron-induced amidation of isolated olefins with formamide have been reported recently(1, 2, 3). It has been noticed (2) that chemical yields of the 1:1 addition products of isolated olefins and formamide are nearly the same in the acetone-initiated photochemical reactions and the γ-ray-induced cases. Since yields are fairly high in both cases, the two methods may be of synthetic utility. On the other hand, the ketone-initiated photochemical addition of formamide to dienes led to relatively poor yields of the 1:1 adducts (4). Thus, the acetone-initiated photochemical addition of formamide to 4 - vinylcyclohexene , 1, 5-cyclooctadiene and norbornadiene afforded low yields of the 1:1 addition products. We have found that the γ-ray-induced addition of formamide to these dienes leads to increased yields of the amides, and accordingly is of potential synthetic use. The reactions studied can be formulated as follows:



(I)

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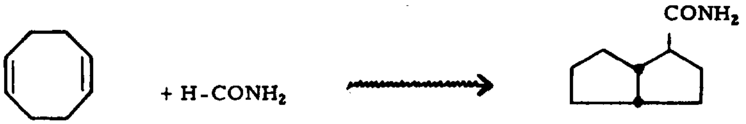
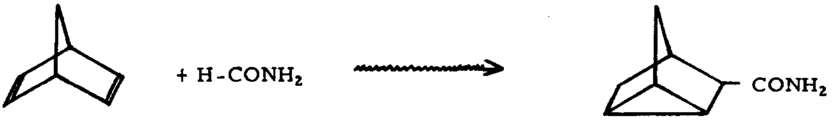


(II)



(III)

It should be noted that in the three cases described a 1:1 adduct is obtained as the major product of the reaction. A selective amidation of the terminal double bond of 4-vinylcyclohexene took place in 35% yield (G = 3), whereas exo-cis-bicyclo-(3.3.0)-octane-2-carboxamide (II) (5) was obtained in 50% yield (G = 3.5) from the reaction of 1,5-cyclooctadiene and formamide. The major product (75%; G = 5) obtained from the reaction of norbornadiene and formamide was a derivative of nortricyclene (III) (6).

The difference in the results obtained in the photochemical and the γ-ray-induced amidation reactions of dienes is due, most probably, to the different mechanisms operating in both cases. Though they both involve the generation of a carbamoyl radical$\cdot CONH_2$ in solution (1, 2) which is subsequently trapped by the diene, the mode of generation of this radical is different in both cases. In the photochemical reactions (which are usually initiated by a ketone) the carbamoyl radical results from hydrogen atom abstraction from formamide by the excited carbonyl compound, whereas in the γ-ray-induced reactions this radical is generated by direct radiolysis of formamide. The excited ketone molecules which are present in the ultraviolet-irradiated mixture interact with the diene leading to a variety of by-products (7), and therefore yields of the desired adducts of the diene and formamide are lowered. In the latter case (where a ketonic sensitizer is absent) the diene is not affected to a great extent during the radiolysis process due to its low concentration in the reaction mixture, and therefore is available for the desired addition reaction.

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