KINETICS OF 1,3-DIPOLAR CYCLOADDITION REACTIONS OF ARYL- AND DIARYLDIAZOMETHANES

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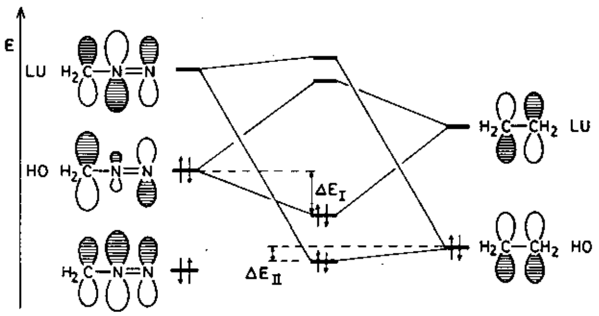
Dedicated to Tetsuo Nozoe on the Occasion of His Seventy-seventh Birthday

The cycloadditions of diazomethane and its aryl derivatives to olefins are HO(1,3-dipole) - LU(dipolarophile) controlled. Accordingly, electron-attracting substituents in the dipolarophile or electron-releasing substituents in diazomethane accelerate the addition. The log k_2 for the reactions of substituted phenyldiazomethanes with ethyl acrylate and norbornene obey Hammett relations with $\rho = -1.5$ and -0.8. Substituents influence the rate constants of diphenyldiazomethane less.

MO perturbation theory (PMO) offers an elegant interpretation of reactivity sequences and regioselectivities of concerted cycloadditions.[1,2] 1,3-Dipolar cycloadditions of diazomethane to substituted ethylenes turned out to be a crucial test, because the predominance of the HO(diazomethane) - LU(ethylene) interaction is so strong that the second frontier orbital interaction can be neglected (Fig. 1). A linear relation of log k_2 with the reci-

Figure 1



procal energy distance of HO(diazomethane) – LU(alkene) was achieved for ethylene and 14 derivatives.[3] Ethyl acrylate reacts 10^7 times faster than butyl vinyl ether, whereas enamines are inert.

Not only the decrease of ethylene π-MO energies by electron-attracting substituents, but also the lifting up of diazomethane orbitals by electron-releasing substituents should accelerate the cycloaddition. We measured the kinetics of aryldiazomethane cycloadditions to ethyl acrylate in DMF at 25°C by spectrophotometry. The slower rates of the additions to norbornene were followed by a volumetric method ; the remaining diazoalkane in samples withdrawn was determined by nitrogen evolution with trichloroacetic acid in 2-methoxyethanol.

Table 1. Rate Constants for Aryldiazomethane Cycloadditions to two Dipolarophiles in DMF at 25°C

$RC_6H_4\overset{-}{C}H-\overset{+}{N}\equiv N$ R =	λ_{max}(nm); ε	Ethyl acrylate 10^5k_2 (l mol^{-1}sec^{-1})	Norbornene
p-CN	459; 47	1 250	3.39
m-Cl	477; 27	5 980	7.02
p-Cl	484; 30	7 990	8.57
H	488; 24	13 100	8.94
m-CH_3	490; 25	14 300	9.41
p-CH_3	488; 27	22 200	12.6
p-OCH_3	507; 29	46 300	19.3
p-$N(CH_3)_2$	523; 36	122 000	48.2

The PMO prediction is borne out by the data of Table 1. One observes a 98-fold rate increase versus ethyl acrylate and a 14-fold increase towards norbornene in going from p-cyanophenyl to p-dimethylaminophenyl-diazomethane.

The k_2 values for ethyl acrylate are by 10^3 greater than those for norbornene due to the lower LU energy ; a larger energy gain ΔE_I in the creation of the new MOs of the transition state of ethyl acrylate addition causes a higher rate constant (Fig. 2). Why do substi-

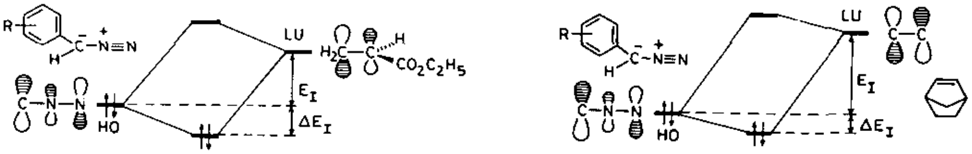
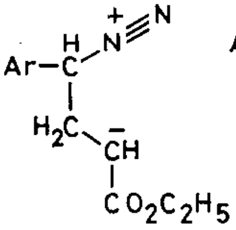


Figure 2

tuents in phenyldiazomethane affect the addition rate to acrylic ester significantly higher than the one to norbornene ? The greater FMO energy separation in the latter case leads to a smaller ΔE_I which is subject to less change than in the case of acrylic ester .

The data of Table 1 fit the Hammett equation with $\rho = -1.52$ (correlation coefficient $r = 0.983$) for ethyl acrylate and -0.83 ($r = 0.955$) for norbornene; they conform well to the early transition state of a concerted cycloaddition.[2] The following arguments speak against a two-step mechanism of these cycloadditions:

1. Diazoalkanes are predominantly nucleophilic; electron-attracting substituents stabilize the ground state. The esters 2 with ethyl acrylate could be formed via the zwitterionic intermediate 1. The observed substituent effect could result from the loss of ground state stabilization; the late transition state should be close to the structure of 1. Although the negative sign of ρ is correct, its absolute size is smaller than expected for 1.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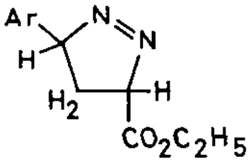
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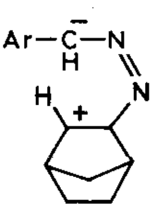
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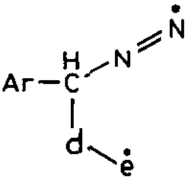
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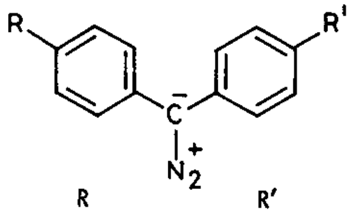
2. In contrast to acrylic ester, norbornene is nucleophilic and would require a zwitterion of type 3. The opposite of the anticipated substituent effect in Ar was observed.

3. The occurence of the diradical intermediate 4 in the combination with a dipolarophile d=e is inconsistent with the structure-rate relation on substituent variation of d=e.[3] Larger ρ values should again account for the suppression of substituent effects of Ar in the genera-

tion of 4. No loss of nitrogen accompanies the cycloaddition.

Table 2. Rate Constants for Cycloadditions of Diaryldiazomethanes to Norbornene in DMF at 25°C (volumetric method)



R	R'	$10^5 k_2$ (l mol^{-1} sec^{-1})
NO_2	NO_2	0.41
NO_2	H	0.61
Cl	Cl	1.42
Cl	H	1.28
H	H	1.13
CH_3O	H	1.68
CH_3O	CH_3O	2.93
$N(CH_3)_2$	$N(CH_3)_2$	2.75 (in cyclohexane)

The cycloadditions of diaryldiazomethanes are somewhat slower than those of aryldiazomethanes. Substituent effects (Table 2) are smaller than in the monoaryldiazomethane series. p-Dimethylaminophenyldiazomethane reacts 5.6 times faster than the p-chloro compound ; the corresponding substituent effect in the diaryldiazomethane series amounts to 1.9. Probably the propeller-like twisting of diaryldiazomethane leads to a weaker ground state conjugation.

REFERENCES

1. R. Sustmann, Tetrahedron Lett., 2717 (1971) ; R. Sustmann and H. Trill, Angew. Chem., Int. Ed. Engl., 11, 838 (1972).

2. R. Huisgen, J. Org. Chem., 41, 403 (1976).

3. J. Geittner, R. Huisgen, and R. Sustmann, Tetrahedron Lett., 881 (1977).

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