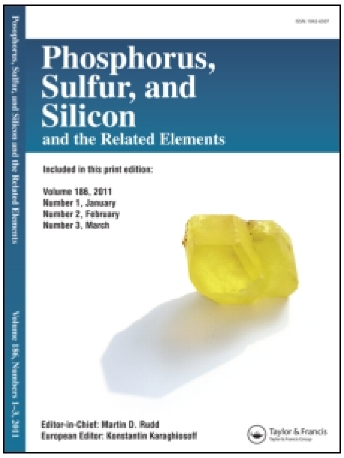

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The Rich Chemistry of Fulvalene Ylides. A Dichotomy in Phosphonium Salt/Ylide Hydrolysis and the Development of a New Synthesis of Azulenes

Declan G. Gilheany[a]; Padraig G. Kelly[a]; Catherine A. Mitchell[a]; Brian J. Walker[b]; John F. Malone[b]; Joanne Blaney[b]; Raymond Wilson[b]
[a] Department of Chemistry, St. Patricks College, Maynooth, Co., Kildare, Ireland [b] School of Chemistry, Queens University, Belfast, N. Ireland

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THE RICH CHEMISTRY OF FULVALENE YLIDES. A DICHOTOMY IN PHOSPHONIUM SALT/YLIDE HYDROLYSIS AND THE DEVELOPMENT OF A NEW SYNTHESIS OF AZULENES.

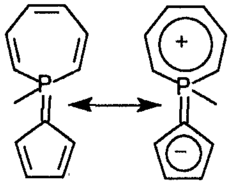
DECLAN G.GILHEANY*, PADRAIG G.KELLY, CATHERINE A.MITCHELL
Department of Chemistry, St.Patricks College, Maynooth,
Co.Kildare, IRELAND

and

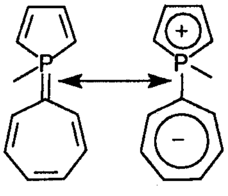
BRIAN J.WALKER*, JOHN F.MALONE, JOANNE BLANEY and
RAYMOND WILSON, School of Chemistry, Queens University,
Stranmillis Road, Belfast, N.IRELAND.

Abstract A series of fulvalene ylides was synthesised. Only weak aromatic effects were found across the ylide bond. Their chemistry includes the first example of a dichotomy in phosphonium salt/ylide hydrolysis, interesting dynamic nmrs of the adducts with dimethyl acetylenedicarboxylate and a new synthesis of azulenes.

We have previously reported[1-4] on the synthesis and reactivity of various fulvalene ylides, named because of their similarity to fulvalenes. As well as their intrinsic interest as new compounds, they were expected to give insight on the nature of the ylide bond from the degree of aromatic character generated by any conjugation through phosphorus and by comparison of potentially aromatic species, e.g. (1), with potentially antiaromatic ones, e.g. (2). Some of these systems displayed interesting chemistry e.g. the first Stevens rearrangement at phosphorus[2].



(1)



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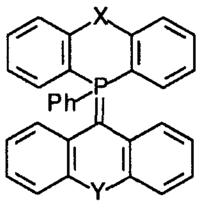


(3)

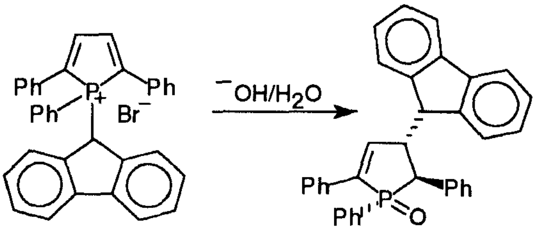
* to whom correspondance should be addressed

SPECTROSCOPY AND X-RAY CRYSTALLOGRAPHY

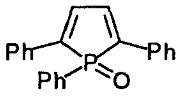
Comparison of the tetrabenzannelated derivatives (3: X,Y = CH=CH or bond) with analogues incapable of conjugation (3: X, Y = CH_2-CH_2 or bond) by $^1H/^{13}C/^{31}P$-nmr and uv showed that there are electronic interactions between the ring systems at each end of the ylide bond. However structural effects are small as shown, for example, in the X-ray crystal structure determination of ylide (3: X = CH=CH, Y = bond) where only a very small amount of planarisation of the seven-membered ring is apparent. In addition it was difficult to quantify these small effects due to the high degree of benzannelation in these compounds. On the other hand the chemical investigation of some of these fulvalene ylides proved to be very fruitful.

DICHOTOMY IN THE HYDROLYSIS OF YLIDES AND THEIR PARENT SALTS

To date the alkaline hydrolysis of an ylide has always been found to give the same products (alkane + phosphine oxide) as the hydrolysis of its parent phosphonium salt[5]. In the first example of a deviation from this rule, salt (4) (a fulvalene ylide precursor), on treatment with aqueous base, gives the rearranged phosphine oxide (5), shown by x-ray crystal structure determination. The hydrolysis is a very fast reaction and competes with the generation of the ylide. On the other hand the derived fulvalene ylide itself hydrolyses normally to phosphole oxide (6) and fluorene. This can be rationalised by consideration of the trigonal bipyramidal intermediates involved.



(4) (5)



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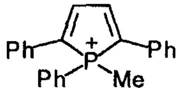
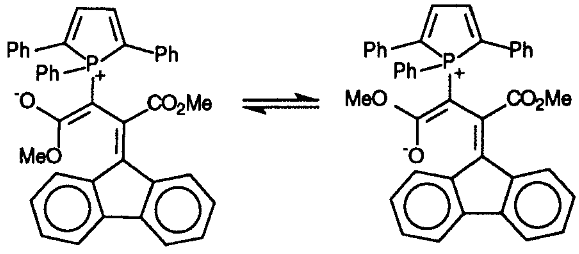


(7)

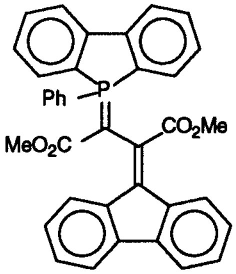
These observations prompted us to reexamine the other examples of very fast phosphonium salt hydrolyses[6,7] and we have found that the methyltriphenylphospholium salt (7) does not give the normal hydrolysis products, as previously assumed[7], but a mixture of the diastereomers of the product analogous to (5) with, in this case, phenyl migration.

DNMR OF ADDUCTS WITH DIMETHYL ACETYLENEDICARBOXYLATE

Some of these ylides proved to be quite unstable so, to help in their characterisation, we trapped them with dimethyl acetylenedicarboxylate (DMAD) - a well known reaction of ylides[8] wherein the alkyne inserts into the P=C bond to give adducts (e.g. 8 and 9 characterised by X-ray crystallography). Also it is expected[9] that ylide/DMAD adducts should show temperature dependent nmrs due to restricted rotation around the bond to the alpha-carbomethoxy group as in (8a)/(8b), which was indeed found to be the case. However more interesting was the comparison of adducts (8)/(9), in that the rate of rotation was found to be significantly higher for (8) than for (9).



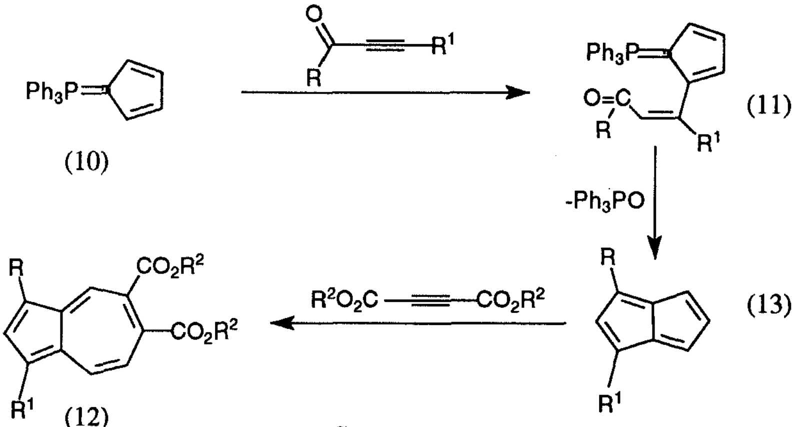
(8a) (8b)



(9)

A NEW SYNTHESIS OF AZULENES

The investigation of the interaction of fulvalene ylides and DMAD also allowed us to develop a new synthesis of substituted azulenes. The route is shown in outline in Scheme 1. Although ylide (10) is extremely stable and does not undergo the Wittig reaction[10], it is subject to electrophilic addition with an activated alkyne to give the monoadduct (11)[11]. We have found that when treated with a further equivalent of alkyne the *E*-isomer of monoadduct (11) yields the substituted azulene (12) in 30-40% yield (which is respectable for an azulene synthesis). The assumed pathway for azulene production is *via* the reactive pentalene (13) for which there is literature precedent[12].



Scheme 1

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