

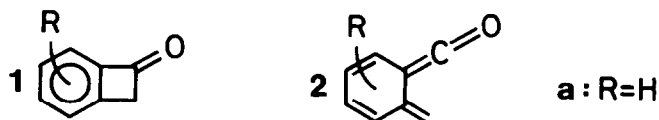
THERMAL ADDITION REACTIONS TO BENZOCYCLOBUTENONES STUDIED BY FLASH PHOTOLYSIS

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Summary: Ortho-quinoid vinylketenes 2 have been generated through flash photolysis of benzocyclobutenones 1. A kinetic study of intermolecular addition reactions of 2 competing with the recyclization 2 → 1 reveals strikingly different substituent effects for the addition of methanol and of dienophiles.

Cycloaddition reactions with vinylketenes have received a great deal of attention in recent years [1]. Benzocyclobutenones 1 which can be prepared efficiently through flash vacuum pyrolysis of 2-methylbenzoyl chlorides [2] are valence isomers of the ortho-quinoid vinylketenes 2. With the aim to engage ketones 1 in thermal cycloaddition reactions we have investigated the reactivity of their valence isomers 2 making use of the fact that these intermediates are also formed by irradiation of the ketones 1 [3].



Upon irradiation of the parent ketone 1a in ether its valence isomer 2a is formed as a light absorbing transient with a lifetime of 170 ms at room temperature [4]. Neither the absorbance of this transient [5] nor its lifetime is affected by careful removal of oxygen through degassing. The first order decay rate constants k_1 observed for 2a and the second order rate constants k_2 for the reaction of 2a with several added trapping agents are reported in Table 1. The transient 2a is rapidly quenched by methanol, the reaction being of first order in 2a but of higher order in alcohol (entry 2 and 3 in Table 1) [6]. In contrast, the reaction of 2a with maleic anhydride is of first order both in 2a and in dienophile. The same second order rate law is assumed to hold for the other examples given in Table 1. Activation parameters have been determined for the intramolecular decay 2a → 1a ($\log A = 11.7$; $E_a = 14.8$ kcal/mol) and for the reaction of 2a with maleic anhydride ($\log A = 7.3$; $E_a = 4.4$ kcal/mol) leading to an isokinetic temperature of 36° for 0.01 M and of 252° for a 1 M solution of dienophile in di-n-butyl ether.

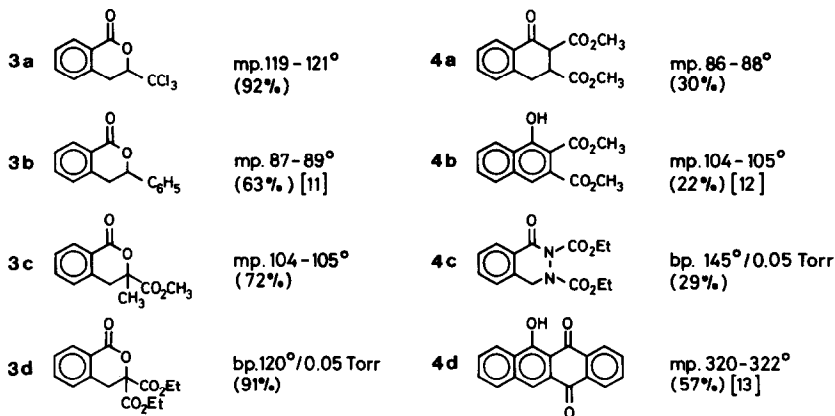
Table 1 Decay of transient 2a formed upon flash photolysis of 1a (0.004 M) in dry ether at 23±1° a).

entry	reagent	conc.	k_1/s^{-1}	$k_2/M^{-1}s^{-1}$
1	none	-	6.0	
2	methanol	1 M	178	
3	"	25 M (neat)	190'000	
4	chloral	0.01 M	133	12'700
5	diethyl mesoxalate	0.01 M	7'800	780'000
6	maleic anhydride	0.005 M	80	14'000 b)
7	" "	0.01 M	125	
8	" "	0.05 M	650	
9	" "	0.10 M	1'470	
10	dimethyl fumarate	1.0 M	189	183
11	dimethyl maleate	1.0 M	13	7
12	ethyl vinyl ether	1.0 M	6.7	1

a) The reproducibility of the observed k-values was ±5%.

b) Averaged value of entries 6 to 9.

Unlike simple ketenes, the intermediate 2a does not react with electron rich olefins such as ethyl vinyl ether (last entry in Table 1). It rather behaves as an electron rich diene system giving adducts with activated carbonyl groups and standard dienophiles. Encouraged and guided by the kinetic data in Table 1 we have succeeded to trap 2a formed thermally from ketone 1a. Thus from equimolar mixtures of 1a with chloral, benzaldehyde, methyl pyruvate, and diethyl mesoxalate upon heating in sealed ampoules at 160° the isocoumarine derivatives 3a - 3d were formed in high yield [8]. Similarly, the cycloadducts 4a - 4d were obtained from 1a at 160° with the following dienophiles: a) dimethyl fumarate, b) dimethyl acetylenedicarboxylate, c) diethyl azodicarboxylate, d) naphthoquinone [9].



In addition to 1a the substituted benzocyclobutenones 1b - 1i [2] have been submitted to flash photolysis. In each case a light absorbing transient of supposed structure 2 was observed. In Table 2 the first order rate constants k_1 for intramolecular cyclisation 2 \rightarrow 1, the pseudo first order rate constants k_1' for the reaction of 2 with 1 M methanol in ether and the second order rate constants k_2 for the addition of 2 to maleic anhydride (MA) in ether are reported.

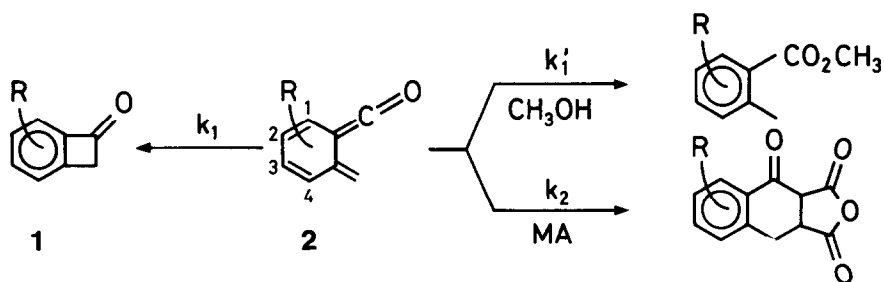
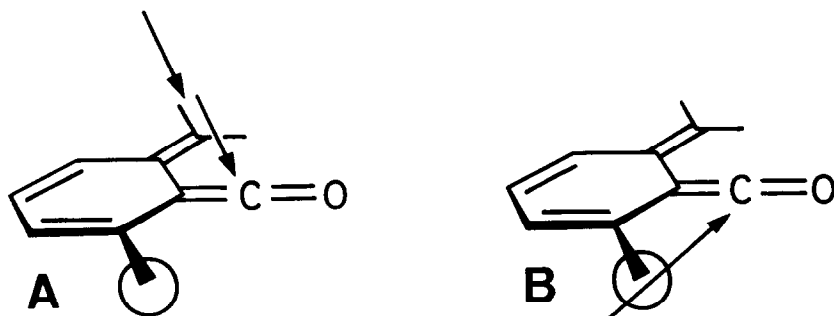


Table 2 Rate constants for the reactions of transients 2 in dry ether at $23 \pm 1^\circ$ (The reproducibility of the observed k -values was $\pm 5\%$).

	substituents				k_1/s^{-1}	k_1'/s^{-1}	$k_2/\text{M}^{-1}\text{s}^{-1}$
	1	2	3	4			
<u>a</u>	H	H	H	H	6.0	172	14'000
<u>b</u>	H	H	CH_3	H	3.9	118	12'000
<u>c</u>	H	H	CH_3O	H	9.9	137	30'000
<u>d</u>	CH_3	H	CH_3	H	6.9	≤ 0.1	17'000
<u>e</u>	CH_3	H	CH_3O	H	17.3	≤ 1	26'000
<u>f</u>	CH_3O	H	CH_3	H	1.2	≤ 0.1	6'000
<u>g</u>	H	CH_3	CH_3	CH_3	97	67	52'000
<u>h</u>	CH_3	CH_3	CH_3	CH_3	283	≤ 10	46'000
<u>i</u>	CH_3O	CH_3	CH_3	CH_3O	11	≤ 0.1	5'000

All intermediates 2a - 2i are reactive toward maleic anhydride while only those lacking a substituent adjacent to the ketene function (2a, 2b, 2c and 2g) show a rate enhancement with methanol. From this we conclude that the approach of the two reagents follows a different stereochemical course: The absence of a substantial substituent effect in the addition of maleic anhydride is in accord with an *out of plane* approach of the reagent according to A. The strong inhibition of the reaction with methanol exclusively by substituents in ortho position to the ketene function indicates a strong preference for an *in plane and exo* approach of the nucleophile according to B.



Differences in intramolecular reactivity (k_1 -values) seem to reflect steric rather than electronic effects, the highest rate being observed with the fully substituted derivative 2h.

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Notes and References

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- [4] A conventional μ s flash photolysis apparatus has been used except for the very short lived transients which have been generated by excitation with a Nd glass laser (353 nm, 50 mJ/pulse, 20 ns).
- [5] The spectrum of the transient intermediate is in agreement with the one observed at 77 K by Hacker and Turro [3b].
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- [9] Recently it has been reported that 4b, 4d, and analogous cycloaddition products are formed from homophthalic anhydride [10]. Our results indicate that 1a/2a are likely intermediates in these conversions.
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