

Cyclobutadiene radical cations and 2-azapyrylium ions

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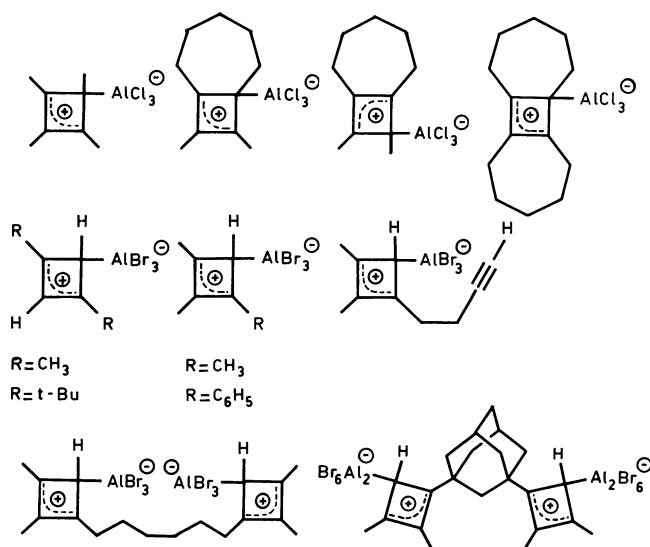
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Abstract - The preparation and structural elucidation of cyclobutadiene radical cations and 2-azapyrylium ions is reported. Both types of species are generated from the readily available σ aluminum halide cyclobutadiene complexes by photolysis and reaction with nitrosyl chloride, respectively. The conformations and configurations of a number of tetraalkyl substituted cyclobutadiene radical cations have been studied by ESR spectroscopy: they are found to be π - and not σ -radicals, and therefore they are the first members of the class of cyclic delocalized 3π -electron systems. Some aspects of the chemistry of cyclobutadiene radical cations are also dealt with. The di-, tri-, and tetraalkyl substituted 2-azapyrylium ions constitute a basically new heteroaromatic system. In some reactions mixtures of isomeric 2-azapyrylium ions are obtained. The structural elucidation is achieved by ^{13}C NMR spectroscopy and X-ray crystallography and a reaction mechanism is presented.

INTRODUCTION

The chemistry of α aluminum halide cyclobutadiene complexes has reached a stage of considerable maturity. Complexes of this kind, which are readily prepared from the appropriate alkynes and Lewis acids in a one-step procedure, react with a large number of substrates to give rise to a remarkable variety of products (ref. 1). The structure of the firstly prepared complex, the aluminum trichloride σ complex of tetramethylcyclobutadiene **1** (AlCl_3) was established unambiguously by X-ray crystallography (ref. 2, 3). The corresponding aluminum tribromide and dialuminum hexachloride and hexabromide complexes have also been prepared and their chemistry investigated (ref. 4). A few representative examples of aluminum halide cyclobutadiene complexes are shown in Scheme 1. "(Note a)"

Scheme 1



Note a: The aluminum halide between parentheses indicates the group which is attached to the cyclobutadiene moiety. The methyl group is represented by a line.

RESULTS AND DISCUSSION

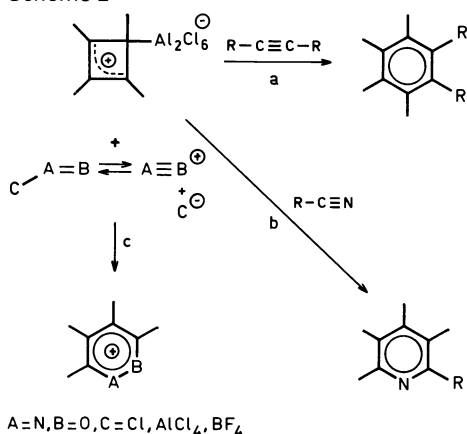
2-Azapyrylium ions

The cycloaddition of aluminum halide σ complexes of cyclobutadienes with carbon-carbon triple bonds and carbon-nitrogen triple bonds leads to benzenes (via isolable Dewar-benzenes) and pyridines, respectively. The scope of the reaction scheme was extended by using positively charged heteroatom-heteroatom triple bonds or "triple-bond equivalents" (covalent compounds of the structure $C-A=B$ in equilibrium with their ionic form $A=B^+C^-$) in order to synthesize existing or new positively charged heteroaromatic ring systems. The results obtained with NO^+ as the heteroatom-heteroatom triple-bond containing species provide 2-azapyrylium ions (Scheme 2, path c), which are heteroanalogues of both pyrylium and pyridinium ions. Surprisingly, no systematic in depth study has been made of these species although a few reports have dealt with this (polyarylated) heterocycle, however without proper structural elucidation (ref. 5, 6).

The best procedure consists of dropwise addition of a standard solution of nitrosyl-chloride in CH_2Cl_2 to a cold ($-70^\circ C$) solution of a dialuminum hexahalide σ complex of a cyclobutadiene, followed by slowly warming to room temperature. The complexes used and the 2-azapyrylium ions obtained (yields 60-85%) are shown in Scheme 3.

The structure of the 2-azapyrylium ions has been established by UV and NMR spectroscopy and by X-ray crystallography. The nearly colourless crystals of the tetrachloroaluminate salt of tetramethyl 2-azapyrylium ion have the bond lengths shown in Fig. 1, which agrees with the canonical structure 1 to be the most important one.

Scheme 2



Scheme 3

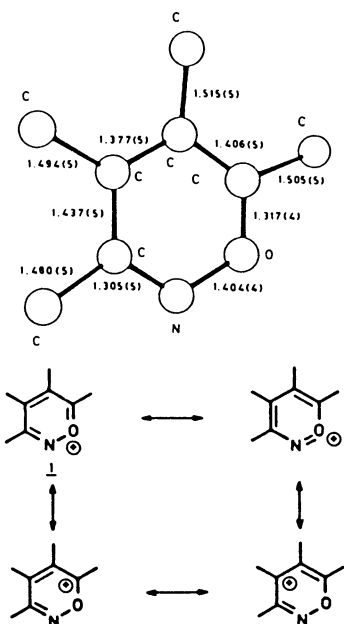
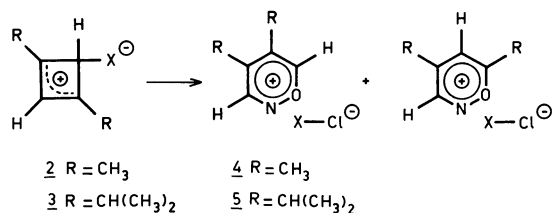
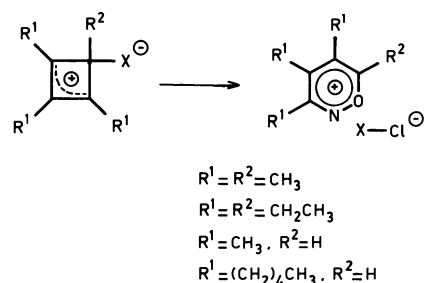
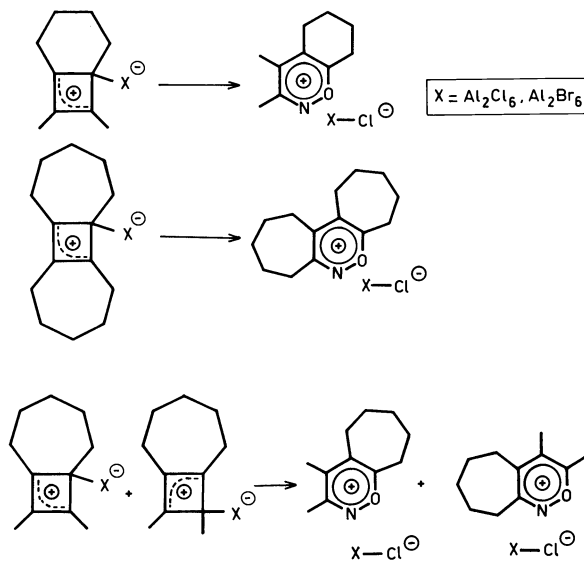


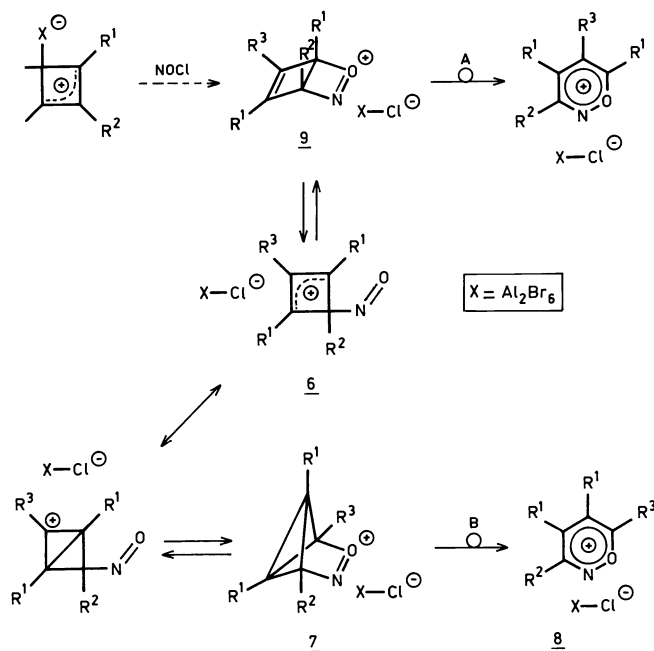
Fig. 1 Bond lengths (Å) and canonical structures of the 3,4,5,6-tetramethyl-2-azapyrylium cation



The UV spectrum of the tetramethyl 2-azapyrylium tetrachloroaluminate shows an absorption at λ_{\max} 270 nm ($\log \epsilon$ 3.92), which strongly resembles those of 1,2,4,6-tetramethylpyridinium-perchlorate (λ_{\max} 268 nm, $\log \epsilon$ 3.87) and 2,4,6-trimethylpyrylium perchlorate (λ_{\max} 285 nm, $\log \epsilon$ 4.08). " (Note b) " A detailed analysis of the ^{13}C and ^1H NMR spectra of the 2-azapyrylium ions (ref. 7) (e.g. the lowest field absorptions of the ring-carbons are 197.5, 180.2 and 156.7 ppm for 3,4,5,6-tetramethyl 2-azapyrylium, 2,4,6-trimethylpyrylium and 1,2,4,6-tetramethylpyridinium ions, respectively) is also in agreement with the conclusion that 2-azapyrylium ions are flat (6π electron containing), aromatic ring systems.

Mechanism of formation. Very remarkably, two isomeric 2-azapyrylium ions are formed in both the reaction of σ complexes 2 and 3 with nitrosylchloride: the substitution pattern of the rearranged ions 4 and 5 differ from the precursor σ complexes in the sense that the alkyl groups are 1,2-positioned in the products and 1,3-positioned in the starting materials. A very recent precedent (ref. 8) for this type of substituent shuffle is available in the reaction of the aluminum trichloride σ complex of 1,3-di-*t*-butylcyclobutadiene with ethylcyanoformate to give ethyl 4,5-di-*t*-butyl-2-picolinate and ethyl-3,6-di-*t*-butyl-2-picolinate. The reaction mechanism shown in Scheme 4 is similar to the one proposed in the case of the isomeric pyridines.

Scheme 4

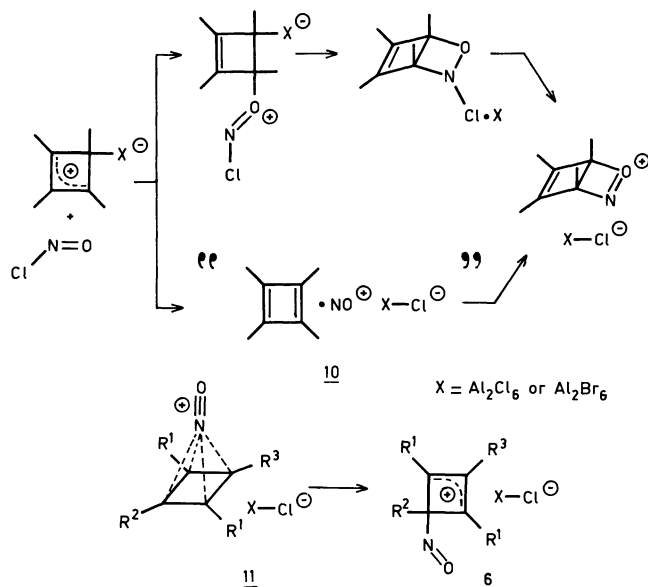


Implicit in this mechanism is the now soundly established fact that the intermediate cyclobutenyl cation 6 has some homocyclopropenium ion character (ref. 3, 9) so that ring closure can lead to the benzvalene-type structure 7, which on aromatization gives the rearranged 2-azapyrylium ion 8. It should be mentioned that structures analogous to the Dewarbenzene type intermediate 9 and benzvalene-type intermediate 7 have in comparable cases been measured by NMR spectroscopy and even been isolated (ref. 10).

It is of interest to speculate about the more intimate details of the first reaction step shown in Scheme 4. A plausible possibility is a Lewis acid-Lewis base reaction between Cl^- of nitrosylchloride and aluminum halide of the cyclobutadiene σ complex with formation of the "cyclobutadiene. $\text{NO}^+\text{X-Cl}^-$ " complex 10, which is redefined in Scheme 5 as a heteroatom substituted pyramidal cation 11; collapse of the latter leads to cyclobutenyl ion 6. As known, pyramidal cations can formally be considered as being the result of the interaction of a positive fragment such as CH^+ as the apex and a 4e system (e.g. cyclobutadiene) as the base of the pyramid (ref. 11). Using the concept of isolobality (ref. 12) CH^+ can be replaced by other fragments such as CO, BH, etc. and because NO^+ is electronic with CO,

Note b: Due to the solvent system used (methylene chloride containing 0.1 M acetic acid anhydride-aluminum trichloride) no measurements below 254 nm could be made and therefore no comparison with the short wavelength absorptions of the pyridinium and pyrylium ions.

Scheme 5



it might also be considered as isolobal. Very recently the relevant orbital energies of NO^+ and CO have been reported (ref. 13); it can be concluded that the stabilizing interaction for a pyramidal structure, i.e. the interaction between the LUMO of NO^+ and the HOMO of cyclobutadiene is stronger than for CO with cyclobutadiene (ref. 7). It is suggested therefore that the pyramidal cation 11 is more likely to exist than the long-sought pyramidal cyclobutadiene-CO complex. The interaction diagram of NO^+ with cyclobutadiene is shown in Fig. 2.

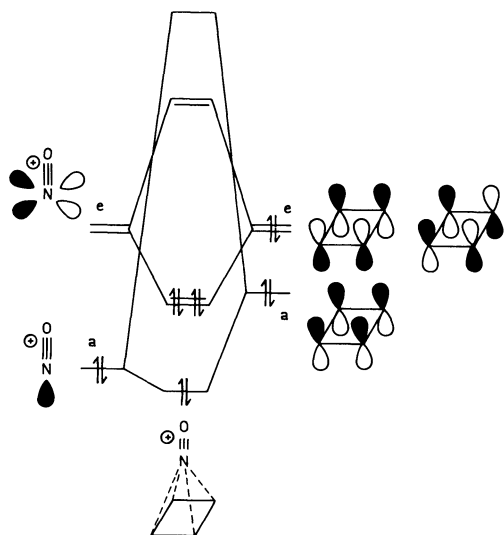
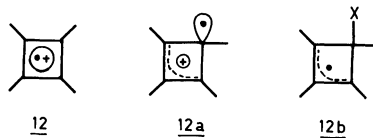


Fig. 2 Interaction diagram of NO^+ with cyclobutadiene.

Scheme 6



Cyclobutadiene radical cations

The dynamic process in aluminum trichloride σ complexes of peralkylated cyclobutadienes, involving consecutive 1,2-shifts of the aluminum trichloride moiety along the cyclobutadiene ring, is caused by thermal splitting of the carbon-aluminum bond (ref. 14). A photochemically induced homolysis of the carbon-aluminum bond has also been discovered some years ago (ref. 15) and constitutes the basis of the synthesis of cyclobutadiene radical cations. In principle one can conceive of three reasonable structures for the radical species that is generated by photolysis of the aluminum halide σ complex of e.g. tetramethylcyclobutadiene: the π -radical 12, the σ -radical 12a and the β -X substituted cyclic allyl radical 12b (X being unknown), Scheme 6; in the latter two cases rapid equilibration processes must occur in order to account for the symmetry of the ESR spectrum (ref. 16). Possibility 12b has been excluded by recording the ESR spectrum of the radical

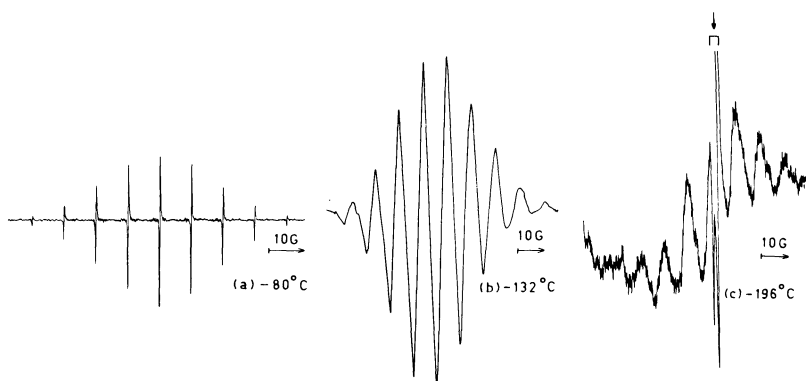


Fig. 3 ESR spectra of the tetramethylcyclobutadiene radical cation at various temp. (The arrow points to a paramagnetic impurity in the Dewar).

species at -80° , -132° and -196°C and although the solid-phase spectra are somewhat broadened, it is clear that the hfs (a_{H} (12H) = $8.75 \pm 0.05\text{G}$) and the symmetry of the ESR spectrum remain unchanged in this temperature range (Fig. 3). It is concluded that the species is intrinsically symmetrical because an equilibration process for 12b (and probably also for 12a) is very unlikely to be rapid on the ESR time scale at -196°C . The structure 12a was excluded by measuring the ^{13}C hfs's in the case of the tetraethylcyclobutadiene radical cation (which could not be done in the case of the tetramethyl derivative due to low persistence at -80°C ; vide infra) being 3.7, 4.4 and 5.0 G. Although we are unable to assign the different hfs's to the ring, α or β carbon atoms, all three values are small and near the value of 3.83 G predicted by the Yonezawa-Kawamura-Kato equation for the cyclobutadiene radical cation (ref. 17). For a σ radical of type 12a a value of 22-30 G is expected for the ring carbon hfs (ref. 18). In conclusion, tetraalkyl-substituted cyclobutadiene radical cations are π - and not σ -radicals. Tentative explanations for the difference in electronic nature between cyclobutadiene radical cations (π -radicals) and cyclopropenyl radicals (σ -radicals) have recently been given (ref. 19).

The persistence of alkyl substituted cyclobutadiene radical cations strongly depends on the method of generation and the size of the alkyl substituents. For example, photolysis of a separately prepared aluminum trichloride σ complex of tetraethylcyclobutadiene (method A, ref. 15, 16) and photolysis of a mixture of alkyne (3-hexyne) and aluminum trichloride (method B, ref. 20) both lead to the tetraethylcyclobutadiene radical cation, the persistence being at least a factor of 60 larger (at -55°C) in favour of method A. Tetraneopentyl and tetra-1-adamantyl cyclobutadiene radical cations can only be prepared via method B; the preferred conformation 13 of the former species is shown in Fig. 4.

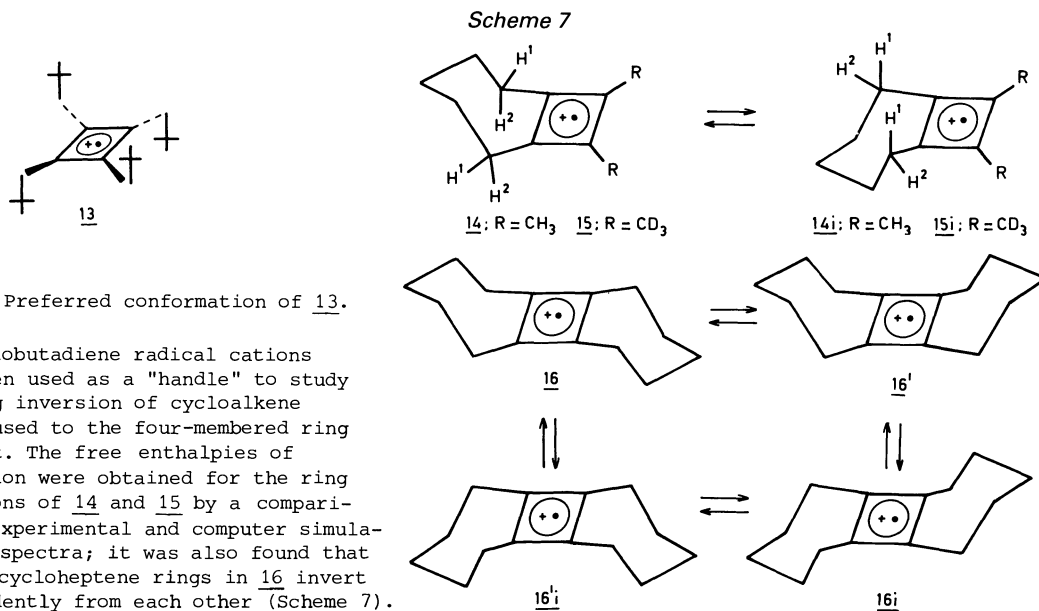
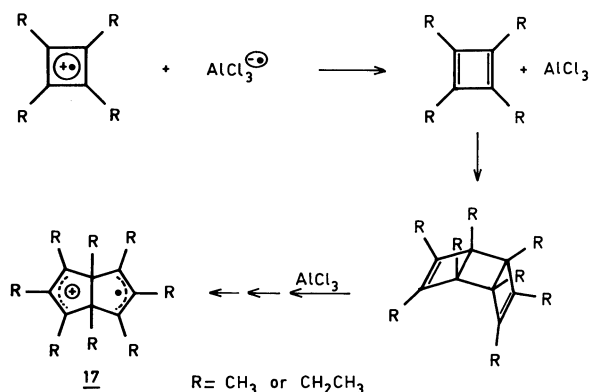


Fig. 4 Preferred conformation of 13.

The cyclobutadiene radical cations have been used as a "handle" to study the ring inversion of cycloalkene rings fused to the four-membered ring fragment. The free enthalpies of activation were obtained for the ring inversions of 14 and 15 by a comparison of experimental and computer simulated ESR spectra; it was also found that the two cycloheptene rings in 16 invert independently from each other (Scheme 7).

The cyclobutadiene radical cations (prepared by method A, *vide supra*) decay thermally to secondary radical cations. The structure of these species was shown to be the dimeric radical cation 17 ($R = \text{CH}_3$) (ref. 19, 21) and the decay process found to be second-order ($R = \text{C}_2\text{H}_5$). A possible mechanism is shown in Scheme 8. Results of preliminary preparative photolysis and electrolysis experiments on the aluminum chloride σ complex of tetramethylcyclobutadiene are in agreement with the proposed structure of the dimeric radical cations.

Scheme 8



Finally, it should be pointed out that the cyclobutadiene radical cations constitute not only examples of cyclic delocalized 3π -electron systems but they also fill the gap between known 2π (the dications of cyclobutadienes) and 4π (the cyclobutadienes) electron systems in the four-membered ring series.

ACKNOWLEDGEMENT

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