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THE SYNTHESIS AND CHEMISTRY OF 3-PHENYL-2-PROPYNYLMULTIAMINES

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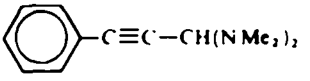
Abstract The reaction of phenylacetylene with $HC(NMe_2)_3$ and $C(NMe_2)_4$ yielded $PhC{\equiv}CCH(NMe_2)_2$ and $PhC{\equiv}CC(NMe_2)_3$, respectively. The reactions of the latter two compounds with acetic acid and methanol are discussed.

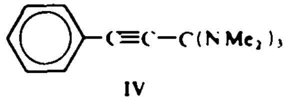
IN RECENT years, a number of reports have been published describing the reactions of carbon acids with *gem*-multiamines and related compounds.[1-3] However, reactions of *gem*-multiamines with acetylenic carbon acids have not been described. Furthermore, to our knowledge, the products expected of such a reaction have not been prepared by any method. In this paper is described the reaction of phenylacetylene with tris(dimethylamino)methane, I, and tetrakis(dimethylamino)methane, II, and some of the chemistry of the 3-phenyl-2-propynylmultiamines produced.

RESULTS AND DISCUSSION

Phenylacetylene reacts readily with I and II at 80° without solvent to yield N,N,N',N'-*tetramethyl*-3-*phenyl*-2-*propynylidenediamine*, III, and N,N,N',N',N'',N''-*hexamethyl*-3-*phenyl*-2-*propynylidynetriamine*, IV, respectively.



III



IV

Reaction of the multiamines with a second mole of phenylacetylene is apparently much slower than the first, being observed not at all with III. Compound IV reacts slowly with excess phenylacetylene giving rise to a complex mixture displaying an uninterpretable NMR spectrum.

Compound IV, an atmosphere-sensitive, low-melting solid, exhibited a sharp singlet in the NMR at τ 7·41 and a weak absorption in the IR at 2220 cm^{-1}, corroborating the structural assignment. Compound III had the expected singlets in the NMR at τ 7·63 and 6·43 in the ratio 12:1 but its IR absorption in the acetylene region was too weak to be meaningful. Its Raman spectrum, however, showed a strong absorption at 2217 cm^{-1} characteristic of a disubstituted acetylene. Additional structural evidence for III was obtained by amination of phenylpropargylaldehyde, yielding an NMR exhibiting the expected resonances.*

As might be expected, the compounds III and IV are rather acid-sensitive and the

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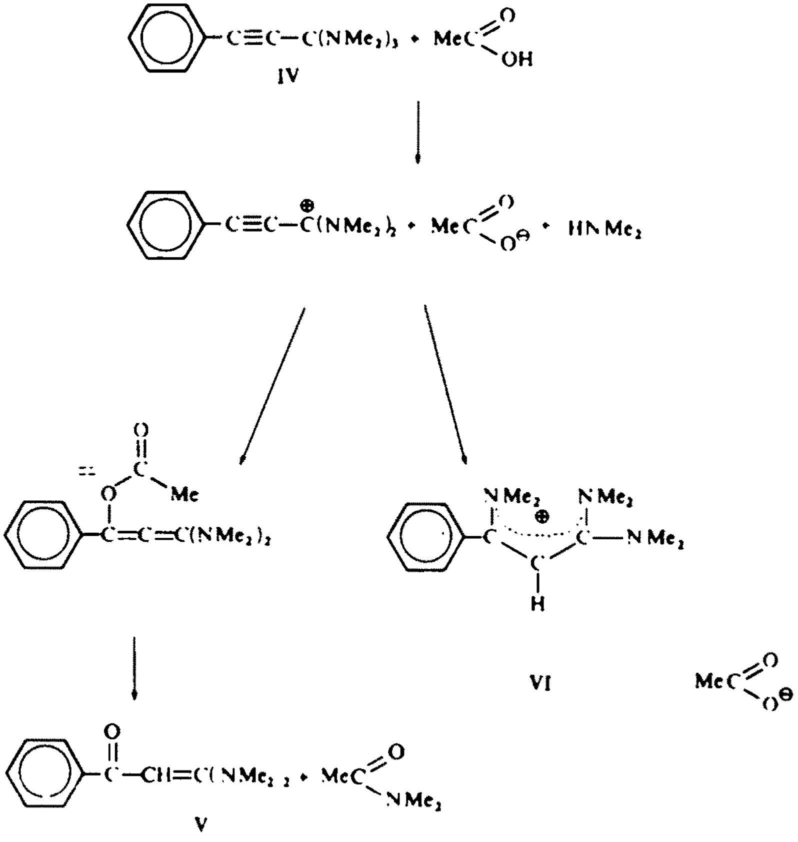
* This experiment was carried out in an NMR tube, benzene solvent, dimethylamine, no catalyst, room temp, and it is interesting to note that by our interpretation of the NMR, amination of the CO function is accompanied by similar amounts of addition to the triple bond.

remainder of this paper deals with the results of their reaction with acetic acid (pK_a 4·8) and methanol (pK_a 16).

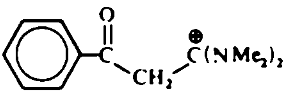
Compound IV reacts rapidly with acetic acid in benzene solution producing three products, dimethylacetamide, 3,3-*bis(dimethylamino)acrylophenone*, V, and 1,3,3-*tris(dimethylamino)-1-phenylallylium acetate*, VI. Compound V is produced in about 80% yield while VI is produced in about 10% yield. The dimethylacetamide was not isolated but identified by its NMR only. Scheme 1 describes a plausible mechanistic sequence for this reaction. Consistent with this mechanism is the observation that when the reaction is run in the presence of an excess of dimethylamine, the only product observed in the NMR is the allylium salt, VI.

SCHEME 1

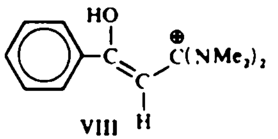


The structural assignment of V rests primarily on its NMR spectrum and its independent synthesis on an NMR tube scale from acetophenone and II in benzene.[2] The NMR spectrum of the resulting solution was identical to that obtained for V.

An interesting feature of V is the manner in which it is protonated by acetic acid in benzene solvent. NMR suggests the protonation takes place on the number 2 carbon yielding ion VII rather than on the oxygen to yield ion VIII [NMR exhibits singlets at τ 7·49 and 7·59 (6:1) benzene solvent, TMS internal standard]. One might

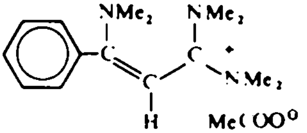


VII



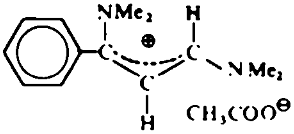
VIII

expect VIII to be favoured due to the possibility of sharing the charge between a larger number of atoms including oxygen. A plausible explanation is that the planar configuration required in VIII to maximize orbital overlap is inhibited by steric pressures so the molecule cannot take advantage of additional sharing of charge. This observation is echoed in the NMR spectrum of the allylium salt, VI, which displays not three dimethylamino environments but two at τ 7·17 and 6·91 in the ratio 2:1. This suggests the molecule might best be approximated by structure VI-A in which the ω nitrogens are kept out of the allyl plane by steric repulsions.



VI-A

N,N,N',N'-Tetramethyl-3-phenyl-2-propynylidenediamine, III, also reacts rapidly with acetic acid and the only isolable product of this reaction is 1,3-*bis(dimethylamino)*-1-*phenylallylium acetate*, IX. Small amounts of dimethylacetamide were observed in the NMR spectrum but the corresponding acrylophenone was not visible nor was



IX

any isolated. All four Me environments of this allylium salt are visible in the NMR as distinct, somewhat broadened, single resonances.

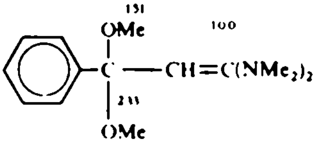
The reactions of compounds III and IV with the weaker acid, methanol, are also of interest, particularly because of their contrast with the acetic acid reactions. Compound III reacts with methanol replacing one dimethylamino group with a methoxyl group yielding 1-*methoxy*-N,N-*dimethyl*-3-*phenyl*-2-*propynylamine*, X. Furthermore, the reaction is completely reversible. Addition of dimethylamine to the methoxylated product, X, will reform the original diamine, III. The structural

III X

assignment of X rests primarily on its NMR spectrum and Raman spectrum, which exhibits a strong absorption at 2221 cm^{-1}.

The reaction of compound IV with methanol appears to be similar, at least in the first stage, to the reaction with III. One dimethylamino group is replaced by one

OMe group yielding 1-*methoxy*-N,N,N′,N′-*tetramethyl-3-phenyl-2-propynylidenediamine*, XI. If this reaction is reversible, the equilibrium must lay far to the right, since addition of excess dimethylamine to XI does not cause a noticeable reappearance of IV. Unfortunately, compound XI could not be obtained free of a secondary product. Compound XI further reacts adding a molecule of methanol to yield a final product having the empirical formula, $C_{15}H_{24}N_2O_2$. The NMR spectrum of this compound indicates two NMe_2 groups in separate environments, two OMe groups in the same environment, and one olefinic proton. Structure XII, 3,3-bis(dimethylamino)-acrylophenone dimethyl ketal, is consistent with this NMR and consistent with the mass spectrum for which the principal fragmentations are shown below:



XII

EXPERIMENTAL

Proton NMR spectra were obtained from a Varian Model A-60 or A-56-60 spectrometer. Raman spectra were obtained on a Cary 81 spectrophotometer using neat liquids in 2 mm cells and appropriate optics. Reagents were the best commercial grades available or prepared by previously reported methods (I,[4] II[5]). M.ps and b.ps were uncorrected. All operations were carried out under an atmosphere of dry N_2.

Synthesis of N,N,N′,N′-*tetramethyl-3-phenyl-2-propynylidenediamine* (III). A mixture of 3·00 g (0·0294 mole) phenylacetylene and 3·74 g (0·0258 mole) of I, in a 25 ml round bottom flask is heated 18 hr at 80° under an atmosphere of dry N_2. Distillation (b.p. 68–71°/0·15 mm) yields 4·5 g (87%) of III exhibiting in its NMR spectrum singlets at τ 7·63, 6·43 and a complex multiplet between τ 3·15 and τ 2·40 in the expected ratio of 12:1:5 (benzene-d_6 solvent, TMS internal standard). The Raman spectrum of III displays a strong absorption at 2217 cm^{-1}. (Found: C, 76·9; H, 8·9; N, 13·7. $C_{13}H_{18}N_2$ requires: C, 77·2; H, 9·0, N, 13·9%.)

Synthesis of N,N,N′,N′,N″,N″-*hexamethyl-3-phenyl-2-propynylidynetriamine* (IV). The triamine is prepared by the same method as the diamine above starting with II and is obtained in 88% yield, b.p. 95°/0·2 mm, m.p. 30·5 31·5°. Its NMR spectrum displays a sharp singlet at τ 7·41 and a complex multiplet between τ 2·41 and τ 3·09 in the ratio of 18:5, and its IR spectrum displays a weak absorption at 2220 cm^{-1}. (Found: C, 73·4; H, 9·4; N, 17·3; mol wt 246 ± 5 (cryoscopy in benzene). $C_{15}H_{23}N_2$ requires: C, 73·4; H, 9·5; N, 17·1%; mol wt 245)

Reaction of N,N,N′,N′,N″,N″-*hexamethyl-3-phenyl-2-propynylidynetriamine* (IV) *with acetic acid*. To a soln of 3·00 g (0·0122 mole) of IV in 10 ml benzene in a 50 ml flask is slowly added a soln of 0·735 g (0·0122 mole) AcOH in 10 ml benzene. A white ppt of VI gradually forms 0·35 g (10%). The ppt is collected and recrystallized from CH_2Cl_2–benzene, m.p. 216–218 , its NMR spectrum exhibits a complex multiplet between τ 2·32 and 2·91, singlets at τ 5·30, 6·91, 7·17 and 8·05 in the expected ratio of 5:1:6:12:3 ($CDCl_3$ solvent, TMS internal standard). (Found: C, 66·9; H, 8·6; N, 13·9. $C_{17}H_{27}N_3O_2$ requires: C, 66·9; H, 8·9; N, 13·8%).

The filtrate from above is evaporated and the residual oil distilled, b.p. 143°/0·2 mm, yielding 2·1 g (79%) V which exhibits in its NMR spectrum a complex multiplet between τ 2·57 and 2·87, a singlet at τ 4·86 and a broad singlet at τ 7·49 in the ratio 5:1:12. (Found: C, 71·5; H, 8·4, N, 12·8; mol wt 218 mass spec. $C_{13}H_{18}N_2O$ requires: C, 71·5; H, 8·3; N, 12·8%; mol wt 218).

Reaction of N,N,N′,N′-*tetramethyl-3-phenyl-2-propynylidenediamine* (III) *with acetic acid*. To a soln of 1·00 g (0·00495 mole) of III in 10 ml ether is added a soln of 0·90 g (0·015 mole) AcOH in 10 ml ether. Compound IX appears as a second liquid phase, which is washed with pentane and dried at reduced press. The allylium salt appears to hold two molecules of AcOH and exhibits the following NMR spectrum: A complex multiplet between τ 2·30–2·80, doublets centered at τ 3·21 and 4·40 (*j* = 13), singlets at τ-5·67, 6·52, 6·77, 7·06 and 8·01 in the ratio of 5:1:1:3:3:3:3:9. Also visible is a singlet at τ-5·67 accounting for the two protons of the AcOH ($CDCl_3$ solvent, TMS internal standard). When the acetate anion is exchanged for

$BPh_4^{\ominus}$ in aqueous media a homogeneous recrystallizable ppt is obtained, m.p. 198 199 from MeCN MeOH. The NMR of the tetraphenylboron salt is similar to the acetate. (Found. C, 85·1; H, 7·8; N, 5·5. $C_{37}H_{39}N_2B$ requires: C, 85·0; H, 7·5; N, 5·4%.)

Reaction of N,N,N′,N′-*tetramethyl-3-phenyl-2-propynylidenediamine* (III) *with methanol.* To 1·43 g (0·0071 mole) of III in a round bottom flask is added 12 ml MeOH. The MeOH is evaporated at 80 mm press and this procedure is repeated 6 times. The final residue is distilled, b.p. 65 /0·1 mm, yielding 1·0 g (75%) of X. The Raman spectrum of X exhibits a strong absorption at 2221 cm^{-1} and the NMR spectrum exhibits a complex multiplet between τ 2·39 and 3·09, singlets at τ 5·33, 6·69 and 7·60 in the ratio 5:1:3:6 (benzene-d_6 solvent, TMS internal standard). (Found C, 76·2; H, 8·0; N, 7·9; mol wt 189 mass spec $C_{12}H_{15}NO$ requires: C, 76·2; H, 8·0; N, 7·4%; mol wt 189)

Reaction of N,N,N′,N′,N″,N″-*hexamethyl-3-phenyl-2-propynylidynetriamine* (IV) *with one mole of methanol.* To a soln of IV in 20 ml benzene is slowly added in 1 ml aliquots a 20% MeOH soln in benzene. Throughout the addition, and for a ½ hr following the final addition, a stream of dry N_2 is passed rapidly through the soln. The reaction mixture is monitored via NMR and the MeOH addition is stopped when the optimum quantity of product is observed. The solvent is removed at reduced press and the residual oil distilled, b.p. 96 97 /0·5 mm, to yield 1·5 g of XI (contaminated with 18% of secondary product see below). The NMR spectrum of XI exhibits a complex multiplet between τ 2·33 and 3·04, and singlets at τ 6·53 and 7·40 in the ratio 5:3:12, and its Raman spectrum exhibits a strong absorption at 2211 cm^{-1}

Reaction of N,N,N′,N′,N″,N″-*hexamethyl-3-propynylidynetriamine* (IV) *with excess methanol.* To a soln of 2·67 g (0·0109 mole) of IV in 10 ml ether is added a soln of 3 g MeOH in 10 ml ether and the mixture allowed to stand at room temp for 3 hr. The solvent and excess MeOH are removed at reduced press and the residual oil distilled, b.p. 91 93 /0·2 mm, yielding 2·43 g (85%) of XII (Found: C, 68·1; H, 9·1; N, 10·2; mol wt 264 mass spec $C_{15}H_{24}N_2O_2$ requires: C, 68·2; H, 9·2; N, 10·6%; mol wt 264), the NMR spectrum of which exhibits a complex multiplet between τ 2·12 and 3·03 and sharp singlets at τ 5·86, 6·89, 7·66 and 7·82 in the ratio 5:1:6:6:6 (benzene-d_6 solvent, TMS internal standard).

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