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### High-performance liquid chromatographic separation of gas-phase benzylation products of aniline

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The aim of this work was to develop a high-performance liquid chromatographic (HPLC) system able to separate all the possible products of the gas-phase benzylation of aniline.

The mechanism of benzylation has been studied by several workers<sup>1</sup> owing to its importance in the synthesis of aromatic ketones. Speranza and co-workers<sup>2</sup> have recently investigated gas-phase benzylation using a nuclear decay technique which is able to eliminate some environmental factors (*e.g.*, the effects of solvent, catalyst, etc.) that strongly influence the reaction in the liquid phase<sup>2</sup>. They allowed [1,4-<sup>3</sup>H<sub>2</sub>]benzene to decay in the presence of carbon monoxide and traces of a nucleophilic substrate, such as ethanol or benzene. Under these conditions the benzoyl cation (C<sub>6</sub>H<sub>5</sub>CO<sup>+</sup>) was formed, which then reacted with the substrate. They are now studying the reaction of tritiated benzene with another nucleophilic aromatic reagent, aniline. Here some different reactions are possible, leading to biphenyl, diphenylamine, benzanilide, 2-, 3- and 4-aminobenzophenone and 2-aminobiphenyl.

It was therefore necessary to separate these substances and their precursors. Although in the literature some HPLC separations of different series of aromatic amines<sup>3</sup> and ketones<sup>4</sup> have been reported, so far no separation of mixtures containing both aromatic amines and ketones has been reported. In this paper we describe an HPLC separation of the possible reaction products.

## EXPERIMENTAL

### *Chromatographic equipment*

The HPLC apparatus consisted of a Perkin-Elmer Series 3B liquid chromatograph, equipped with a Rheodyne 7105 injection valve, a Perkin-Elmer LC-75 variable-wavelength UV-visible detector with Autocontrol and a Perkin-Elmer 561 recorder.

### Materials

Methanol was of HPLC grade (Carlo Erba, Milan, Italy). All other reagents were of RPE grade (Carlo Erba). Solutions were filtered before use through a Millipore MF filter (0.30  $\mu\text{m}$ ). Water was distilled and Millipore-filtered.

Standards of biphenyl, diphenylamine, 2-, 3- and 4-aminobenzophenone and benzanilide were kindly provided by G. Occhiucci (Istituto di Chimica Nucleare, CNR, Rome, Italy).

### Chromatography

HPLC analysis was performed with the following chromatographic systems: a Spherisorb ODS column ( $d_p$  5  $\mu\text{m}$ ; 150  $\times$  4 mm I.D.; packed by Violet, Italy), eluted (A) with 50 mM phosphate buffer (pH 3.0)-methanol (50:50) initially, then with gradient elution to 75% methanol in a 30-min linear programme, and (B) with 50 mM phosphate buffer (pH 3.0)-methanol (55:45) initially, then with gradient elution to 70% methanol in a 20-min linear programme, and finally with isocratic elution with phosphate buffer (pH 3.0)-methanol (30:70) for 10 min.

All elutions were carried out at a flow-rate of 1 ml/min. Detection was carried out at 270 and 360 nm.

### RESULTS

A chromatogram of the possible benzylation products detected at 270 nm is shown in Fig. 1; the elution conditions used were as in B above. In fact, peaks 3 and 4 are completely overlapping when system A is used. All the compounds are separated

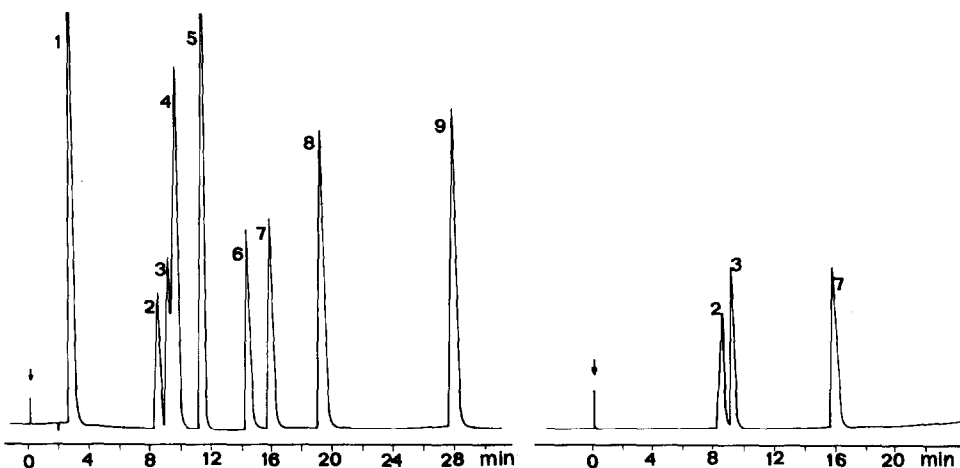


Fig. 1. Chromatograms of gas-phase benzylation products of aniline with UV detection at 270 nm (0.16 a.u.f.s.). Solvent programme B. Peaks: 1 = aniline; 2 = 4-aminobenzophenone; 3 = 3-aminobenzophenone; 4 = benzanilide; 5 = benzene; 6 = 2-aminobiphenyl; 7 = 2-aminobenzophenone; 8 = diphenylamine; 9 = biphenyl.

Fig. 2. Chromatogram of gas-phase benzylation products of aniline with UV detection at 360 nm (0.16 a.u.f.s.). Solvent programme B. Peaks: 2 = 4-aminobenzophenone; 3 = 3-aminobenzophenone; 7 = 2-aminobenzophenone.

in this system, except 3-aminobenzophenone and benzanilide, which are not completely resolved. However, if the same separation is monitored at 360 nm (Fig. 2) only 2-, 3- and 4-aminobenzophenone are detected. Hence it is possible to detect 3-aminobenzophenone without interference from benzanilide.

In conclusion, two chromatographic separations carried out with the same elution system, but with different wavelengths of detection, allow all the compounds under examination to be resolved.

#### REFERENCES

- 1 H. Gore, in G. A. Olah (Editor), *Friedel-Crafts and Related Reactions*, Vol. III, Interscience, New York, 1964, p. 1.
- 2 G. Occhiucci, A. Patacchiola, C. Sparapani and M. Speranza, *J. Chem. Soc. Chem. Commun.*, (1982) 1269.
- 3 H. Johnson, Jr., S. F. Cernosek and R. M. Gutierrez Cernosek, *J. Chromatogr.*, 161 (1978) 259.
- 4 P. R. Young and H. M. McNair, *J. Chromatogr.*, 119 (1976) 569.