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DIFFERENCES IN REACTIVITY AND SELECTIVITY BETWEEN RADICAL ADDITIONS AND CYCLOADDITIONS

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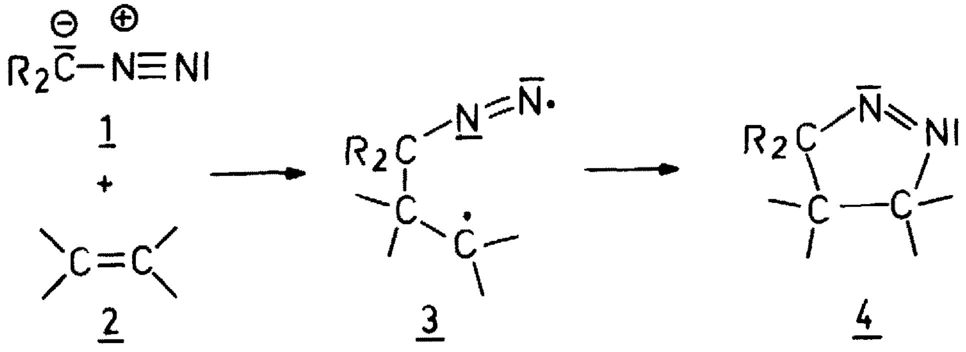
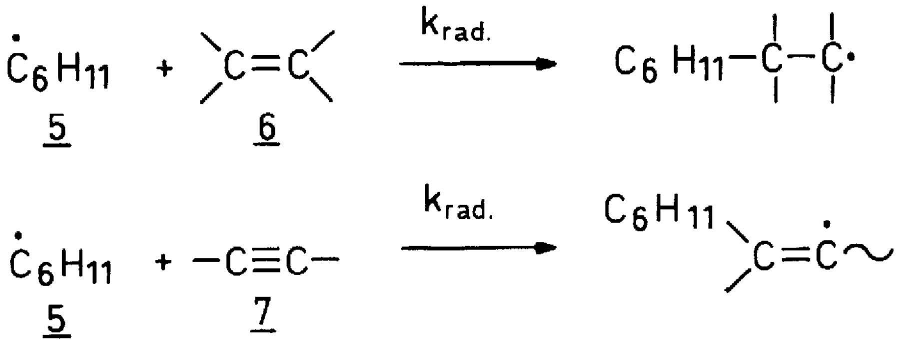
Summary: Alkenes and alkynes show one-bond reactivity with radicals and two-bond reactivity with diazomethane.

Although vast experimental evidence has been accumulated by Huisgen¹⁾ in favour of a symmetry allowed²⁾ concerted pathway of 1,3-dipolar cycloadditions, two-step mechanisms via diradicals as intermediates are still discussed³⁾. As an example, it was presumed that additions of diazoalkanes 1 to alkenes 2 could give diradicals 3, which recombine in a fast reaction step yielding products 4³⁾.



In diradicals 3 alkene substituents do not influence the stability of the nitrogen centred radical (diazenyl radical). Therefore rates of two-step cycl additions should be mainly dependent upon the substituent effect on the formation of the carbon centred radical (alkyl radical) of 3. In order to study this substituent effect we have measured addition rates of a cyclohexyl radical (5) to alkenes 6 and alkynes 7 using the "mercury method"[4].



In Table I addition rates of the cyclohexyl radical (5) are compared with cycloaddition rates of diazomethane (1, R=H), measured by Huisgen[5]. Alkenes 6 and alkynes 7, that are substituted at only one carbon atom show similar effects on the rates of radical additions and cycloadditions. With substituents at both carbon atoms of 6 or 7 the reactions are no longer comparable, because now the rate of the radical reaction is decreased by steric effects to a much larger extend than that of the cycloaddition:

1. With a cyclohexyl radical cinnamic ester, phenyl propiolic ester and crotonic ester react slower but with diazomethane they react faster than styrene.
2. Compared to methacrylic ester the methyl group in crotonic ester reduces the addition rate of the cyclohexyl radical by a factor of 75. In cycloadditions with diazomethane the rate difference between methacrylic ester and crotonic ester amounts only to a factor of 8.

Table I

Rel. addition rates of a cyclohexyl radical (k_{rad}) and of diazomethane (k_{cycl}) with alkenes and alkynes at 298 K.

	k_{rad}	k_{cycl} [a]
$H_2C{=}CHCO_2C_2H_5$	6.7	2520
$H_2C{=}CCH_3CO_2C_2H_5$	5.0	116
$HC{\equiv}CCO_2CH_3$	2.1	1120
$H_2C{=}CHC_6H_5$	≡ 1.0	≡ 1.0
$HC{\equiv}CC_6H_5$	0.25	0.061
$C_6H_5CH{=}CHCO_2C_2H_5$	0.44	5.9
$C_6H_5C{\equiv}CCO_2C_2H_5$	0.20	8.9
$CH_3CH{=}CHCO_2C_2H_5$	0.067	14

a) Data from ref. 5).

3. Cyclohexyl radicals attack cinnamic ester predominately at the carbon atom, that is substituted by an ester group. Diazomethane reacts with quite opposite regioselectivity[6)].

These different reactivities and selectivities of the substituents demonstrate the difference between one-bond reactivity of radical additions and two-bond reactivity of cycloadditions[7)]. In radical additions only one carbon atom is attacked forming one new bond, whereas in cycloadditions with diazomethane both carbon atoms of the double or triple bond are attacked in the transition state.

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