Cyclobutadienyl dications as intermediates in the rapid degenerate rearrangements of 4-halo-1,2,3,4-tetrasubstituted cyclobutenyl cations

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the results of the electron density on the phosphorus atom (e_p), the adjacent carbon atom (e_c) and the net charge of the odd-ligand (q_x) are summarized. With respect to e_c we note that of the compounds which are reactive in the Wittig reaction, 2 has the lowest e_c value. The next lower value of 1.470 occurs in 3, which is unreactive and has the same e_p value as 2. Concerning the e_p values we notice that the largest one belongs to the (unknown) compound 4. At the same time this compound shows a smaller e_c value than the "critical" value of 1.470. Therefore we must conclude that 4 will not react in the Wittig reaction.

Table I Parameters used in the semi-empirical calculations.

orbital	γ_{ii} (eV)	α_{core} (eV)	β_{c-c} (eV)
C_{2p}	11.13	-11.16	-2.32
P_{3d}	6.3	-2.86	

Furthermore, Table II also shows that the percentage of dipolar structure ($\sim$ net odd-ligand charge q_x) cannot be conclusive for reactivity in the Wittig reaction, since 5 has

Table II Calculated electron densities and comparison with reactivities.

compound	e_p	e_c	q_x	reactivity in the Wittig reaction
1	0.389	1.626	—	yes
2	0.255	1.486	-0.809	yes
3	0.257	1.470	-0.800	no
4	0.484	1.418	-0.276	?
5	0.179	1.278	-0.900	no

the largest net odd-ligand charge and is still unreactive. The fact that the e_p value is so much higher in 4 can be understood in terms of aromaticity: 4 has 4 electrons, making it anti-aromatic. This compound will therefore try to reduce the number of electrons in the ring system by donating extra electron density to the phosphorus atom. This phenomenon is in contrast with 5 which has 6 electrons and therefore tries to preserve the electrons in the ring. This is in excellent agreement with the calculated value of 5.9 electrons in the ring.

Cyclobutadienyl dications as intermediates in the rapid degenerate rearrangements of 4-halo-1,2,3,4-tetrasubstituted cyclobutenyl cations

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Abstract. Based on ^{13}C NMR chemical shifts at variable temperatures it is suggested that cyclobutadienyl dications form essential intermediates in the rapid equilibration of 4-halo-1,2,3,4-tetra-substituted cyclobutenyl cations.

Recently¹, we published the ^{13}C NMR spectrum of the 1,2,3,4-tetraphenylcyclobutenyl cation (I). Comparison of the sum of all relevant chemical shifts of I with the reported values of a compound, supposed to be the 1,2,3,4-tetraphenylcyclobutadienyl dication (II) indicated similar amounts of positive charges.

On repeating Olah's original experiment (dissolution of 1,2-dibromo-1,2,3,4-tetraphenylcyclobutene in SO_2ClF/SbF_5 at -60°), we obtained a much better resolved CMR spectrum. The chemical shift of the carbons of the four-membered ring was found at 19.6 ppm*. All phenyl rings were found to be equivalent and showed signals at 44.95, 55.28, 60.88 and 72.41 ppm. These peaks were assigned to the *para*, *ortho*, *meta* and α -carbons, respectively.

Warming this solution to -20° resulted in a down-field shift of the four-membered ring signals by about 9 ppm. This effect was no artifact as was shown by the unchanged positions of the aromatic signals as well as the lock substance with respect to the carrier frequency.

From these results, it appears that at -60° as well as at -20° , we have observed rapidly equilibrating degenerate monobromo cations. At more elevated temperatures ionic contributions (IV) become more important with respect to covalent structures (III). (See scheme).

Scheme 1

Analogous conclusions have been arrived at quite recently by Henrichs and Peterson² in a study of CMR chemical shifts in substituted tetramethylene halonium ions**.

PPP calculations on the tetraphenylcyclobutadiene dication using a symmetrical propeller model in which the phenyl rings are turned out of the plane of the four-membered ring by 45° , yield about 0.3 unit of positive charge on each of the cyclobutadiene carbons. Also taking into account the intrinsic substituent effect of the phenyl ring³, one would

** Detailed application of their equation 1 did not seem to be appropriate in the present case because of the relatively large uncertainties in the substituent effects, exerted by bromine.

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* All shifts were measured relative to $C_2F_4Br_2$ and subsequently transferred to the CS_2 scale.

predict the four-membered ring carbons at -5 ppm relative to CS_2 .

In this respect it might be of interest to reconsider the reported tetramethylcyclobutadiene dication, obtained by warming a solution of 4-chloro-1,2,3,4-tetramethylcyclo-

butenyl cation. The experimental shift at -75° proved to be -14.4 ppm compared with a predicted value of about -35 ppm. In our opinion, the possibility of interconversion between mono- and di-cations cannot be excluded for this case.

Photochemical additions of *o*-quinones and benzil to conjugated alkenynes

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Abstract. Phenanthraquinone (PQ) and tetrachloro-*o*-benzoquinone were added photochemically to the double bond of various substituted alkenynes (1), yielding dihydrodioxin derivatives (2, 5); in some cases oxetane derivatives (4) were isolated too. Generally the photochemical addition occurred non-stereospecifically. Reversible additions of PQ to the double bond were established. Thermal additions of tetrachloro-*o*-benzoquinone occurred with retention of configuration. The photochemical addition of benzil to conjugated alkenynes and to alkenes, however, led to oxetanes (6) only.

Results

9,10-Phenanthraquinone. Irradiation of a solution of 9,10-phenanthraquinone (PQ) with excess of an alkyne (1) in benzene in all cases gave addition to the double bond, generally affording a *cis-trans* mixture of 2-(1-alkynyl)-2,3-dihydro-1,4-dioxin derivatives (2) (see Table I). Addition of PQ to 1-ethynylcyclohexene (H and *cis* $\text{C}\equiv\text{CH}$) even afforded the *trans* adduct (3) as the sole product:

Table I Some results of the photoaddition reactions of PQ^a.

Alkyne 1	Ratio reactants	Adduct	Yield %	m.p. (°C) ^b	Product remarks
$\text{R}^1=\text{R}^2=\text{R}^3=\text{R}^4=\text{H}$	15	2	21	108–109	
$\text{R}^1=\text{R}^4=\text{H}$ $\text{R}^2 + \text{R}^3 = (\text{CH}_2)_4$	2	2 $\equiv$ 3	13	211–212	<i>cis/trans</i> < 0.05
$\text{R}^1=\text{R}^3=\text{R}^4=\text{H}$ $\text{R}^2 = \text{CH}_3$	11	2	50	175–176	
$\text{R}^1=\text{R}^2=\text{R}^4=\text{H}$ $\text{R}^3 = \text{CH}_3$ (<i>cis</i>)	40	2	57	155–156	<i>cis/trans</i> = 4 ^b
$\text{R}^1=\text{R}^2=\text{R}^4=\text{H}$ $\text{R}^3 = \text{OCH}_3$ (<i>cis</i>)	16	2	50	124–130	<i>cis/trans</i> = 1
$\text{R}^1=\text{R}^2=\text{R}^4=\text{H}$ $\text{R}^3 = \text{OCH}_3$ (<i>cis</i>)	16	4	13	137–139	<i>cis/trans</i> = 5

^a Other adducts 2 were obtained from the reaction of PQ with: 1-octen-3-yne: m.p. 209–210°C, yield 11%; 2-hexen-4-yne (*cis* + *trans*): 117–118°C – 21%; 3-hexen-1-yne (*cis* + *trans*): oil – 31% and 4-methyl-3-hexen-1-yne (*cis* + *trans*): oil – 44%

^b 4% of the recovered enyne was isomerized.

^c Melting points given are uncorrected.

¹H-NMR, IR, UV and MS spectral data were in conformity with the structures assigned^{1–6} (see Table II).

Photolyses of PQ with 1-methoxy-1-buten-3-yne and 3-penten-1-yne gave also oxetanes (4) in 13 and 8% yield respectively, as judged from spectral data^{6,7} (see Table II).

In general considerable amounts of chromatographically highly polar material was found, presumably RH adducts^{9–11}, and other hydrogen-abstraction reaction products; these were not investigated. As has been found for some activated alkynes^{12–14} no addition of PQ to the triple bond was observed. Recovery of non-reacted *cis*- or *trans*-1-(methylthio)-3-hexen-1-yne and of *cis*-penten-1-yne in the reaction with PQ showed some *cis-trans* isomerization of the alkyne.

Tetrachloro-*o*-benzoquinone. Irradiation of some alkenynes with tetrachloro-*o*-benzoquinone gave analogous dihydro-1,4-dioxin adducts (5) (see Tables III and IV).

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