Journal of Chromatography, 481 (1989) 477–479
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 838

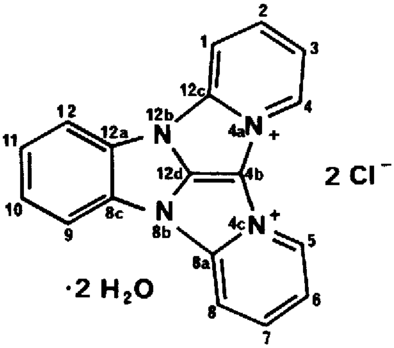
Letter to the Editor

2-Trichloromethylbenzimidazole, a selective chromogenic reagent for the detection of some azines on thin-layer plates

Addendum

Sir,

In a previous study[1], some azines were detected on thin-layer chromatographic (TLC) plates using their reaction with 2-trichloromethylbenzimidazole (TCMB). The structure of the product of the reaction of TCMB with pyridine shown here was suggested[1]. In this addendum, the analytical and spectral evidence that confirms this structure are presented.



EXPERIMENTAL

4a,4c,8b,12b-Tetraazadibenzo[a,f]indano[1,2,3-cd]pentalene-4a,4c-diinium dichloride dihydrate

TCMB (234 mg, 1 mmol, freshly recrystallized from chloroform) was dissolved in pyridine (790 mg, 10 mmol, 99.8% chromatographic standard purity). An amaranth product was precipitated after several minutes. After 5 h, the solid product was filtered off and washed with diethyl ether and acetone and dried under vacuum over phosphorus pentoxide until the odour of pyridine had disappeared. The yield was 122 mg (31%); m.p. >360°C.

The crude product was purified by preparative TLC on precoated Polyamid 11 F_{254} aluminium sheets, 0.2 mm thick (Merck). The chromatograms were developed in acetic acid–water (1:9, v/v). The amaranth zone ($R_F = 0.51$) was scraped from the plate and eluted with methanol. The characteristics were as follows.

Elemental analysis: found, C 54.71, H 4.18, N 13.61, Cl 17.70; calculated for $C_{18}H_{12}N_4Cl_2 \cdot 2H_2O$, C 54.26, H 4.12, N 14.32, Cl 18.12%.

0021-9673/89/$03.50

Electron impact mass spectrometry (EI MS) (LKB 9000A, 70 eV, 250°C); m/z (intensity, %): 286 (1.0) 285 (23.8), M^+ 284 (100.0), 283 (64.1), M^{2+} 142 (1.1).

High-resolution EI MS (Finnigan-MAT 8200, resolution 7000): M^+ m/z 284, found 284.1056, calculated for $C_{18}H_{12}N_4$ 284.1062; M^{2+} m/z 142, found 142.0523, calculated for $C_9H_6N_2$ 142.0531.

Field desorption (FD) MS (Varian-MAT 711, J_E = 20 mA): m/z (intensity, %), 285 (33.5), M^+ 284 (100.0).

^1H NMR (Jeol JNM-100, 100 MHz, CH_3OH-d_4, hexamethyldisiloxane as internal lock, 25°C): δ (ppm), 6.5–9.6 (m).

IR (Specord IR-75, KBr pellets): ν (cm^{-1}), 3400sb (H_2O), 3090w, 3040w, 3015m (C–$H_{arom.}$), 1635s (C=N), 1630m, 1605s, 1590m, 1540m, 1510s (C=C and C=N of aromatic rings), 1460m, 1440m, 1390m, 1305w, 1205m, 1185m; 765m, 745s (2-substituted pyridie).

UV (Pye Unicam SP 700, CH_3OH): $\lambda_{max.}$ (nm) (log $E^{1\%}_{1\,cm}$), 210 (2.86), 240 (2.97), 350 (2.67), 520 (2.53).

The same procedure was repeated using pyridine-d_5 (of NMR solvent grade) and the deuterium-labelled product was obtained, with the following characteristics.

EI MS (70 eV, 20°C): m/z (intensity, %), 294 (6.1), 293 (34.6), M^+ 292 (100.0), 291 (27.3), 290 (61.9), 289 (10.0), 288 (11.3), M^{2+} 146 (9.9).

IR (KBr pellets): ν (cm^{-1}), 2700 mb (^2H_2O), 2270 m (C–$^2H_{arom.}$).

DISCUSSION

The proposed structure shown above is confirmed by the analytical and spectral data. The high polarity and m.p. of the examined compounds are indicative of an ionic structure.

In the mass spectra of the product (EI and FD), the molecular ion of the cationic fragment at m/z 284 (no chlorine) was found and its formula was determined as $C_{18}H_{12}N_4$ using high-resolution EI MS.

The formula $C_{18}H_{12}N_4Cl_2 \cdot 2H_2O$ was confirmed by elemental analysis. Therefore, the identified product must be a dication.

The molecular ion M^{2+} is converted into the base ion M^+ after the addition of an electron under EI ionization conditions: $M^{2+} + e^- \rightarrow M^+$. This phenomenon, characteristic of negative ionization MS, was also observed in the EI mass spectra of some dications, *e.g.*, diquat dibromide.

The UV and ^1H NMR spectra confirm the aromatic character of the molecule.

The band characteristics of aromatic C–H, C=C and C=N bonds was found in the IR spectrum. The bands typical of 2-substituted pyridines were present. No N^+–H band was observed.

In the EI mass spectrum of the deuterium-labelled compound, the M^+ ion of the octadeuterated derivative at m/z = 292 was observed. In the IR spectrum the bands characteristic of ^2H_2O and C–^2H were found.

The above evidence indicates that the structure shown is the most probable for the major product of the reaction of TCMB with pyridine.

ACKNOWLEDGEMENTS

The authors express their gratitude to Halina Jelin and Jerzy Zakrzewski for valuable assistance.

Institute of Industrial Organic Chemistry,
Annopo 16, 03-236 Warsaw (Poland)

LESZEK KONOPSKI*
BOLESŁAW JERZAK

1 L. Konopski and B. Jerzak, *J. Chromatogr.*, 363 (1986) 394–396.

(First received May 25th, 1989; revised manuscript received July 28th, 1989)