

AN ICR STUDY ON THE STRUCTURE OF THE $C_6H_6O^{+}$ ION FROM PHENETOLE

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Abstract—The $C_6H_6O^{+}$ ion from phenetole is generated by hydrogen transfer predominantly from the terminal-position, but also to some extent from the position next to oxygen. Deuterium labelling and ion-molecule reactions show that both transfers occur to the oxygen atom and not to the aromatic ring. The $C_6H_6O^{+}$ ion is thus formed exclusively in the phenolic structure.

INTRODUCTION

In recent years several attempts have been made to elucidate the structure of the $C_6H_6O^{+}$ ion, generated from the molecular ion of phenyl ethyl ether by loss of ethylene, i.e. to differentiate between a phenolic and a cyclohexadienone structure. These have included the use of metastable ion characteristics, substituent effects, kinetic data, deuterium labelling and deuterium isotope effects.^{1a-d} All point to the phenolic structure of the $C_6H_6O^{+}$ ion, but in an indirect and not always convincing way.

Direct proof for the phenolic structure of the $C_6H_6O^{+}$ ion from phenyl ethyl ether can in principle be obtained from its behaviour in ion-molecule reactions. We have studied this with an Ion Cyclotron Resonance spectrometer using its powerful double resonance technique² shown below.

RESULTS AND DISCUSSION

Reaction of the $C_6H_5DO^{+}$ ion from phenyl 2,2,2-trideuteroethyl ether (1) with neutral 3,5-dimethyl pyridine

The ICR spectrum of phenyl 2,2,2-trideuteroethyl ether is very simple under the conditions given in Fig 1.

The large peak at m/e 95 corresponds to the $C_6H_5DO^{+}$ ion and the small peak at m/e 94 to the $C_6H_6O^{+}$ ion. These must be due to non-specific transfer of a side-chain hydrogen atom, because it has been shown earlier that the molecular ion of phenyl pentadeuteroethyl ether produces exclusively the $C_6H_5DO^{+}$ ion, indicating no exchange between side-chain and ring hydrogen atoms.^{1b}

A similar phenomenon has been reported for other phenyl alkyl ethers.³

When the present ion is generated from the



Fig 1. ICR spectrum of phenyl 2,2,2-trideuteroethyl ether, $\omega_1/2\pi = 153.6$ kHz, 2×10^{-6} Torr, 20 eV. Further instrumental conditions relevant to this and following figures are described in the experimental part.

molecular ion by migration of a deuterium atom directly to the oxygen atom, *i.e.* when it has an oxygen-deuterated phenol structure, one should expect that it is capable of donating a deuteron to base. Therefore, the ICR spectrum of 3,5-dimethyl pyridine has been taken because of its suitable

molecular weight (Fig 2) to check whether the behaviour of this possibly suited deuteron acceptor is not too complicated.

Its appearance turns out to be very simple under the applied conditions; in addition to the fragments generated from the molecular ion by unimolecular decompositions, there is only one ion present, arising from an ion-molecule collision, *i.e.* the $(M+H)^+$ -ion at m/e 108.

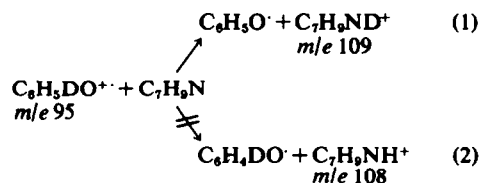
When a mixture of our trideuterated phenetole and 3,5-dimethyl pyridine is introduced in the ICR cell, it is of special interest to note that the ICR spectrum then contains a peak at m/e 109, thus indicating that indeed a $(M+D)^+$ ion of 3,5-dimethyl pyridine is generated (Fig 3).

Double resonance shows, that neutral 3,5-dimethyl pyridine accepts exclusively a deuteron from the $C_6H_5DO^+$ ion in an exothermic reaction (Fig 4a and Eq. 1), but not a proton (Fig 4b and Eq. 2).*†

*†A negative signal in the double resonance technique, *i.e.* a decrease in product ion intensity, has been associated with exothermic or thermoneutral reactions. See J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.* **48**, 1783 (1968).

*†Reaction 1 is exothermic by 23 kcal/mol, if the following assumptions and data are used: (a) Although the proton affinity of 3,5-dimethyl pyridine in the gas phase is not yet known, it seems very likely that it will approach that of pyridine, having a proton affinity of 225 ± 2 kcal. M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz and R. W. Taft, *J. Am. Chem. Soc.* **94**, 1369 (1972); (b) Heats of formation: $\Delta H_f^\circ(C_6H_5O^+) = 173$ kcal/mol, $\Delta H_f^\circ(C_6H_5O) = 9$ kcal/mol and $\Delta H_f^\circ(H^+) = 366$ kcal/mol. We have neglected the fact, that in reaction 1 not a proton, but a deuteron is transferred, which seems reasonable because the heats of formation of H^+ and of D^+ differ only by 1 kcal/mol. See for these data J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl and F. H. Field, *Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions*, NSRDS-NBS 26, U.S. Government Printing Office, Washington, D.C. (1969); (c) The value $\Delta H_f^\circ(C_6H_6O^+) = 173$ kcal/mol actually refers to the molecular ion of phenol. The heat of formation of the $C_6H_6O^+$ ion from phenyl ethyl ether appears to be larger, as one can deduce from its A.P. measurements, so that reaction 1 will be even more exothermic.

See for the A.P. measurements R. G. Gillis, G. J. Long, A. G. Moritz and J. L. Occolowitz, *Org. Mass Spectrom.* **1**, 527 (1968) and M. M. Bursey and C. E. Parker, *Tetrahedron Letters* 2211 (1972). For a discussion on this difference also see D. H. Williams, R. G. Cooks and I. Howe, *J. Am. Chem. Soc.* **90**, 6759 (1968).



Yet our ICR spectrum shows the presence of $C_7H_9NH^+$. This originates partly without interference of phenetole fragments (*cf.* Fig 2) but also by transfer of a proton from the $C_6H_5O^+$ ion to neutral 3,5-dimethyl pyridine as clearly shown again by double resonance (Fig 4b). Because of the small amount of $C_6H_5O^+$ ions this is a minor process (Figs 1 and 3).

Because the $C_6H_5DO^+$ ion acts exclusively as a D^+ donor, this rules out a cyclohexadienone structure (3), because (apart from a small isotope

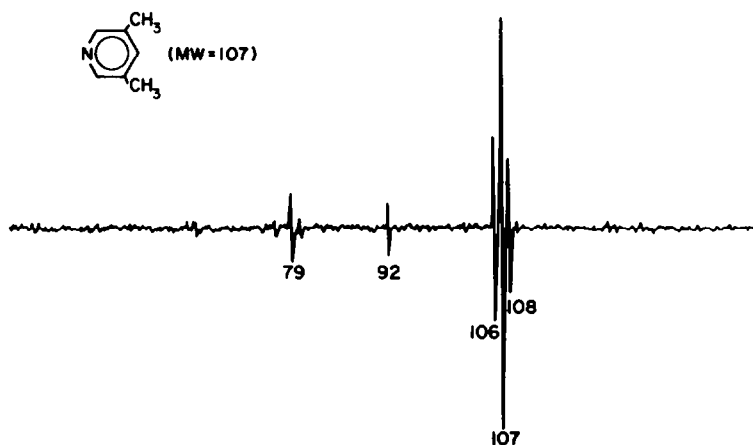


Fig 2. ICR spectrum of 3,5-dimethyl pyridine, $\omega/2\pi = 153.6$ kHz, 2.4×10^{-6} Torr, 20 eV.

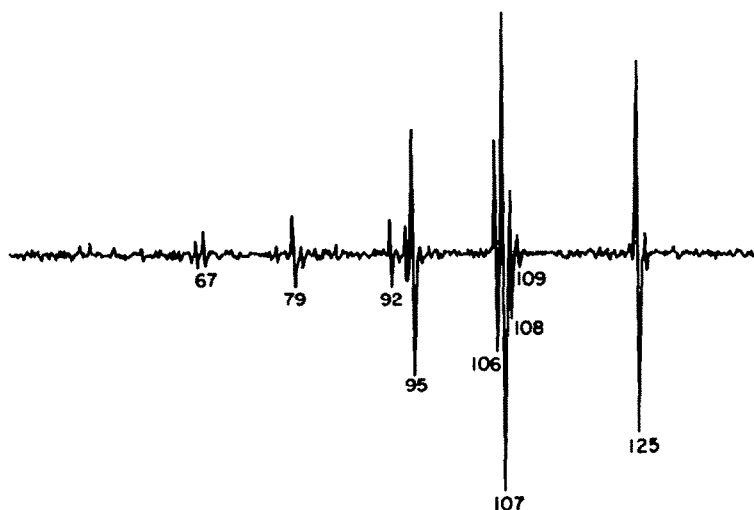
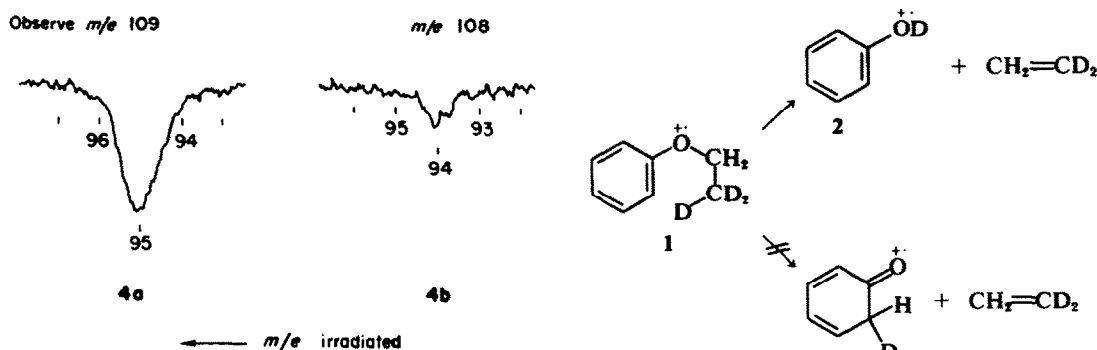


Fig 3. ICR spectrum of a mixture of phenyl 2,2,2-trideuteroethyl ether (2×10^{-6} Torr) and of 3,5-dimethyl pyridine (2.4×10^{-6} Torr), $\omega_1/2\pi = 153.6$ kHz, 20 eV.



Figs 4a and 4b. The double resonance spectra of the $(M+D)^+ = m/e$ 109 and of the $(M+H)^+ = m/e$ 108 ions of 3,5-dimethyl pyridine (2.4×10^{-6} Torr), mixed with phenyl 2,2,2-trideuteroethyl ether (2×10^{-6} Torr). Both ions are observed with $\omega_1/2\pi \times 153.6$ kHz while frequency ω_2 is swept through the mass range m/e 93–96. The irradiating voltage is 0.1 V and the electron energy 20 eV.

effect) this should be an equally good H^+ donor whether it isomerises to a phenol* or not.

Reaction of the $C_6H_5DO^+$ ion from phenyl 1,1-dideuteroethyl ether with neutral 4-t-butyl pyridine

As described above we have studied whether the $C_6H_5DO^+$ ion from phenyl 1,1-dideuteroethyl

ether is capable of donating either a deuteron or a proton or both to a base. In this case we have chosen 4-t-butyl pyridine as base because of its higher molecular weight, so that there is a better chance of separating in the double resonance experiment the translationally heated ions $C_6H_5DO^+$ and $C_6H_5O^+$, the latter now being present in excess (Fig 5).

The ICR spectrum of 4-t-butyl pyridine contains in addition to peaks arising from unimolecular decompositions of its molecular ion, a small peak at m/e 136 due to a $(M+H)^+$ ion (Fig 6).

A mixture of our dideuterated phenetole and 4-t-butyl pyridine gives a peak at m/e 137, showing that indeed in an ion-molecule reaction the $(M+D)^+$ ion of 4-t-butyl pyridine is generated (Fig 7).

Double resonance shows, that the $C_6H_5DO^+$ ion although present in small amounts, does indeed transfer a deuteron to neutral 4-t-butyl

*The heat of formation of the cyclohexadienone ion is estimated to be 26 kcal/mol higher than that of its phenolic tautomer, so that on isomerization a vibrationally and rotationally excited phenolic ion can be generated, which then could be collisionally desactivated in the ICR cell. R. G. Gillis, G. J. Long, A. G. Moritz and J. L. Ocolowitz, *Org. Mass Spectrom.* 1, 527 (1968).

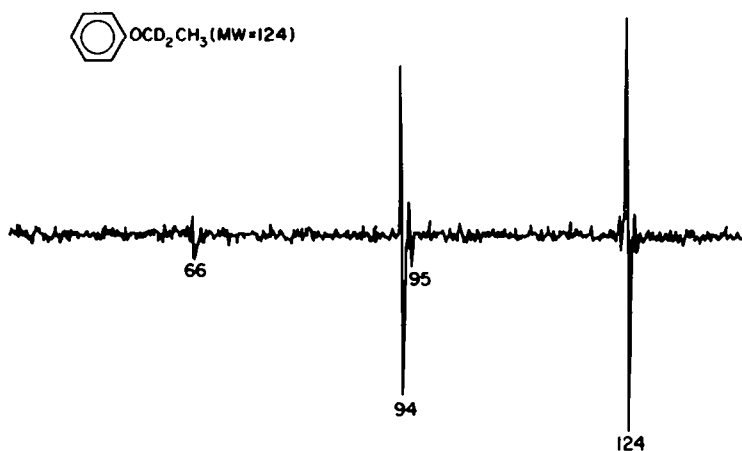


Fig 5. ICR spectrum of phenyl 1,1-dideuteroethyl ether, $\omega_1/2\pi = 153.6$ kHz, 6.8×10^{-6} Torr, 20 eV.

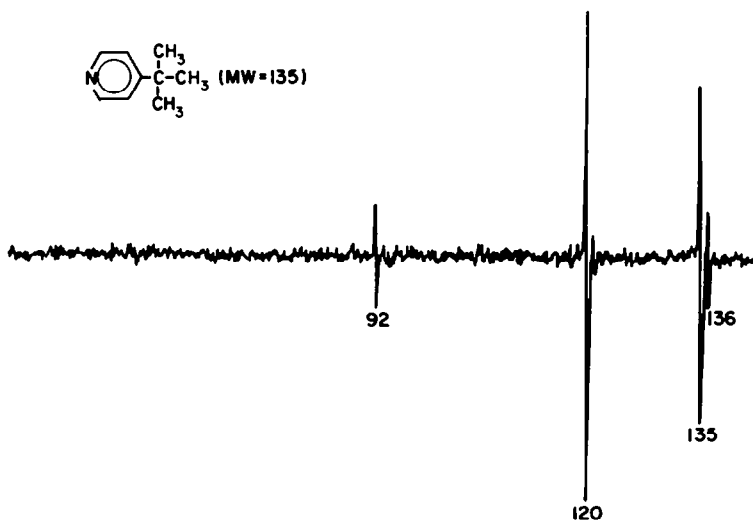
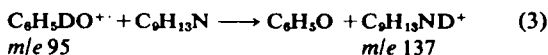


Fig 6. ICR spectrum of 4-t-butyl pyridine, $\omega_1/2\pi = 153.6$ kHz, 4.8×10^{-6} Torr, 20 eV.

pyridine in an exothermic reaction (Fig 8a and equation 3).*



Under the same conditions the more abundant $\text{C}_6\text{H}_6\text{O}^+$ ion appears to donate a proton to neutral 4-t-butyl pyridine, but the double resonance signal also has a shoulder at a position, where the ion *m/e* 95 should give a peak when it transfers a proton to neutral 4-t-butyl pyridine (Fig 8b). Its height however, as far as can be estimated, is not larger than expected for the ^{13}C -isotope of the

$\text{C}_6\text{H}_6\text{O}^+$ ion (the estimated intensity of *m/e* 95 relative to that of *m/e* 94, derived from 3 scans as given in Fig. 8b, is $\sim 8 \pm 2\%$, which is very close to the calculated value of 6.6%). We may therefore assume, that the $\text{C}_6\text{H}_5\text{DO}^+$ ion is only capable of donating a deuterium to 4-t-butyl pyridine, which again supports a phenolic structure.

These results suggest that hydrogen transfers from the 1 and 2 positions of the ethyl chain are exclusively to the oxygen atom.

Obviously, the suggestions of Djerassi³ (based upon the work on phenyl *n*-butyl ether) "that the initial structures of the $\text{C}_6\text{H}_6\text{O}^+$ ions would be the ionized 2,4-cyclohexadienone for hydrogen transfer from the 1 and 2 positions" are not applicable to the phenyl ether system.

It should be noted that Djerassi has also postu-

*^dSee footnotes ^a and ^b, p. 386. The proton affinity of 4-t-butyl pyridine in the gas phase is not yet known.

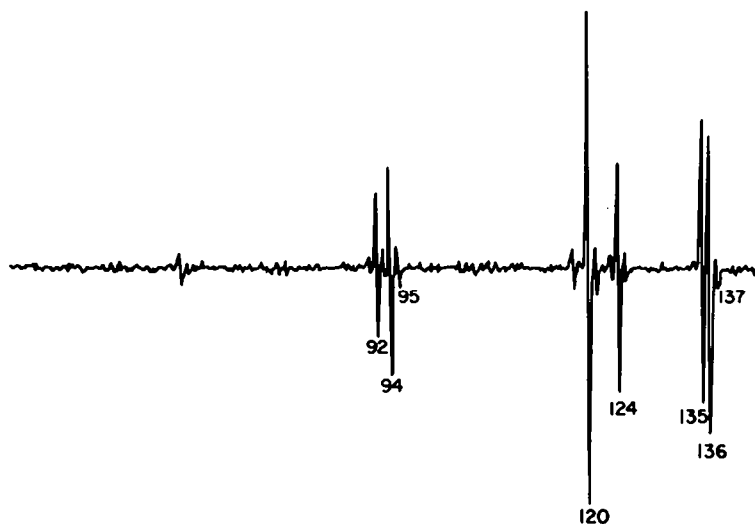


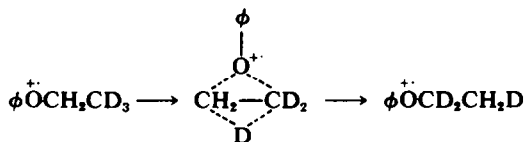
Fig 7. ICR spectrum of a mixture of phenyl 1,1-dideuteroethyl ether (4×10^{-6} Torr) and of 4-t-butyl pyridine (1×10^{-3} Torr), $\omega_1/2\pi = 153.6$ kHz, 20 eV.

ated the ionized phenol structure but then exclusively for hydrogen transfer from the 3 and 4 positions.

The problem remains, why in our case transfer of a methylene hydrogen atom to the oxygen in the molecular ion of phenetole should result in the loss of ethylene.

Hydrogen scrambling in the ethyl chain prior to fragmentation* seems unlikely considering the recent work of Djerassi on phenyl *n*-butyl ether.³

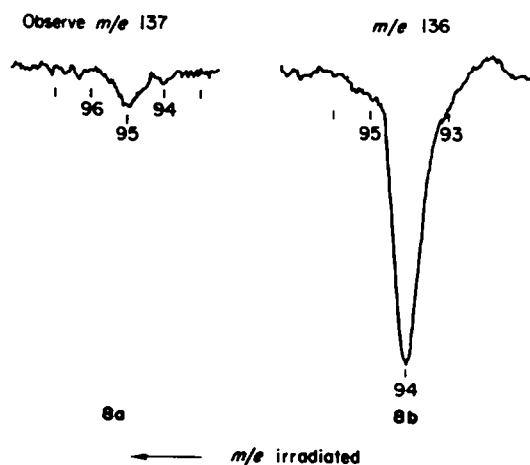
A different explanation could be an interchange of the phenoxy group and one of the original methyl hydrogen atoms in some of the molecular ions prior to fragmentation, perhaps *via* the intermediate:



Such a positional interchange of groups, separated by two carbon atoms, has also recently been

*See refs 6a–g, quoted in ref 3.

*C. B. Theissling, N. M. M. Nibbering and Th. J. de Boer, in *Adv. in Mass Spec.*, Vol. 5, p. 642. A. Quayle, Ed., Institute of Petroleum, London (1971). In all molecular ions of the 2-phenoxyethyl halides the phenoxy group and the halogen atom were equally distributed over the two side-chain carbon atoms prior to formation of the $C_6H_6O^+$ -species. In the present case this holds only for a part of the molecular ions, probably due to the difference in bond strengths of the C–H– and C–X bonds.



Figs 8a and 8b. The double resonance spectra of the $(M+D)^+ = m/e$ 137 and of the $(M+H)^+ = m/e$ 136 ions of 4-t-butyl pyridine (1×10^{-5} Torr), mixed with phenyl 1,1-dideuteroethyl ether (4×10^{-6} Torr). Both ions are observed with $\omega_1/2\pi = 153.6$ kHz, while frequency ω_2 is swept through the mass range m/e 93–96. The irradiating voltage is 0.1 V and the electron energy 20 eV. The very weak signal at m/e 94 in Fig. 8a corresponds with proton transfer of the $C_6H_6O^+$ ion to the natural ^{13}C and ^{15}N isotope of 4-t-butyl pyridine.

found by us in the molecular ions of 2-phenoxyethyl halides† and of benzylicyanide⁴ (interchange of phenoxy group and halogen atom and of phenyl group and nitrogen atom, resp.) and in the $(M-CH_2OH)^+$ -ion from 2-methyl-2-phenyl-propane-1,3-diol⁵ (interchange of phenyl and hydroxyl groups).

EXPERIMENTAL

All measurements were made using a Varian V-5903 ICR spectrometer (serial number 126) fitted with the standard flat three-section cell (cross-section 1.27×2.54 cm; one of the drift plates of the analyzer region extends to the end of the ion collector region) and equipped with a dual inlet system. All experiments were performed at ambient temperature. The electron energy was set by use of a digital voltmeter and pressures were determined from the ion pump current meter. The emission current was $0.14 \mu\text{A}$ (Figs 1 to 5) and $0.20 \mu\text{A}$ (Figs 6 to 8b), giving total ion currents within the ranges 4×10^{-12} – 1×10^{-11} A (Figs 1 to 6) and 2.5 – 5×10^{-11} A (Figs 7 to 8b).

The latter range is somewhat too high and therefore not ideal as shown by K. R. Jennings,⁶ but it appeared to be necessary because of the low abundances of the ions under investigation (*m/e* 95 and *m/e* 137; see Figs 7 to 8b and text). The electron collector voltage was zero.

Typical cell voltages were: trap, $+0.41$ V (Figs 1 to 6) and $+1.03$ V (Figs 7 to 8b); analyzer, split, $+0.02$ V and $+0.28$ V (Figs 1 to 8b); source, split, -0.33 V and $+0.50$ V (Figs 1 to 8b). The rf level of the marginal oscillator was set so as to produce no change in total ion current at resonance.

Single resonance spectra were obtained in the field modulation mode (amplitude 20 G) with a sweep rate of 5 min., response 0.1 sec.

In the ion cyclotron double resonance experiments square wave modulation was employed and the spectra were recorded with a sweep rate of 10 min., response 10 sec (sweep width of the frequency of the irradiating oscillator ~ 35 kHz). The irradiating oscillator was applied to the source region.

During the scans, the total ion current was also monitored as recommended by K. R. Jennings⁶ by connecting the output of the electrometer, which measures the total ion current, to a digital voltmeter. It appeared, that the total ion current dropped $< 1\%$ at the peaks.

Phenyl 2,2,2-trideuteroethyl ether was obtained by reduction of phenyl 2-bromo-2',2'-dideuteroethyl ether, described earlier,^{*} with LAH , in ether, and then purified (GLC) using a 10 percent silicone rubber SE-30 column. The sample appeared to contain 95.5% d_3 and 4.5% d_2 molecules, as derived from the peak heights in the molecular ion mass range of its ICR spectrum (Fig 1);

these peak heights were determined from slow scans (3x) through this mass range and then divided by the masses of the corresponding ions⁷ before they were used to calculate the deuterium content.

Phenyl 1,1-dideuteroethyl ether was obtained from phenyl 2-chloro-1,1-dideuteroethyl ether, described earlier^{*} by reduction with LAH in THF and then purified by GLC as above. From its ICR spectrum (Fig 5) it was calculated that the sample contained 92.7% d_2 and 7.3% d_1 molecules, in excellent agreement with previous deuterium content measurements of the starting sample.^{*}

3,5-dimethyl pyridine was a trade product of Merck and 4-t-butylpyridine was available in our laboratory.

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¹⁶G. C. Goode, R. M. O'Malley, A. J. Ferrer-Correia, R. I. Massey, K. R. Jennings, J. H. Futrell and P. M. Llewellyn, *Int. J. Mass Spec. Ion Phys.* 5, 393 (1970).

*See footnote ¹/p. 389.