Tetrahedron Letters No. 40, pp 3491 - 3494, 1975. Pergamon Press. Printed in Great Britain.

STABLE RADICAL DICATIONS

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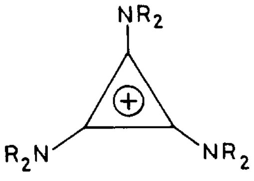
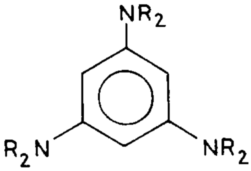
(Received in UK 21 July 1975; accepted for publication 22 August 1975)

While organic radical cations have frequently been generated in solution or even isolated, very little is known about (mono-)radical <u>di</u>cations[1]. This is understandable since generation of such a species necessitates removal of an electron from a positively charged closed-shell precursor which would not normally possess a high-lying HOMO.

Trisamino-cyclopropenium ions **A** are remarkable exceptions to this rule as indicated by a comparison of calculated HOMO-levels of **A** and **B**:



A



B

E^{HOMO}: $\alpha + 0.38\ \beta$[2)]

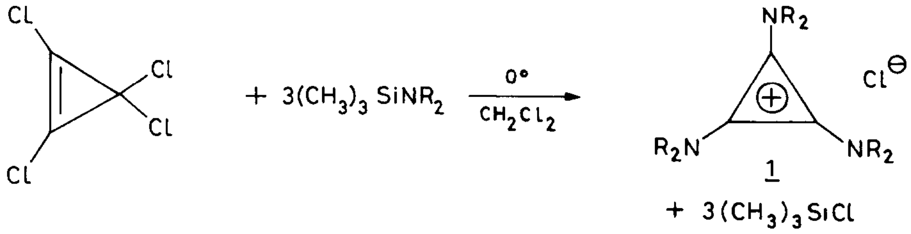
E^{HOMO}: $\alpha + 0.45\ \beta$[2)]

It can be seen that within HMO-approximations the highest occupied orbital of **A** falls within the same energy range as the degenerate HOMOs of neutral **B** which notoriously behaves as an electron-rich and highly oxidizable compound[3)].

By ESR-measurements Gerson and Yoshida were indeed able to show[1)] that a representative of **A** ($R=CH_3$) could be oxidized electrochemically to a deep red radical dication. However, under their reaction conditions this species proved elusive and could not be isolated and characterized further.

We now report a convenient and high-yield synthesis of the first stable tris-dialkylamino-cyclopropenium radical dications. Our procedure involves two steps starting from commercially available tetrachlorocyclopropene:

a) Synthesis of tris-dialkylamino-cyclopropenium chlorides according to (1):



(1)

a) R = CH_3 b) R = C_2H_5 c) R = $\text{-}(CH_2)_2\text{-}$

Recently, Yoshida synthesized several tris-dialkylamino-cyclopropenium salts by reaction of tetrachlorocyclopropene with secondary amines[5]. The new exchange procedure (1) offers considerable advantages over this conventional method:

(i) the reaction proceeds, like a titration, instantaneously and quantitatively

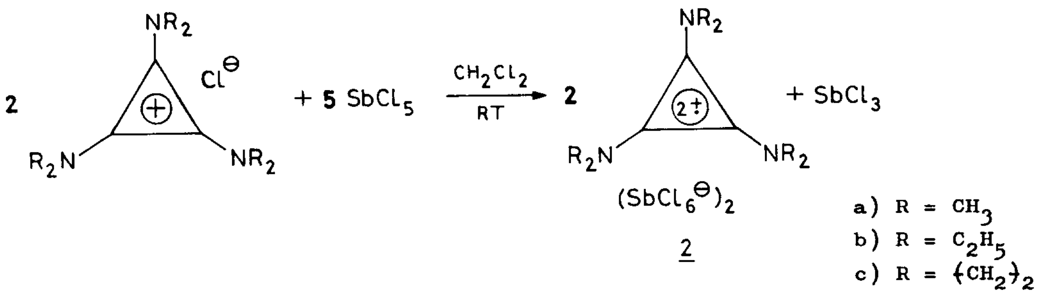
(ii) work-up is greatly facilitated and simply consists in precipitation of 1 with Et_2O or, alternatively, removal of CH_2Cl_2 and $(CH_3)_3SiCl$ i.V.

(iii) salts 1 are obtained in anhydrous form which is important for the oxidation step to follow (c.f. below).

(iiii) Finally the successful synthesis of 1b (and a number of further examples[4]) - inaccessible by Yoshida's route[5,6] - indicates the <u>superior scope</u> of reaction (1).

Salts 1a-c all show intense broad IR-bands at 1540 cm^{-1} which are highly characteristic of tris-dialkylamino-cyclopropenium salts[5]. Above 200° they can be volatilized into a mass spectrometer and give simple spectra with the corresponding tris-dialkylamino-cyclopropenium ions as parent peak (c.f. table I).

b) In the second step cpds. 1 are oxidized according to (2):



a) R = CH_3
b) R = C_2H_5
c) R = $\text{-}(CH_2)_2\text{-}$

Thus, addition of $SbCl_5$[7] to solutions of anhydrous[8] salts 1 in abs. CH_2Cl_2 precipitates analytically pure radical dications 2 as brick-red microcrystals in yields > 90% (c.f. table I). Cpds. 2 are stable in the atmosphere for at least several hours but gradually decompose in the course of weeks so that only freshly prepared samples should be used for experimental purposes.

Apart from a small bathochromic shift of the characteristic ring vibration[5] the IR-spectra (KBr) of radical dications 2 are virtually identical with their precursor salts. Due to the unpaired electron NMR-signals of 2 are broadened beyond detection in CD_3CN. After addition of Zn to these solutions their red color vanishes and the NMR-spectra of 1 are observed.

The characteristic red color of radical dications 2 is due to an intense UV-absorption at 500-540 nm (c.f. scheme I). MO theory predicts that this absorption should arise from allowed transitions between the degenerate substituent orbitals (e") to the half-occupied HOMO of a_2" symmetry (c.f. also loc. cit. 1)).

Table I

Physical data of compounds 1 - 2

cpd.	mp. °C	IR[a] (cm^{-1})	UV λ_{max} (log ε) (nm)	NMR[d]	MS (70 EV)
1a	128	1540	235[b] (4.25)	6,78 (s)	168 (M^+-Cl); base peak
1b	oil	1535	236[b] (4.21)	6,50 (q) 8,70 (t) ratio 2:3	252 (M^+-Cl); base peak
1c	oil	1540	242[b] (4.30)	6,48 (m) 7,97 (m) ratio 1:1	246 (M^+-Cl); base peak
2a	169 (dec.)	1565	508[c] (qual.)		
2b	133 (dec.)	1550	521[c] (qual.)		
2c	130 (dec.)	1550	532[c] (qual.)		

a) characteristic ring vibration
b) measured in CH_2Cl_2
c) measured in CH_3CN. Because of rapid decomposition in this solvent the precise extinction could not be determined
d) measured in $CHCl_3$

The ESR-spectrum of 2a was also measured in CH_3CN[9] and shown to be identical with the spectrum recorded by Gerson et.al.[1] thus confirming their structural assignment.

By virtue of their twofold positive charge and their half-occupied HOMO radical dications of type 2 may be expected to complex with various nucleophiles and electronrich compounds. This intriguing aspect has already received partial experimental support and will be particularly emphasized in our future work.

Acknowledgement:

Stimulating discussions with Dr. W. Schmidt and the experimental contributions of C. Schlierf and W. Schmucker are gratefully achnowledged.

Notes and References

1) F.Gerson, G.Plattner and Z.Yoshida, Mol.Phys. 21 (6), 1027 (1971).
2) Assuming $\alpha_N = \alpha + \beta$[1].
3) *For leading references see P.Menzel and F.Effenberger, Angew.Chem.* 87, 71 (1975).
4) Further applications and experimental details will be reported in a forthcoming full paper.
5) Z.Yoshida, Topics in Current Chemistry 40, 47 (1973).
6) The reaction stops after exchange of two chlorines[5].
7) After conversion of salts 1 to the corresponding fluoborates oxidation is equally well effected by (excess) Br_2, $NOBF_4$ and NO_2BF_4 in CH_2Cl_2.
8) Salts 1 are hygroscopic and should be sheltered from atmospheric moisture. Otherwise reaction (2) may yield impure products because of partial hydrolysis of $SbCl_5$.
9) We thank Dr. G.Neugebauer, Max-Planck-Institut für medizinische Forschung, Heidelberg, for measurement of this spectrum.