STUDIES ON SOME ORGANOPHOSPHORUS COMPOUNDS

BY

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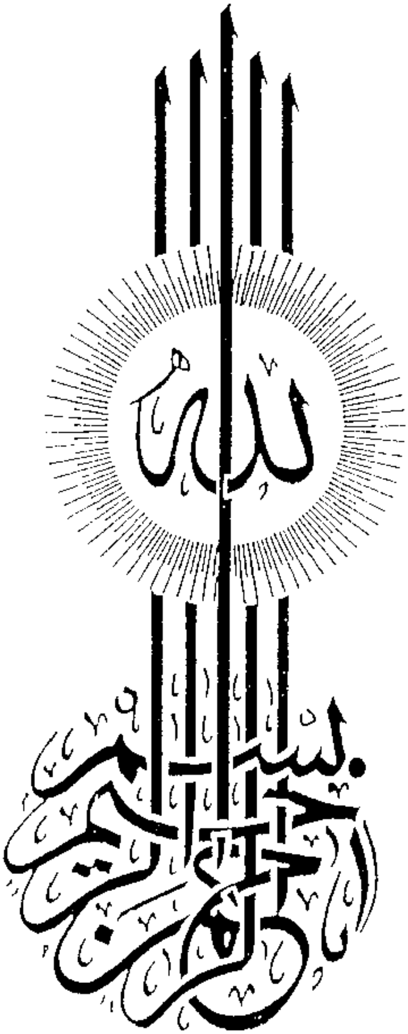
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Synthesis of some oxaphosphetanes via Wittig's Reaction

SUMMARY

Charge transfer complexes between triphenylphosphine, triethylphosphite as donor and maleic, itaconic and citraconic anhydrides as acceptor are studied.

These complexes have been followed up using both the i.r and the U.V spectra.

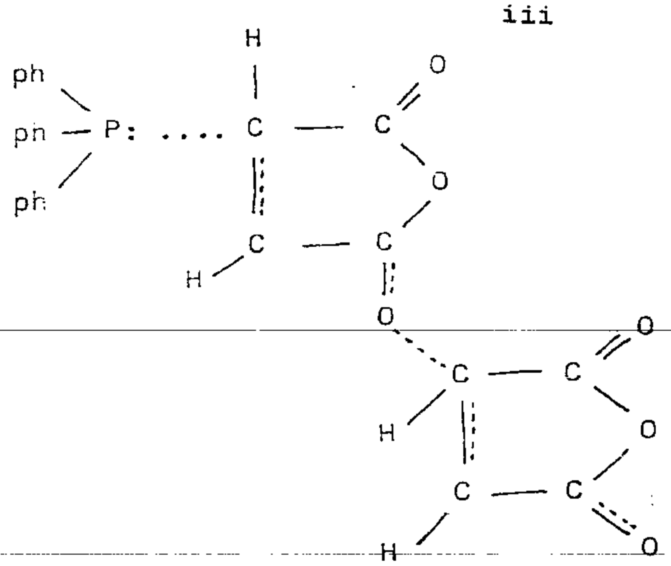
In the IR measurements, maleic, itaconic and citraconic anhydrides are used as acceptors, and triphenylphosphine as donor (Fig. 3). Both maleic and itaconic anhydrides give intermediate colour complexes (red shift). However, citraconic anhydride failed to give any colour.

The U.V spectra have been used to verify the equilibrium constant (K) as well as ratio of donor to the acceptor using modified Bensi-Hildebrand equation.

In the case of triphenylphosphine the maximum absorption, Fig. (4) and Fig. (5) shows a clear maximum at 0.4 (1/ D). This indicates that ratio of A:D is 2:1. Citraconic anhydride proved to be inactive in our hands as confirmed by i.r and U.V spectra.

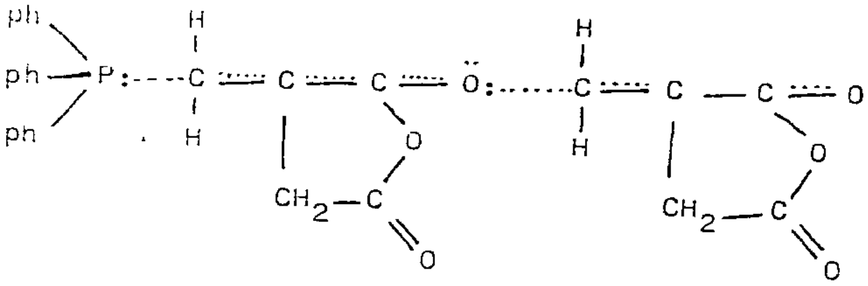
In the case of triethylphosphite (D), maleic and itaconic anhydride (A), the maximum absorption (Fig. 10) and (Fig. 16) shows a clear maximum at 0.7 (1/ D). So the ratio of A:D is reversed i.e the complex can be formed as D_2A.

It is clear that in the case of triphenyl phosphine the complex is DA_2, while in the case of triethylphosphite the ratio can be safely written DAA , where the two acceptor molecules in this complex are anhydride (A) and the second molecule of triethylphosphite (A').



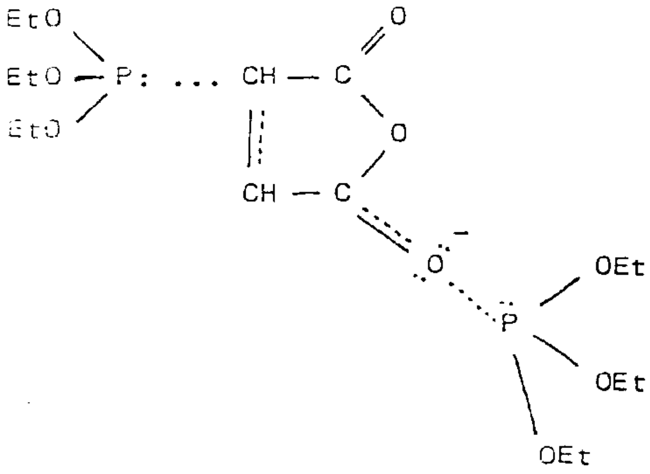
DA_2

maleic anhydride
complex

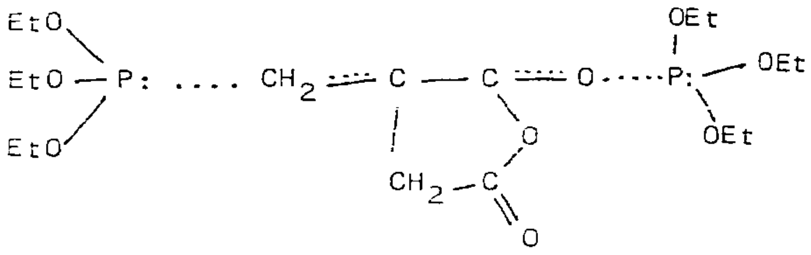


**Itaconic
anhydride
complex**

DAA'



Maleic anhydride
complex



**Itaconic
anhydride
complex**

INTRODUCTION

Definition of the term "Complex" in organic chemistry:

Foster in his book[1], defined the term "complex" as a substance formed by the interaction of two or more component molecules (and/or ions), which may have independent crystal structure and which will reversibly dissociate into its components, at least partially, in the vapour phase and on dissolution.

Charge transfer (Electron Donor-Acceptor) complexes:

The complexes presently discussed are formed by the weak interaction of electron donors with electron acceptors. Using valence-bond theory, a rational explanation of many of the ground-state properties has been given in terms of a structure which involves mainly dispersion, dipole and similar forces together with a usually small contribution from a covalent dative structure in which one electron has been transfered from the donor to the acceptor component of the complex.

Mulliken[2,3] has called all electron donor-acceptor interactions (electron) donor-acceptor complexes. Interaction in which covalent (σ) bonds are formed, are automatically included. In other contexts such products would simply be considered as new covalent compounds.

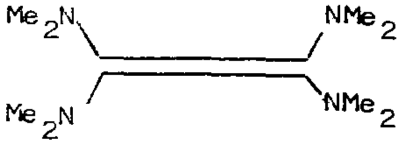
Charge-transfer complexes usually involve simple integral ratios of the components, the enthalpy of formation is usually of the order of a few KCal/mol or less, and the rates of formation and decomposition into the components are so high that the reactions appear to be instantaneous by normal techniques. An electronic absorption extra to the absorption of the components is often observed. This is the result of an intermolecular charge-transfer transition involving electron transfere from the donor to the acceptor.

Electron Donors and Electron Acceptors:

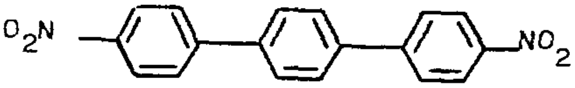
The components of the complex have been described as electron donors and electron acceptors. Mulliken[2] divided even-electron donor and acceptor species into increvalent and sacrificial types. Increvalent donors are lone-pair (n)-donors such as aliphatic amines, amine oxides, ethers, phosphines, sulphoxides, alcohols, iodides. Some of these interact strongly with electron acceptors. Sacrificial donors are compounds which donate an electron from bonding orbital. They include σ-donor such as hydrocarbons, specially small cyclic hydrocarbons. These are very weak electron donors. By contrast, π-donors such as aromatics, particularly polycyclic systems and systems containing electron-releasing groups, may be strong donors. Relatively little work has been reported on aliphatic π-donor hydrocarbons. It is doubtful whether the colours obtained by the addition of tetranitromethane to olefins are the result of charge-transfer complex formation[4].

Increvalent acceptors are of the vacant orbital type, for example B $(hal)_3$ and Al $(hal)_3$. The binding of electron donors (particularly n-donors) to such acceptors is often so strong that covalent binding results. However, with other vacant orbital acceptors such as Ag^+, weak charge transfer complexing may occur. Sacrificial acceptors may be of the σ or π-type. σ-Acceptors include the hydrogen halides, the weakly accepting halo-substituted paraffins and the more strongly accepting halogens e.g. I_2, Br_2, ICl, ICN. π-Acceptors are the most common organic acceptors. They include aromatic systems containing electron-withdrawing substituents such as nitro, cyano and halo, also acidanhydrides, acid chlorides and quinones[5].

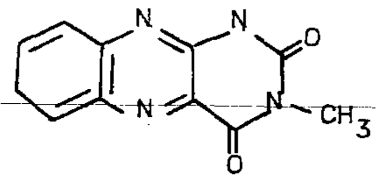
Although this division into electron donor and electron acceptor species may be made, it must be emphasized that the terms are only relative. A single species may for example behave both as a donor and as an acceptor. This may possibly occur in self-complexes of benzene[6]. Similarly, it has been suggested that the larger condensed polycyclic aromatic hydrocarbons, which are good donors, should also be good acceptors.[7] Evidence for such behaviour has been obtained from interactions of pyrene, anthracene with the very strong electron donor tetrakis (dimethylamino)-ethylene (1). Likewise 4,4-dinitro-p-terphenyl (2) has been shown to have the characteristic properties of an electron donor and an electron acceptor as demonstrated by its various charge-transfer complexes[8]. 1,3-Dimethylalloxazine (3) has also been shown to complex with electron donors and electron acceptors[9].



(1)



(2)

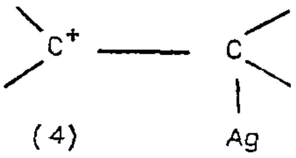


(3)

Historical Development:

For many years, chemists recognized that addition products may be obtained from stable compounds, the formation of which is contrary to the normal rules of valency. Sudborough[10] had depicted the products as having structures in which the component molecules were covalently bonded together.

Briegleb[11] suggested that the hydrocarbon-nitro-compound adducts were the result of the electrostatic attraction between the localized dipoles of the nitro groups and the induced dipoles in hydrocarbons. Pauling suggested that the Ag^+-ethylene complex (4) is stabilized by resonance between a structure involving no covalent bonding between the two moieties and a structure of the type(4).



(4)