A Dialkylideneammonium Cation analogous to an Allene

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WE here describe some salts containing a new class of cation, $[R_2C:N:CR_2]^+$, formally analogous to allenes[1] $R_2C:C:CR_2$.

An interesting relationship exists between unsaturated organic compounds and cations formally derived from them by replacing a multiply-bonded carbon atom by a positively charged nitrogen, *e.g.* between alkynes $RC\vdots CR$ and nitrilium cations[2] $[RC\vdots NR]^+$, or alkenes $R_2C:CR_2$ and imonium cations[3] $[R_2C:NR_2]^+$. Such cations apparently have the same shape and essentially the same bond multiplicity as the isoelectronic carbon compound, even though in principle the skeletal bond order could be lowered, and the shape at nitrogen changed, by contributions from carbonium ionic forms such as $R\overset{+}{C}{=}NR$ or $R_2\overset{+}{C}{-}NR_2$.[4]

The compounds $Ph_2C:N:CPh_2{}^+BCl_4{}^-$ (decomp. 125—140°) and $Ph_2C:N:CPh_2{}^+SbCl_6{}^-$ (m.p. 158—162° with decomp.) separated immediately (as oils, which when washed with toluene and hexane and pumped dry gave microcystalline powders) from reactions at 20° between toluene solutions of BCl_3 (or $SbCl_5$; 1 mol.) and $Ph_2C:NCClPh_2$ (1 mol.). $Ph_2C:NCClPh_2$ (m.p. 183—186°) is itself a new compound which was prepared from $Ph_2C:NLi$[5] and Ph_2CCl_2 in refluxing benzene during 12 hr., and recrystallised from toluene–hexane. The tetrachloro-aluminate $Ph_2C:N:CPh_2{}^+AlCl_4{}^-$ (decomp. 140—160°) was prepared similarly from $AlCl_3$ and $Ph_2C:NCClPh_2$ in benzene or toluene at 60—70° for 1 hr. The empirical formulae of the dialkylideneammonium salts were confirmed by elemental analyses, and their ionic constitutions by the molar conductivities[6] (24—27 $cm.^2\Omega^{-1}mole^{-1}$) of their M/1000 solutions in $PhNO_2$. Their i.r. spectra at frequencies above *ca.* 800 $cm.^{-1}$ were nearly identical, with the most significant band a moderately strong absorption centred at 1845 $cm.^{-1}$, which we assign to the skeletal stretching vibration $\nu_{C:N:C}$. Differences below 800 $cm.^{-1}$ could be attributed to vibrations of the anions. A structure $Ph_2C:N{\cdot}\overset{+}{C}Ph_2$, with only one double C:N bond, might have been expected to absorb near 1600 cm.$^{-1}$ ($\nu_{C:N}$), as does the covalent intermediate $Ph_2C:NCClPh_2$. The skeletal stretching frequencies may be compared with $\nu_{C=N=B}$ at 1786 cm.$^{-1}$ for the isoelectronic $Ph_2C=N=BPh_2$,[7] $\nu_{C:C:C}$ at at 1950—1970 cm.$^{-1}$ for allenes $R_2C:C:CR_2$,[8] $\nu_{C:C:N}$ at 1998 cm.$^{-1}$ for the ketimine $Ph_2C:C:NMe$,[9] and $\nu_{N:C:N}$ at 2128—2152 cm.$^{-1}$ for carbodi-imides $RN:C:NR$.[8]

Our compounds are, we believe, the first examples of a cation $R_2C:N:CR_2^+$ isoelectronic with allenes and containing linearly co-ordinated nitrogen. Their co-ordination chemistry, currently being explored, is expected to be of interest in view of the diversity of the modes of interaction of allenes[1,10] and their analogues[9] with transition elements, and in view of the interest of ligands with a formal positive charge.[11]

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