Tetrahedron Letters No. 10, pp 785 - 788, 1975. Pergamon Press. Printed in Great Britain.

PREPARATION AND REACTIONS OF QUATERNARY ALDAZINES

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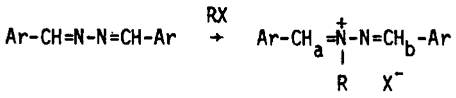
(Received in UK 20 January 1975; accepted for publication 31 January 1975)

Results of quaternising arylaldazines (1) by the usual alkylating agents (RX, R_2SO_4) to form azinium salts (2) are ill-defined[1] and no pure salts of this type appear to have been isolated in contrast to azinium salts (2; R=H, X=Cl, Br, I) of hydrogen halides which are well documented[2]. We have found that triethyloxonium tetrafluoroborate[3] effectively quaternises aldazines to give azinium salts (2; R=Et, $X=BF_4$). In a typical preparation benzalaldazine (PhCH:N-N:CHPh) was made to react with the reagent ($Et_3O^+\ BF_4^-$) in dry dichloromethane with stirring for 24 h and the product (2; Ar=Ph, R=Et, $X=BF_4$) was obtained as a pale-yellow substance after removal of the solvent below 30^0 or by addition of ether to the mixture at -20^0 and purified by washing with dry ether (cf. table). Structural confirmation rests upon elemental and spectral analysis: i.e. bands at 1635, 1605 cm^{-1} ($-CH{=}\overset{+}{N}Et-$ and -CH=N- respectively[4]) and at 1060 cm^{-1} (BF_4^-); the p.m.r. spectrum (in CF_3CO_2D) showed the typical ethyl resonances (t at 8.2 and q at 5.25τ), a complex multiplet (1.5-2.5τ, 10Ar-H's), and two singlets at 1.05(H_a) and 1.2τ(H_b; cf. 2). Quaternisation was also achieved by heating benzaldazine in methyl fluorosulphonate to give (2; Ar=Ph, R=Me, $X=FSO_3^-$). No quaternary salts were isolated from arylaldazines with negative groups or from aryl or alkyl ketazines or alkylaldazines.

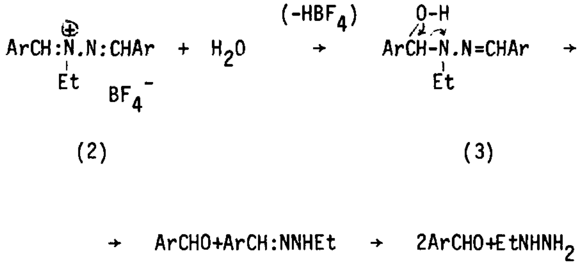


$$\mathrm{Ar{-}CH{=}N{-}N{=}CH{-}Ar} \xrightarrow{RX} \mathrm{Ar{-}CH_a{=}}\underset{\underset{R}{|}}{\overset{+}{\mathrm{N}}}\mathrm{{-}N{=}CH_b{-}Ar}\quad X^-$$

(1) (2)

The behaviour of these novel azinium salts towards certain nucleophiles was found to be of potential synthetic interest. For instance, on boiling an aqueous ethanolic solution of the salts (2) for ca. 4 h, hydrolysis to give the parent aldehyde occurred quantitatively.

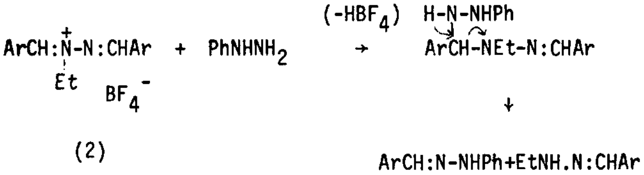
presumably by way of an unstable carbinolamine (3) as shown. Although aldazines hydrolyse in mineral acids[5] this method would allow an 'azine-protected aldehyde' to be regenerated under very mild conditions.



$$\underset{(2)}{ArCH:\underset{Et}{\overset{\oplus}{N}}.N:CHAr\ \ BF_4^-} + H_2O \xrightarrow{(-HBF_4)} \underset{(3)}{ArCH(\overset{}{O\text{-}H})\text{-}\underset{Et}{N}.N=CHAr} \rightarrow$$

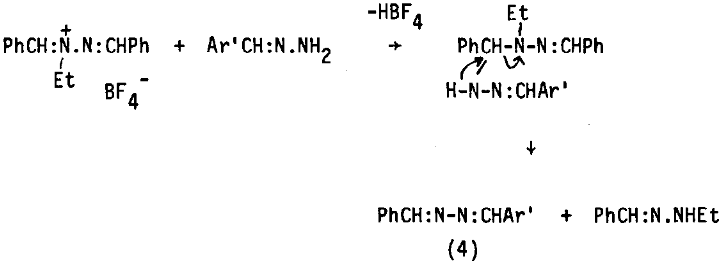
$$\rightarrow ArCHO+ArCH:NNHEt \rightarrow 2ArCHO+EtNHNH_2$$

A mild exothermic reaction occurred when a dichloromethane solution of phenylhydrazine was added to the azinium salts (2; Ar=Ph, p-MeOC$_6$H$_4$ or p-MeC$_6$H$_4$) in the same solvent. On cooling, needles of the corresponding phenylhydrazone (60-70%) separated and aryl ethylhydrazone was obtained on driving off the solvent. A mechanism analogous to the previous one is envisaged.



$$\underset{(2)}{ArCH:\underset{Et}{\overset{+}{N}}\text{-}N:CHAr\ \ BF_4^-} + PhNHNH_2 \xrightarrow{(-HBF_4)} \overset{H\text{-}N\text{-}NHPh}{ArCH\text{-}NEt\text{-}N:CHAr} \rightarrow ArCH:N\text{-}NHPh+EtNH.N:CHAr$$

It was thought that azinium salts might react with arylhydrazones under similar conditions in an analogous manner and provide a novel synthesis of the rather inaccessible unsymmetrical azines as shown:



$$PhCH:\underset{Et}{\overset{+}{N}}.N:CHPh\ \ BF_4^- + Ar'CH:N.NH_2 \xrightarrow{-HBF_4} \underset{H\text{-}N\text{-}N:CHAr'}{PhCH\text{-}\overset{Et}{N}\text{-}N:CHPh} \rightarrow \underset{(4)}{PhCH:N\text{-}N:CHAr'} + PhCH:N.NHEt$$

Although the reaction has only been carried out with the 1,4-diphenyl azinium salt (2; Ar=Ph) it promises to be of wider scope in view of the results obtained so far. Chromatography (alumina) using light petrol and ethyl acetate (3:1) separated the ethyl hydrazone from the following unsymmetrical azines {4; Ar' = p-MeC$_6$H$_4$, m.p. 112° (65%)[6];

p-$MeOC_6H_4$, m.p. 80° (57%)[6]; m-$NO_2C_6H_4$, m.p. 134° (50%)[7]; 2-$HOC_{10}H_6$, m.p. 130° (57%)*}. Conventional methods for making unsymmetrical azines are often unsatisfactory[8] or demand complex starting materials[9].

1,4-Diaryl-2-ethyl-2-azonia-3-azabuta-1,3-diene tetrafluoroborates:

$ArCH{=}\overset{+}{N}(Et).N{:}CHAr\ BF_4^-$

Ar*	Reaction Time (h)	Yield %	M.p. °C
Ph	24	92	148
o-$MeOC_6H_4$	24	50	235
m-$MeOC_6H_4$	24	80	182
p-$MeOC_6H_4$	24	70	240
p-MeC_6H_4	24	87	190
2-Furyl	3	66	194
2-Thienyl	3	91	189

Aldoximes (ArCH:NOH; Ar = Ph, p-MeC_6H_4) also quaternised when treated with the reagent in CH_2Cl_2 to give the corresponding white, crystalline salts ($ArCH{:}\overset{+}{N}HOEt\ BF_4^-$)[10] which in hot aqueous ethanol regenerated the parent aldehyde practically quantitatively. The hydrolysis mechanism is analogous to that given for the azines above involving the intermediacy of an unstable ethanolamine (ArCHOHNHOEt) which breaks up into the aldehyde and ethyl hydroxylamine (NH_2OEt). However, since many other aldoximes gave oily salts with the ethylating reagent which were difficult to purify, this method is not generally convenient for oxime fission.

We thank Allen and Hanbury for a studentship (to S.S.M.) and Dr. D. Bishop for useful discussions.

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10. The structure follows from the treatment of the quaternary oxime with $NaBH_4$ to give the corresponding O-ethylated compound, ArCH:NOEt.

* The structure of all new compounds was confirmed by analytical and spectral data.