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STERIC AND ELECTRONIC EFFECTS OF SUBSTITUENTS AT ARSENIC ON THE DECOMPOSITION OF ARSONIUM BETAINES

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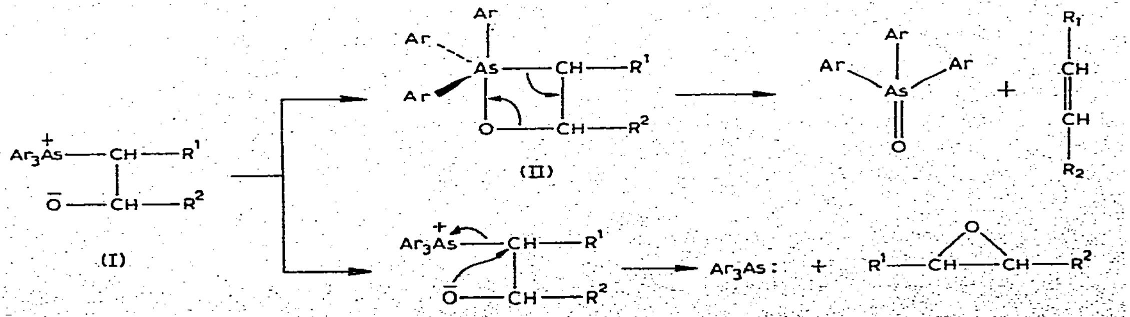
Summary

In contrast to the behaviour of the analogous phosphonium betaines, neither the presence at arsenic of the electron-withdrawing 2-furyl substituent nor enclosure of the arsenic in the strained dibenzarsolium ring system promote betaine collapse via attack of betaine oxygen at the arsonium centre. Thus both 2-furyl(methyl)diphenylarsonium iodide and 5-methyl-5-phenyldibenzarsolium iodide on treatment with benzaldehyde and ethanolic sodium ethoxide give exclusive formation of olefin epoxide and tertiary arsine.

Introduction

It has been established that arsonium betaines I can collapse in two ways; (*i*) by intramolecular nucleophilic attack of the betaine oxygen at the arsonium centre to form the arsine oxide and olefin via the pentacovalent arsorane II; and (*ii*) by intramolecular attack of the betaine oxygen at the carbon adjacent to arsenic to form the olefin epoxide with displacement of triarylarsine (Scheme 1).

SCHEME 1



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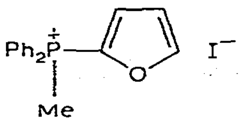
Trippett et al. [1] have suggested that in the transition state for olefin formation from the pentacovalent arsorane II, breaking of the As—C bond is in advance of other electron shifts, and the α-carbon bears a fractional negative charge. If the group R^1 is electron-withdrawing [1,2], this negative charge is stabilised, and olefin formation is favoured, even when the electropositive character of the arsenic atom is reduced by the presence at arsenic of electron-donating *p*-methoxyphenyl substituents. In the absence of such a strongly electron-withdrawing group on the α-carbon, the alternative mode of decomposition of the betaine is favoured, to give the olefin epoxide and triarylarsine.

In our work on the factors affecting the mode of decomposition of phosphonium betaines [3-5], we have shown that the presence of the electon-withdrawing 2-furyl substituent at phosphorus promotes rapid intramolecular collapse of the betaines to form the normal Wittig products. Thus the reaction of the salt III with benzaldehyde in ethanolic sodium ethoxide gives styrene and the phosphine oxide IV in 50—60% yield. In contrast, the analogous reaction of methyltriphenylphosphonium iodide yields predominantly the rearranged phosphine oxide V. In this case, betaine collapse is relatively slow, and an alternative route is favoured, involving protonation of the betaine followed by an effectively irreversible dehydration to a vinylphosphonium salt, which undergoes hydrolysis with rearrangement to give V. Rapid betaine collapse to form normal Wittig products also occurs if the phosphorus is contained in the strained dibenzophospholium ring system. Thus the salt VI on treatment with benzaldehyde in ethanolic sodium ethoxide gives the phosphole oxide VII and styrene in 40—50% yield, no rearrangement products being detected. Rapid betaine collapse was attributed to the relief of strain attendant on the formation of the spiro-oxaphosphorane VIII in which both four and five membered rings span apical—equatorial positions.



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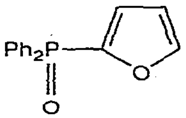

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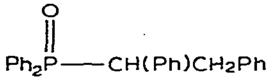

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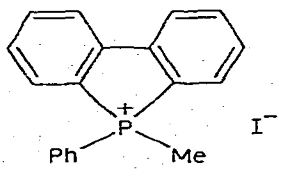

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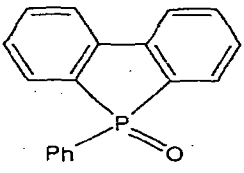

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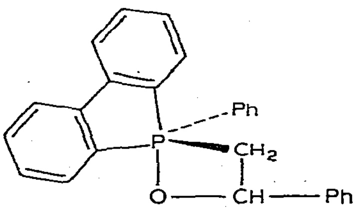
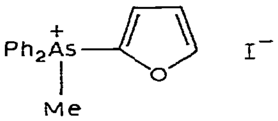


(VIII)

We now report a similar study of the effects of variation in the substituents at arsenic on the mode of decomposition of arsonium betaines in the reaction of arsonium ylides with benzaldehyde.

Results and discussion

Trippett et al. [1] have shown that the reaction of methyltriphenylarsonium iodide with benzaldehyde in the presence of ethanolic sodium ethoxide yields styrene oxide and triphenylarsine in high yield. We have repeated this reaction and obtained the same result, no trace of the normal Wittig products, styrene and triphenylarsine oxide, being detected. Replacement of one of the phenyl groups at arsenic by the more electron-withdrawing 2-furyl substituent did not cause any change in the overall course of the reaction. Thus the salt IX on treatment with benzaldehyde in the presence of ethanolic sodium ethoxide gave 2-furyldiphenylarsine and styrene oxide in 50% yield, and as in the above case no trace of olefin or arsine oxide was detected. Thus the presence of an electron-withdrawing group at arsenic does not facilitate betaine collapse via nucleophilic attack at arsenic, in contrast to the situation observed for the analogous phosphonium betaine. The absence of an electron-withdrawing substituent on the α-carbon is clearly the controlling influence, even when the arsonium centre is made more electropositive. Attempts to increase the number of electron-withdrawing groups at arsenic were unsuccessful, since although the triheteroarylarsines tri-2-furylarsine and tri-2-thienylarsine can be readily prepared by standard methods, due to the electron-withdrawing nature of the heteroaryl substituents they do not react with methyl iodide to form the required methyltriheteroarylarsonium salts, even after a prolonged period of reflux with methyl iodide in a polar solvent such as nitromethane, conditions under which the analogous heteroarylphosphines readily form quaternary salts.



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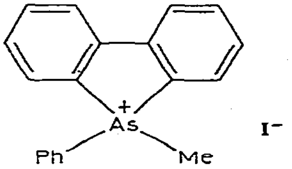

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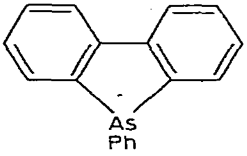

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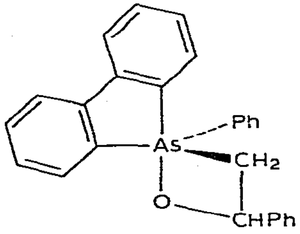

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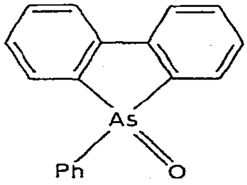

(XIII)

We have also studied the course of the reaction between the dibenzarsolium salt X and benzaldehyde in the presence of ethanolic sodium ethoxide, in order to investigate the effect of enclosing the arsenic in a small, strained ring system. The endocyclic C—As—C bond angle in the parent dibenzarsole XI has been shown to be 88° by an X-ray study [6]. Although a structural study of the salt X has not yet been made, it seems reasonable to assume that salt formation will result in increased ring strain, since the endocyclic bond angle at arsenic will still be of the same order as in the parent dibenzarsole due to the constraints imposed by the ring system, whereas the preferred angle in an arsonium salt should be approximately tetrahedral. Such ring strain would be relieved substantially if betaine collapse occurred via formation of the spiroarsorane XII in which both the four and the five membered ring would span apical—equatorial positions by analogy with related phosphoranes in which the phosphorus forms part of a small ring. In phosphorus chemistry the equilibrium between betaine and phosphorane lies well towards the latter in the case of spirophosphorane formation [7]. Nevertheless, it is apparent that collapse of the spiroarsorane XII to the olefin and arsole oxide XIII will lead to the reintroduction of ring strain, but this should be offset to some degree by the energy of formation of the As=O bond.

However, the reaction of the dibenzarsolium salt X with benzaldehyde in the presence of ethanolic sodium ethoxide gave exclusively styrene oxide and the tertiary arsine XI, and, as in the case of the acyclic methyltriphenylarsonium salt, no traces of the olefin and arsine oxide were detected. Thus, as for the 2-furylarsonium salt IX, the controlling factor still appears to be the absence of an electron-withdrawing substituent on the α-carbon capable of stabilising the partial negative charge which would develop in betaine collapse to the olefin and arsine oxide. In the case of the reaction of the cyclic salt X, another factor is that the observed mode of decomposition of the betaine may be favoured by relief of steric strain on ejection of the relatively strainfree arsine XI from the strained arsonium betaine.

In view of the observed pattern of behaviour of arsonium betaines, it would seem that arsenic has a much smaller tendency than phosphorus to undergo valence shell expansion to form a pentacovalent species. However, a number of pentacovalent arsoranes have been prepared and characterised [8,9]; the apparent reluctance of arsonium betaines to collapse via the pentacovalent arsoranes even when geometrical and electronic factors favour arsorane formation is no doubt due to the relative weakness of As=O compared to P=O.

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. IR spectra were recorded on a Perkin—Elmer Infrared Spectrophotometer in potassium bromide. ^{1}H NMR spectra were recorded at 60 MHz on a JEOL spectrometer. GLC analyses were carried out using a Pye series 104 chromatograph equipped with a 5′ column of 10% Apiezon L on celite, and a flame ionisation detector. TLC separations were carried out on a preparative scale using a 1 mm thickness of silica gel CT on 20 × 20 cm glass plates. Solvents used were petroleum ether (40—60°C) and ethyl acetate. Mass spectra were recorded on an AEI MS30 spectrometer.

Preparation of arsines and arsonium salts

(i). (2-Furyl)diphenylarsine and derivatives. To a solution of n-butyllithium (0.24 mol) in light petroleum (b.p. 40—60°C) (150 ml) was added a solution of furan (20 g, >0.24 mol) in diethyl ether (200 ml) and the resulting mixture

stirred under nitrogen for 2 h. To this was added dropwise a solution of diphenylarsenious chloride (7.25 g, 0.027 mol) in benzene (50 ml), and the resulting mixture heated under reflux for 1 h more. The excess organolithium reagent was then destroyed by the dropwise addition of aqueous ammonium chloride solution (10% w/v, 100 ml). The organic layer was then separated, dried and the solvents removed. The residue was then distilled under reduced pressure to give 2-furyldiphenylarsine, b.p. 133°C at 0.1 mmHg, (5 g, 63%); τ ($CDCl_3$): 2.8 (m, 11H); 3.7 ppm (m, 2H); *m/e* 281 (M^+). The arsine was characterised by conversion into the methiodide by prolonged reflux with an excess of methyl iodide in nitromethane solution. After removal of excess methyl iodide and the nitromethane, the residue was dissolved in water, and the resulting solution washed with ether to remove non-ionic impurities and unreacted arsine. The arsonium salt was then extracted with chloroform from the purified aqueous solution. After drying, the chloroform layer was evaporated to give (2-furyl)methyldiphenylarsonium iodide (IX) m.p. 126—127°C (ex. MeOAc/EtOH). (Found: C, 47.15; H, 3.95. $C_{17}H_{16}AsIO$ calcd.: C, 46.6; H, 3.70%.) τ ($CDCl_3$): 2.0—2.8 (m, 11H); 3.25 (m, 2H); 6.8 ppm (s, 3H).

Treatment of the arsine with hydrogen peroxide in acetone gave 2-furyldiphenylarsine oxide (as the dihydrate), m.p. 104—105°C (ex. hexane/MeOAc). (Found: C, 55.7; H, 5.7. $C_{16}H_{13}AsO_2 \cdot 2H_2O$ calcd.: C, 55.2; H, 4.9%.)

(ii). 5-Phenyldibenzarsole (XI). This was prepared by the reaction of 2,2'-dilithiobiphenyl with phenyldichloroarsine as described by Heinekey and Millar [10]; treatment of the arsine with hydrogen peroxide in acetone gave the oxide XIII, m.p. 158—161°C. On refluxing the arsine with an excess of methyl iodide in nitromethane for 24 h, the salt 5-methyl-5-phenyldibenzarsolium iodide (X) was formed. After recrystallisation from MeOAc/EtOH it had m.p. > 140°C dec. (Found: C, 50.9; H, 3.55. $C_{19}H_{16}AsI$ calcd.: C, 51.15; H, 3.6%.) τ ($CDCl_3$): 1.0—2.7 (m, 13 H); 6.7 ppm (s, 3 H). Treatment of the iodide with aqueous sodium picrate gave the arsonium picrate, m.p. 177—178°C (ex. aq.—EtOH). (Found: C, 54.95; H, 3.45; N, 7.65. $C_{25}H_{18}AsN_3O_7$ calcd.: C, 54.85; H, 3.3; N, 7.65%.)

(iii). Triphenylarsine and derivatives. A commercial sample of triphenylarsine was used, and converted into the methiodide and oxide in the usual way.

Wittig reactions of arsonium salts

General procedure. The arsonium salt (10^{-3} mol) and freshly distilled benzaldehyde (10^{-3} mol) were dissolved in absolute ethanol (2 ml). To this solution was added a solution of sodium ethoxide in ethanol (1 ml) (prepared from sodium (0.23 g) in ethanol (10 ml)), and the resulting solution allowed to stand at room temperature under nitrogen for one week. At the end of this period, the solutions were filtered to remove precipitated sodium iodide, and then analysed by GLC for the presence of styrene and styrene oxide. The solvent was then evaporated, and the residue dissolved in chloroform and applied to a preparative TLC plate (silica gel CT). The plates were developed twice with petroleum ether (40—60°C), and once with ethyl acetate. The bands were extracted, and the pure compounds characterised by comparison with authentic samples.

Results

(i). The reaction of methyltriphenylarsonium iodide with benzaldehyde

under the above conditions gave styrene oxide and triphenylarsine (50%). Styrene was not detected on GLC analysis and triphenylarsine oxide was not detected on TLC analysis.

(ii). The reaction of (2-furyl)methyldiphenylarsonium iodide with benzaldehyde under the above conditions gave styrene oxide and 2-furyldiphenylarsine (48%). Neither styrene nor the arsine oxide were detected in the reaction mixture.

(iii). The reaction of 5-methyl-5-phenyldibenzarsolium iodide with benzaldehyde under the above conditions gave styrene oxide and 5-phenyldibenzarsole (45%). Neither styrene nor the arsine oxide were detected.

The above reactions were repeated on the above scale using a 24 h reflux period. In each case, the same products were isolated in slightly better yield.

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