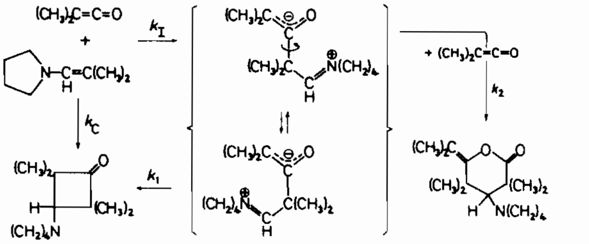
In contrast, the additions of TCNE to anthracene [4] and related Diels–Alder reactions show only a minute solvent dependence. The same is true for 1,3-dipolar cycloadditions of diazoalkanes [5], phenyl azide [6], C-phenyl–n-methylnitrone and azomethine imines to various dipolarophiles. These concerted cycloadditions are characterized by early transition states, *i.e.*, there is hardly any change of solvation energy during the activation process.

A dichotomy of reaction paths was found for diazocarbonyl compounds and enamines. Whereas dialkylaminocyclohexenes produce cycloadducts, the corresponding enamines containing the cyclopentene ring undergo azo coupling which furnishes enaminohydrazones *via* a zwitterionic intermediate. The contrasting dependence of rate on solvent polarity supports different mechanisms [7].



Dimethylketene combines with N-isobutenylpyrrolidine to give a 3-pyrrolidinocyclobutanone as 1:1 adduct and a δ-methylene-δ-lactone as 2:1 adduct. The dependence of the product ratio on the concentration of dimethylketene allows to disentangle a concerted pathway and a rection *via* a zwitterionic intermediate which can be intercepted by a second molecule of dimethylketene (see formula Scheme) [8]. The different solvent dependencies of the two reaction branches confirm the mechanistic divergence.

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Cryptate Inclusion Complexes and the Regulation of Solute–Solvent Interactions

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The uptake of an ion into the intramolecular cavity of a hollow cryptand molecule may greatly affect the properties of *both* the cryptated ion and its counterion.

The resulting *lipophilisation* of one of the ions renders salts soluble in media in which they are otherwise insoluble.

Protection of the cryptated species modifies its physicochemical properties and its chemical reactivity.

Activation of the uncomplexed ion may be produced, which strongly affects its chemical reactivity.

These three major effects, lipophilisation, protection, activation, all result from/in a modification of the solute–solvent interactions experienced by the ionic species subjected to cryptation.

This talk will survey the results of some of the numerous studies which have demonstrated and made use of these effects, covering *inter alia*:

(*a*) physico-chemical properties of cation cryptates;

(*b*) the use of cryptate cations as counterions in X rays studies, solutions of metal anions and clusters *etc.*;

(*c*) cation participation in reaction mechanisms;

(*d*) anion activation in strongly basic systems, in rate and orientation of anionic reactions, in molecular rearrangements, in anionic polymerisation *etc.*

A further consequence of lipophilisation is the use of cryptands as *carriers* in membrane transport phenomena.

When available, comparisons with corresponding crown type or other complexes will be made.