complex, VI, of unknown stereochemistry was isolated.[19] Application of the SST technique to the measurement of the 1,3 iron shift in VI gave the results summarized in Table I. Surprisingly, $\Delta G^{\ddagger}$ (23.9 kcal/mol) for iron migration is slightly greater for this compound than for I. Although significant lowering of the $\Delta G^{\ddagger}$ might have been anticipated for VI relative to I if the norcaradiene mechanism obtains (Scheme II), we feel that these results do not necessarily rule out a possible norcaradiene intermediate for this fluxional process. If, for example, the phenyl group is exo to iron in VI, then steric interactions of the phenyl group with the cyclohexadiene unit in the norcaradiene-like transition state may offset any electronic stabilization of the transition state owing to the C_7 substituents.[18]

Although the detailed mechanism of the 1,3 iron shift cannot be precisely specified for I, it is clear from these results that activation energies for 1,3 iron shifts are higher than those for 1,2 iron shifts in cyclic polyene and polyenyl complexes. ($\Delta G^{\ddagger}$s range from ~7 kcal for $C_8H_8Fe(CO)_3$[20] to ~15 kcal for (η^3-C_7H_7)Fe(CO)(η^5-C_5H_5).[2]) The results obtained in this study and those reported by Mann[7c] demonstrate that spin saturation transfer is a very useful technique for studying relatively "slow" fluxional organometallic systems where thermal sensitivity of the complex precludes the use of standard line-broadening techniques at higher temperatures. Indeed, for these cycloheptatrieneiron tricarbonyl complexes, line broadening would have been observable by ^{1}H NMR only above 140 °C where decomposition is quite rapid.

We are currently applying the spin saturation technique to other organometallic systems which are expected to exhibit fluxional processes with high activation energies.[21]

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(7) An exception appears to be the $C_8H_8M(CO)_3$ systems (M = Cr, Mo, W). Cotton[7b] has reported that the ^{13}C resonances of the ring carbons in this compound broaden and collapse at the same rate—a result consistent only with 1,3 shifts or a random process. More recently, using spin saturation transfer Mann has shown that, for $C_8H_8Cr(CO)_3$, the migration of Cr occurs predominantly by 1,3 shifts, with a possible minor 1,3 component.[7c] (b) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Am. Chem. Soc.*, **96**, 4723, 7926 (1974). (c) B. E. Mann, *J. Chem. Soc., Chem. Commun.*, 626 (1977).
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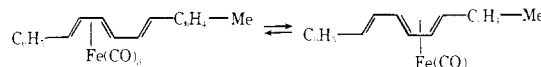
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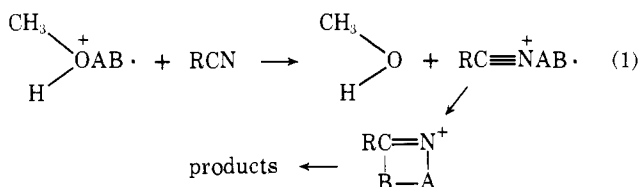
Received October, 17, 1977.

Design of an Ion–Molecule Reaction Specific for Neutral Nitriles

Sir:

Only a few ion–molecule reactions have been observed which are so characteristic of a neutral functional group that the reaction may be used to identify the group. The classical examples of these are the reactions of ionized butadiene with olefins;[1] the metathesis of substituents between ionized and neutral olefins,[2] which may be used to locate double bonds;[3] and the reactions of trihalomethyl cations with neutral carbonyl compounds.[4] Reactions which distinguish between epimers because of their specificity for less hindered isomers[5] are related to this category.

A reaction specific for nitriles was designed as follows. Transfer, not simple addition, pathways are more effective ion–molecule reactions at low pressures. Proton transfers are the best understood transfers. The proton affinity of acetonitrile is 5 kcal/mol greater than that of methanol,[6,7] and, for reasons paralleling those adduced for series of nitrogen-containing[8] and triply-bonded[9] compounds, the proton affinities of nitriles with larger alkyl substituents are greater.[6,7] Thus proton transfer from methanol to all nitriles should be observed, but of course proton transfer is not specific. Since methyl cation affinities have similar trends as proton affinities, with clear exceptions which bound the analogy,[10] we examined other alkyl cations. While a positively charged atom is the primary reaction site in ion–molecule reactions, to create specific reactivity for a functional group, it is necessary to introduce another reaction site into the alkyl group. We chose a radical site. A radical site has little influence on electronic effects of alkyl groups, for the electronic effects of C_2H_5 and C_3H_7 are very similar to those of the analogous radicals from which a hydrogen atom has been removed, $\cdot C_2H_4$- and $\cdot C_3H_5$-, in at least one series of compounds.[11] The most desirable location of the radical site is adjacent to carbenium carbon, for this will permit four-center reactions with the nitrile group; rapid four-center reactions are common; and there is precedent for involvement of triply bonded atoms in a four-center reac-

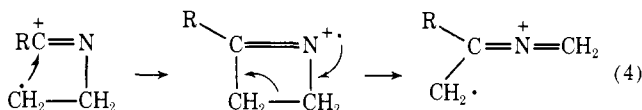tion.[12] The proposed reaction must therefore fit the outline of eq 1.

$$CH_3\!\!>\!\!\overset{+}{O}AB\cdot \; + \; RCN \; \longrightarrow \; CH_3\!\!>\!\!O \; + \; RC\!\!\equiv\!\!\overset{+}{N}AB\cdot \quad (1)$$

$$\text{products} \; \longleftarrow \; \overset{RC\!=\!\overset{+}{N}}{\underset{B\!-\!A}{\big|\;\;\big|}}$$

The simplest model of the reagent ion is the m/z 60 ion produced by loss of CH_2O from 1,2-dimethoxyethane (eq 2).[13]

$$CH_3\overset{+}{O}\cdot \;\cdots\; \longrightarrow \; CH_3\!\!>\!\!\overset{+}{O}CH_2CH_2\cdot \; + \; CH_2O \quad (2)$$
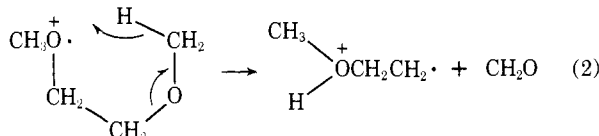
In experiments using a modified Varian 5900 ion cyclotron resonance spectrometer, a range of simple aliphatic nitriles up to C_6 and aromatic nitriles without other functional groups was studied. Labeling experiments confirm the transfer of the central ethylene unit (eq 3). However, it does not transfer

$$RCN \; + \; CH_3\!\!>\!\!\overset{+}{O}CD_2CD_2\cdot \; \longrightarrow \; RCNC_2D_4^{+}\cdot \; + \; CH_3OH \quad (3)$$
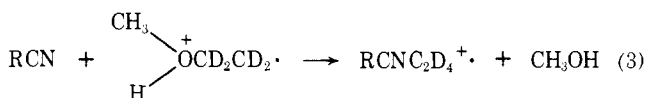
$C_2H_4^{+}\cdot$ to any alkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, ethers, acids, esters, ketones, aldehydes, amines, Schiff bases, alkyl halides, sulfides, sulfoxides, sulfones, isonitriles, thiocyanates, isothiocyanates, cyanates, or nitro compounds which we have examined,[14] except for a slow reaction with acetone observable above 10^{-5}-Torr pressure which is not paralled by reactions with other ketones. This reaction is at least an order of magnitude slower than the reaction with nitriles. We estimate the latter as being on the order of 8 × 10^{-10} cm^3/molecule s, that is, reaction after most collisions. The reaction is sometimes faster than proton transfer and, within the compounds studied, never less than one fourth as rapid; it will be interesting to study nitriles containing other functional groups. This specificity and facility indicate that further internal reaction with the nitrile function probably leads to an easily accessible, stable product ion isomeric with the initially formed M + 28 ion. An obvious choice is shown in eq 4; in it the product is stabilized by formation of both a

$$\overset{+}{RC}\!\!=\!\!N \; \longrightarrow \; \overset{R}{\underset{CH_2\!-\!CH_2}{\big\backslash}}C\!\!=\!\!N^{+}\cdot \; \longrightarrow \; \overset{R}{\underset{CH_2\cdot}{\big\backslash}}C\!\!=\!\!\overset{+}{N}\!\!=\!\!CH_2 \quad (4)$$

center analogous to the $CH_2\!\!=\!\!N^{+}\!\!=\!\!CH_2$ ion observed in the spectra of appropriate amines[15] and also an allylic radical. Since the ion is stable to other ion-molecule reactions in mixtures of nitriles and 1,2-dimethoxyethane, this postulation remains only speculation for the moment.

We have demonstrated here that the body of information[16,17] on ion-molecule reactions has become sufficiently large that one can apply the chemistry to the *design* of specific ion-molecule reagents. In the future it will be possible to expand the collection of these reagents to confirm structural detail of new molecules by mass spectrometric analysis using specifically designed ion-molecule reactions.

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Characterization of Surfactant Vesicles as Potential Membrane Models. Effect of Electrolytes, Substrates, and Fluorescence Probes

Sir:

This communication reports properties of surfactant vesicles, prepared from aqueous dioctadecyldimethylammonium chloride (DODAC)[1] dispersions by sonication, which render them to be the simplest functional membrane model investigated to date.

Sonication dispersed DODAC initially to a turbid and ultimately to an optically transparent solution.[3] In agreement with analogous recent data,[2,4,5] electron micrographs[6] confirmed the presence of closed vesicles. The turbid solution, obtained by sonicating the DODAC dispersion for 30 s,[3] contained bilayer vesicles of 2500–4500 Å in diameter. The optically transparent solution, obtained by sonicating the DODAC dispersion for 15 min,[3] consisted of single compartment vesicles whose diameter, read off from electron micrographs, ranged between 1000 to 1500 Å.[7] All of the experiments described below were carried out on optically transparent solutions of single compartment 1000–1500-Å-diameter bilayer DODAC vesicles.

Aqueous solutions of DODAC vesicles were found to be stable for weeks in room temperature. Absence of unsaturated carbon atoms in the surfactant obviates degradation, a common problem with liposomes.[10] Surfactant vesicles, like liposomes,[10] were lysed upon the addition of 80% alcohol. Effects of electrolytes, however, were found to be more pronounced on surfactant vesicles than on liposomes. Sonication of the "typical" DODAC dispersion[3] in 0.10 M NaCl, for example, resulted in gel formation. Turbidity and subsequent flocculation in 0.10 M NaCl was observed even when the amount of DODAC was reduced by almost tenfold (i.e., 1.5 mg of DODAC in 2.0 mL of 0.10 M NaCl). Conversely, *diluted surfactant vesicles* (fourfold dilution of the "typical preparation"[3] by distilled H_2O) remained stable, albeit turbid, in 0.10 M NaCl. Analogous behavior has been observed for other electrolytes. Increase in turbidity upon the addition of electrolytes corresponds to osmotic shrinkage of the vesicles. It appears, however, that the range of electrolyte concentration