Electrophilic Substitution of Aromatic Compounds by NH_4^+ under Chemical Ionization Conditions

By JAN VAN THUIJL,* WIM C. M. M. LUIJTEN,† and WILLEM ONKENHOUT†

(*Gorlaeus Laboratories, Departments of Organic and*† *Analytical Chemistry, The University, P.O. Box* 9502, 2300 *RA Leiden, The Netherlands*)

Summary Under chemical ionization conditions NH_4^+ protonates certain aromatic compounds PhR (R = –CN, $-NH_2$, –NHMe, $-CH_2NH_2$, and $-CO{\cdot}NH_2$), and acts upon others as an electrophile, substituting $-NO_2$, –Cl, –Br, –I, $-CH_2OH$, –CO·H, –CO·Me, –CO·OH, and –CO·OMe with NH_3^+, presumably *via* a sigma complex.

DURING work on nitroazoles,[1] we observed striking differences between mass spectra obtained under chemical ionization (CI) conditions using methane and ammonia as the ionizing gas.‡ Methane produced the protonated molecular ions MH^+ and fragment ions at m/z $M - 46$, $[MH - HNO_2]^+$, as in aromatic or aliphatic nitro com-

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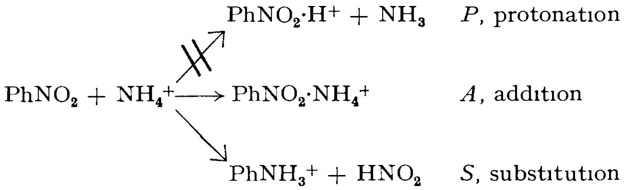
‡ All experiments were performed with an LKB-2091 mass spectrometer equipped with a chemical ionization source. We thank Dr. N. P. E. Vermeulen for technical assistance.

pounds[2] Ammonia caused little protonation but all mass spectra showed the stable adduct ions $[M + NH_4]^+$, and, surprisingly, an abundance of fragments at m/z $M - 29$, apparently due to $[M + NH_4 - HNO_2]^+$

We therefore submitted nitrobenzene to CI mass spectrometry (CIMS) using methane and ammonia Methane caused protonation and also gave the adduct ion $[PhNO_2Et]^+$, but no fragment was observed at m/z 94[2] With ammonia we observed neither the molecular ion nor the ion arising from protonation, P, but a very stable adduct A, m/z 141, and a base-peak fragment S, m/z 94 were observed

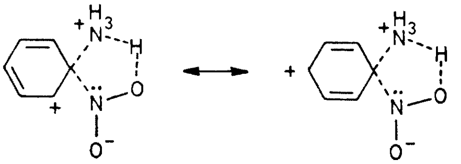


In order to find out whether the substitution is of a more general nature, a number of monosubstituted benzenes was studied by CIMS using NH_3 The results show that nitrobenzene is not an isolated case [see groups (iii) and (iv) below] and that substrates can be divided into four groups, where M represents the molecular ion, A the adduct $[PhR + NH_4]^+$, and S the substitution product ion $PhNH_3^+$ (i) M, and in some cases P, found, little or no A and S *e g* –H, –Me, –OMe,§ –SH, –SMe, $-NH_2$,¶ –NHMe, $-CH_2NH_2$, and –F (ii) M, P, and A observed, little or no S *e g* –CN, –CO Ph, and $-CO\,NH_2$ (iii) M and S observed, little or no P and A *e g* –Cl, –Br, and –I (iv) A and S observed, and in some cases also M and P *e g* $-NO_2$, $-CH_2OH$, –CO·H, –CO Me, –CO OH, and –CO OMe When present, S is always observed at m/z 94, and therefore it represents the anilinium ion $PhNH_3^+$ When the ionizing gas is switched from ammonia to methane, m/z 94 collapses immediately

The ease of formation of potentially good 'leaving molecules' does not appear to play a decisive role in the production of the ion S Thus, benzonitrile does not lose HCN as it does upon electron impact[3] Pentadeuterionitrobenzene yields the ion S at m/z 99, accompanied by a small amount of H/D scrambling as in equation (1) implying that attack

$$C_6D_5NO_2 + NH_4^+ \rightarrow C_6D_5NH_3^+ + HNO_2 \qquad (1)$$

of NH_4^+ occurs at the carbon atom carrying the substituent Moreover, the bulky iodine atom sterically hinders easy complex formation since the fraction of S, relative to the sum of the ions $M + P + A + S$, increases in the order F (0 0), Cl (*ca* 0 4), Br (*ca* 0 7), but is much less for I (*ca* 0·2) Therefore, formation of a sigma complex intermediate (**1**), in at least a number of cases, appears to be established



(1), *A*

Finally, the observation that electron releasing substituents such as –OMe, *para* with respect to the nitro group, promote complex formation, is compatible with electrophilic attack by NH_4^+, to give (**1**) as an intermediate

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§ Phenol has not been considered since its molecular ion appears at the same mass as its potential product ion

¶ Aniline gives some of the adduct ion A Ions P and S have identical compositions

[1] W C M M Luijten and J van Thuijl *Org Mass Spectrometry*, 1979 in the press

[2] A Maquestiau, Y van Haverbeke, R Flammang H Mispreuve, and J Elguero, *Org Mass Spectrometry*, 1979, **14**, 117, J J Brophy V Diakiw, R J Goldsack D Nelson and J Shannon *ibid* p 201, O S Chizhov, V I Kadentsev, G G Palmbach, K I Burstein S A Shevelov, and A A Feinsilberg *ibid*, 1978 **13** 611

[3] H Budzikiewicz, C Djerassi, and D H Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967