ELSEVIER

Journal of Chromatography A, 878 (2000) 235–247

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Gas chromatography–mass spectrometry–Fourier transform infrared spectrometry and high-performance liquid chromatographic characterization of mononitro- and dinitro-isomers from the nitration of *N*,*N*-dimethyldiphenylacetamide

Ladislav Soják[a,*], Alexander Perjéssy[b], Róbert Kubinec[a], Janka Čambáliková[c], Angelo G. Giumanini[d], Giancarlo Verardo[d], Monica M. Magnan[d]

[a]*Institute of Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovak Republic*
[b]*Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovak Republic*
[c]*State Veterinary Institute, Department of Pollutants, Botanická 15, 842 52 Bratislava, Slovak Republic*
[d]*Department of Chemical Sciences and Technologies, University of Udine, 33100 Udine, Italy*

Received 12 October 1999; received in revised form 24 February 2000; accepted 25 February 2000

Abstract

Gas chromatographic retention data, Fourier transform infrared and mass spectrometric (electron impact, electron attachment and methane chemical ionization) profiles are reported for the products of mono- and dinitration of *N*,*N*-dimethyldiphenylacetamide. Differentiations of analytical importance among isomers could be gathered by the study which led to their complete identification.

Keywords: Dimethyldiphenylacetamide; Nitro compounds; Pesticides

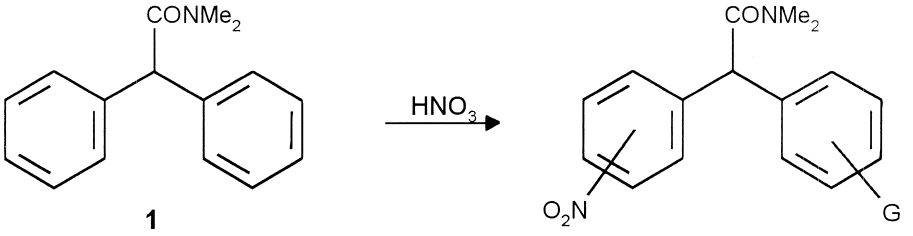
1. Introduction

In the continuing interest in the innovative method of nitration of aromatic substrates in dichloromethane [1,2], which has revealed the chaperon effects of a number of α-substituents, leading to high conversions to *ortho*-nitro derivatives, the study has now moved to the observation of the amide function as the chaperon in the diphenylmethane derivatives, which are characterized by a bulky substituent. A tertiary amide group gives better assurance of avoiding side reactions at the nitrogen center: to this end we selected *N*,*N*-dimethyldiphenylacetamide (**1**). Incidentally, this is a widely used pesticide and therefore a commercially available product. With this relationship in mind, particular attention is therefore paid to the problem of detailed analysis of its nitration products, i.e., the isomeric mononitro **2**–**4** and dinitro compounds **5**–**10** (Fig. 1).

In previous works we solved the problem of the identification of isomers from mono- and dinitration of both phenyl-, diphenyl- [3], and (hydroxy)-diphenylacetic acids [4] by programmed temperature capillary gas chromatography (cGC) with Fourier transform infrared spectrometric (FT-IR) and mass

*Corresponding author. Fax: +421-7-6542-9064.
E-mail address: sojak@fns.uniba.sk (L. Soják)

0021-9673/00/$ – see front matter
PII: S0021-9673(00)00287-9



G = H **2** *ortho-*, **3** *meta-*, **4** *para-*
G = NO_2 **5** *ortho,ortho′-*, **6** *ortho,meta′-*, **7** *ortho,para′-*, **8** *meta,meta′-*, **9** *meta,para′-*, **10** *para,para′-*

Fig. 1. Nitration of *N,N*-dimethyldiphenylacetamide.

spectrometric (MS) detection. In the following study [5] the isothermal GC and FT-IR data of the above methyl arylacetates were generalized. The usefulness of GC–MS–FT-IR and HPLC–UV for the characterization of the diisopropylnaphtalene isomers in an industrial mixture was documented by other authors [6].

The aim of this work is the identification of mono- and dinitro isomers from the nitration of *N,N*-dimethyldiphenylacetamide (**1**) by means of cGC–FT-IR–MS, which is interesting because of the unavailability of GC–MS–FT-IR data as well as of the lack of commercial standard reference materials (none of these nitro compounds were known from literature) or difficult separate independent preparation of these analytes.

2. Experimental

2.1. Materials

N,N-Dimethyldiphenylacetamide (**1**) was provided by Sipcam (Milan, Italy) and purified by crystallization from ethanol to constant melting point before use. Mixed mononitro isomers **2**–**4** were obtained by nitration of **1** with nitric acid in dichloromethane at room temperature; all of the *x,x′*-dinitro derivatives could be obtained as a mixture from a standard nitration of **1** with two equivalents of nitric acid in concentrated sulphuric acid. Full details about these experiments as well as the syntheses and separations of the pure isomers **2**, **4**, **5**, **7** and **10** will be made available in a paper under preparation. They were found to be stable under the gas chromatographic conditions of this work. Their MS spectra, obtained in the direct inlet mode and via GC, were identical.

2.2. GC–MS–FT-IR experiments

GC separation of nitration products of *N,N*-dimethyldiphenylacetamide was carried out with a laboratory-prepared fused-silica capillary column, 6 m×320 μm I.D., coated with OV-1 as the stationary phase, 0.40 μm film thickness. The carrier gas was helium at an inlet pressure of 50 kPa and a linear velocity of 40 cm s^{-1}. Samples were diluted with chloroform and volumes of 0.5 μl were injected onto the column using splitless technique (0.5 min). The injector and detector temperatures were 310°C. The column efficiency was 17 000 plates for *para,para′*-dinitro derivative with the retention factor $k'=92$ at 230°C in a GC run with a flame ionization detection (FID). *n*-Alkanes were added to the mixtures of nitration products in order to evaluate retention indices in isothermal and temperature-programmed separations. Isothermal retention indices were measured at 200, 230 and 250°C, and temperature-programmed indices at column temperatures programmed from 150 to 310°C at 30°C min^{-1}. Retention indices were measured with an average repeatability of ±1 index unit.

A Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph equipped with a FID system, a HP Model 5965A IR detector, and a HP 5971A mass-selective detector was used for obtaining GC, FT-IR and MS data.

In order to obtain the FT-IR spectral data the concentrations of injected samples were higher than those for GC–FID but only as much as needed to preserve the baseline separation of investigated isomers. The FT-IR light-pipe temperature was 310°C. The wave numbers of absorption bands were determined as average values of three different measurements with a reproducibility of 1 cm^{-1}. Data treatment was carried out with a HP Model 59970C Chemstation, equipped with an HP 9000 Series 300 computer.

Mass spectra were recorded by cyclic scanning from 45 to 350 mass units with a cycle time of 0.51 s and a solvent delay of 1 min. A HP 59970C data system was used for data acquisition and elaboration. The transfer line temperature was 280°C. The quadrupole conditions were electron energy 70 eV, emission current 300 μA and ion source temperature 180°C.

Mass spectral data were also independently obtained from a Finnigan Trio 2000 GC–MS system operating at 20 and 70 eV ionization energy [electron impact (EI) positive ion spectra], in the methane chemical ionization (CH_4-CI) mode (CI positive ion spectra) and in the negative ion mode (electron attachment negative ions). The five most intensive peaks detectable in the range 44−(M+2) u and some other interesting peaks for each individual compound were measured and are reported in Table 1.

2.3. HPLC experiments

The measurements were performed using a HPLC system consisting of a Model 2350 HPLC pump (Isco, NE, USA), an Autosampler Marathon-XT (Spark Holland, Emmen, The Netherlands) and a Model 9065 diode array detection (DAD) system (Varian, Sunnyvale, CA, USA). The compounds were separated by a Merck LiChrospher RP-18 column (250 mm×4 mm I.D., spherical particles of 5 μm) and methanol–acetonitrile–water (13:33:54) as mobile phase at a flow-rate of 1 ml min^{-1}. The column efficiency was 8100 effective plates for the retention factor $k'=20.4$ at 21°C. The DAD system recorded in the range 220–360 nm with a scan rate of 11 cycles s^{-1} and resolution of 1 nm. A 10-μl volume of solution was injected into the instrumental system.

3. Results and discussion

3.1. GC

The chromatogram of the nitration products of *N*,*N*-dimethyldiphenylacetamide (**1**) obtained with temperature programming on a capillary column with OV-1 as the stationary phase is shown in Fig. 2. In a short capillary column with an efficiency of 17 000 plates, complete separation of the isomeric mono- and dinitro derivatives as well as a parent compound was obtained in 5 min. The measured values of their retention indices with temperature programming and isothermally at 230°C and their temperature coefficients are given in Table 2. The identification of the compounds corresponding to the individual GC peaks, which were carefully examined along the elution profile for homogeneity, was performed from their complementary data from GC retention properties, IR and MS spectra as well as the comparison with the prepared nitro derivatives. The isomers of mononitro derivatives were eluted in the order *ortho*-, *meta*- and *para*-, whereas the dinitro derivatives emerged in the sequence *ortho,ortho′*-, *ortho,meta′*-, *ortho,para′*-, *meta,meta′*-, *meta,para′*- and *para,para′*-. These retention orders are identical to those of the mono- and dinitro methyl esters of diphenylacetic acid [3], (hydroxy)diphenylacetic acids [4], as well as of isomeric methylbiphenyls and heteronuclearly-substituted dimethylbiphenyls bearing CH_3 groups in both aromatic rings [7].

Since the relationships between the structure and linear retention indices are more complicated than those of logarithmic (Kováts) retention indices [8], the retention indices obtained under isothermal conditions were used for the correlations between the structure and retention behavior as a means of characterization using the principle of additivity of retention increments of the NO_2 group in different structural positions [5]. The increments of the NO_2

Table 1
Mass spectra of compounds **1–10**

Compound (position of nitro group(s) and running number)	Electron impact			Chemical ionization
	Positive ions		Negative ions	
	70 eV	20 eV		
1	167 (100), 165 (82), 72 (63), 239 (M, 54), 152 (34), 168 (30), 166 (25)	167 (100), 72 (45), 239 (M, 40), 168 (14), 165 (7), 15 (3)	167	240 (MH, 100), 241 (20), 72 (3), 167 (3), 134 (2), 46 (1)
2 *Ortho-*	72 (100), 195 (76), 165 (22), 196 (19), 167 (16) 238 (14), 179 (12), 105 (11), 166 (8), 266 (7), 168 (7), 212 (7), 281 (0.2), 284 (M, 0.2), 282 (0.1), 283 (0.1)	195 (100), 72 (93), 196 (28), 238 (20), 167 (18), 179 (12), 168 (11), 266 (7), 212 (7), 105 (7), 285 (0.2), 283 (0.2), 284 (M, 0.1)	46 (100), 284 (M,92), 194 (22), 285 (19), 209 (17), 267 (14), 236 (13), 211 (12), 212 (7)	285 (MH, 37), 46 (34), 237 (13), 74 (7), 240 (7), 255 (6), 72 (4), 210 (3), 182 (1), 180 (0.9), 212 (0.5)
3 *Meta-*	72 (100), 165 (32), 196 (28), 182 (11), 166 (7) 164 (6), 212 (2), 254 (7), 284 (M, 0.6), 239 (0.4)	72 (100), 196 (62), 197 (9), 73 (9), 165 (7), 195 (5), 182 (5), 134 (5), 254 (4), 212 (2), 284 (M, 1), 207 (0.8), 240 (0.3), 268 (0.2)	284 (M,100), 46 (33), 285 (16), 212 (2)	285 (MH, 100), 255 (65), 286 (15), 256 (11), 72 (8), 269 (6), 240 (4), 46 (3)
4 *Para-*	72 (100), 165 (39), 254 (33), 182 (24), 166 (14) 164 (7), 196 (7), 212 (4), 284 (M, 1), 268 (0.3)	254 (100), 72 (82), 255 (16), 196 (13), 73 (9), 182 (7), 166 (7), 165 (5), 212 (4), 284 (M, 2), 281 (0.5), 268 (0.4)	284 (M,100), 212 (24), 46 (23), 285 (18)	285 (MH, 100), 255 (42), 286 (15), 283 (7), 256 (7), 72 (5), 269 (4), 46 (3), 74 (2), 240 (2)
5 *Ortho,ortho′-*	72 (100), 283 (48), 195 (24), 166 (18), 152 (11) 167 (10), 210 (10), 165 (8), 299 (0.4), 329 (M, 0.1), 330 (0.1), 327 (0.1)	72 (100), 283 (58), 195 (54), 240 (49), 166 (37), 210 (22), 194 (21), 167 (20), 16 (11), 266 (8), 299 (0.4), 330 (0.3), 329 (M, 0.1)	46 (100), 329 (M,31), 239 (7), 210 (6), 330 (5), 134 (4)	330 (MH, 100), 46 (15), 331 (15), 300 (7), 196 (7), 120 (6), 74 (4), 72 (3)
6 *Ortho,meta′-*	72 (100), 283 (61), 240 (38), 241 (22), 163 (19) 150 (19), 164 (15), 194 (14), 165 (13), 166 (10), 257 (6), 167 (6), 210 (5), 311 (4), 299 (3), 330 (0.3), 329 (M, 0.2), 328 (0.3)	72 (100), 283 (32), 240 (29), 194 (16), 241 (14), 166 (10), 210 (8), 150 (5), 167 (4), 299 (2), 311 (2), 330 (0.1), 329 (M, 0.1)	46 (100), 239 (64), 329 (M,.62), 254 (31), 312 (21), 310 (9), 294 (8), 282 (7), 210 (7), 134 (5), 299 (4),	330 (MH, 100), 300 (27), 46 (14), 331 (14), 72 (5), 74 (4), 270 (3), 120 (3)
7 *Ortho,para′-*	72 (100), 283 (42), 240 (30), 163 (13), 241 (11) 164 (10), 165 (10), 166 (7), 150 (11), 152 (8), 257 (5), 311 (2), 299 (1), 328 (0.3), 329 (M, 0.2), 330 (0.1)	72 (100), 283 (25), 240 (18), 241 (7), 194 (6), 210 (3), 227 (2), 257 (2), 311 (1), 299 (0.7), 328 (0.2), 330 (0.1), 329 (M, 0.1)	239 (100), 312 (73), 46 (68), 254 (55), 329 (M,36), 210 (15), 299 (11), 281 (9), 211 (8), 282 (3)	330 (MH, 100), 300 (25), 46 (12), 301 (4), 120 (4), 270 (4)
8 *Meta,meta′-*	72 (100), 164 (11), 163 (9), 165 (6), 73 (6) 152 (4), 299 (2), 329 (M, 0.3)	72 (100), 210 (0.9), 211 (0.8), 299 (0.7), 227 (0.7), 299 (0.7), 240 (0.6), 329 (M, 0.1)	329 (M,100), 46 (25), 330 (15), 257 (3), 299 (2)	270 (1), 74 (0.6), 207 (0.4), 330 (MH, 0.3), 300 (0.2), 285 (0.1)
9 *Meta,para′-*	72 (100), 164 (14), 163 (14), 165 (9), 152 (8) 227 (8), 139 (5), 299 (5), 329 (M, 0.2), 330 (0.2)	72 (100), 227 (3), 299 (2), 211 (0.8), 210 (0.7), 228 (0.5), 329 (M, 0.2), 257 (0.2), 283 (0.1)	329 (M,100), 46 (25), 257 (21)	270 (1), 74 (0.5), 207 (0.4), 330 (MH, 0.2), 285 (0.1)
10 *Para,para′-*	72 (100), 227 (11), 163 (7), 164 (6), 165 (6) 152 (5), 139 (3), 211 (2), 299 (2), 257 (1), 329 (M, 0.4)	72 (100), 227 (4), 299 (1), 181 (0.8), 228 (0.6), 257 (0.4), 329 (M, 0.2)	329 (M,100), 257 (70), 46 (19)	207 (0.5), 270 (0.5), 74 (0.4), 330 (MH, 0.1), 300 (0.1)

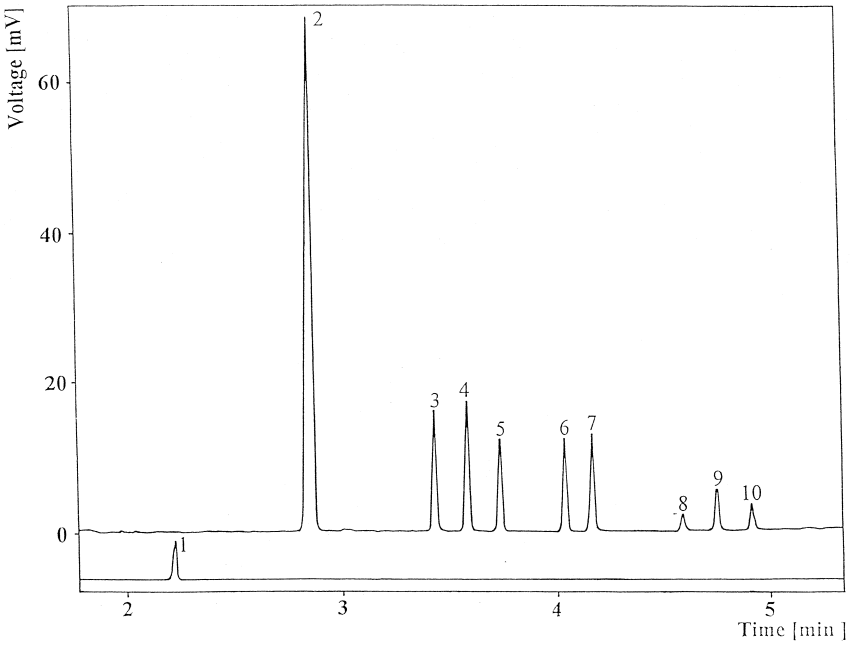


Fig. 2. GC–FID chromatogram of the products from the nitration of *N,N*-dimethyldiphenylacetamide and parent compound. Peak identification as in Table 2.

group to the retention indices of amidic compounds obtained by subtraction of retention index of parent compound from that of corresponding isomer at 200°C are given in Table 3. It is evident that the increments of the NO_2 group of mono- and dinitro derivatives increase in the same direction as the retention of corresponding isomers. This result is analogous to those observed in the case of nitro derivatives of other arylacetates [5].

Quantitatively, the increments of the NO_2 group are substantially lower for *ortho*-mononitro derivative **2** in comparison with those of methyl ester diphenylacetic acid and (hydroxy)diphenylacetic acid, and for *meta*- **3** and *para*- **4** isomers they are similar. Using the principle of additivity [5,8], the values of retention indices of isomeric dinitro derivatives of dimethyldiphenylacetamide calculated from these retention increments of the NO_2 group are in

Table 2
Temperature-programmed retention indices (TP-I), isothermal (230°C) retention indices (I) and temperature coefficients (dI/dT) for compounds **1–10**

GC peak No. (Fig. 1)	Compound (position of nitro group (s) and running number)		TP-I	I	dI/dT
1	Parent	**1**	1970	1997	0.7
2	*Ortho*-	**2**	2194	2213	0.9
3	*Meta*-	**3**	2390	2397	1.0
4	*Para*-	**4**	2446	2449	1.1
5	*Ortho,ortho′*-	**5**	2500	2497	1.3
6	*Ortho,meta′*-	**6**	2608	2597	1.2
7	*Ortho,para′*-	**7**	2658	2641	1.3
8	*Meta,meta′*-	**8**	2828	2792	1.2
9	*Meta,para′*-	**9**	2892	2849	1.4
10	*Para,para′*-	**10**	2963	2907	1.5

Table 3
Increments of the NO_2 group to the retention index ($\delta I_{200}^{OV\text{-}1}$) of mono- and dinitro derivatives of *N,N*-dimethyldiphenylacetamide on OV-1 as stationary phase at 200°C

Compound	$\delta I_{200}^{OV\text{-}1}$
Mononitro derivatives	
Ortho-	212
Meta-	389
Para-	435
Dinitro derivatives	
Ortho,ortho′-	481
Ortho,meta′-	586
Ortho,para′-	623
Meta,meta′-	780
Meta,para′-	833
Para,para′-	886

average by ±20 index units (i.u.) different from experimental values. It must be noted that the correlated analytes are eluted in the broad range of retention indices 1977–2862. The average difference between the retention indices for neighboring eluted isomeric dinitro derivatives of dimethyldiphenylacetamide is 81 i.u., which is four-times higher than the average difference between the experimental and calculated values of their retention indices.

The dI/dT values for **1**–**10** increased from parent amide **1** to the mononitro **2**–**4** and dinitro **5**–**10** derivatives. These values increased in the order *ortho-*<*meta-*<*para-*; *para,x′* derivatives **7**, **9** and **10** showed also higher characteristic dI/dT values.

Preliminary GC identification was then achieved from the observations of the retention properties of prepared isomers and on the basis of structure–retention correlations [5]. Combination of the data from the highly informative detection of capillary column eluates both by FT-IR and MS allowed one to attain the definitive identification of all isomers.

3.2. FT-IR

The GC peak identification and the assignment of the FT-IR data of the nitro derivatives **2**–**10** are given in Table 4.

Similarly to the series of isomeric nitro derivatives of phenyl-, diphenyl- and (hydroxy)diphenylmethylacetates the nitro derivatives of **1** did not exhibit significant differences in the region of the wave numbers of C=O stretching vibrations ($\Delta\tilde{\nu}$=2 cm^{-1}). Also, the region of the wave numbers of symmetrical NO_2 stretching vibrations yielded no useful keys to the identification of positional nitro isomers on the benzene rings, due to the crowding of observed absorption bands within the range of $\Delta\tilde{\nu}$=4 cm^{-1}. Finally, FT-IR data in the region of the wave numbers of asymmetrical NO_2 stretching vibrations appeared the most reliable tool for recognition of the isomeric nitro derivatives. Furthermore, the isomers bearing a *meta*-substituted NO_2 group exhibited in the region of $\tilde{\nu}_{as}$ (NO_2) vibration wave numbers a significant increase $\Delta\tilde{\nu}$=12–17 cm^{-1}, compared to analogous *ortho-* and *para*-substituted isomeric congeners. This increase is much higher than it was observed in the case of previously investigated phenyl-, diphenyl- and (hydroxy)diphenylmethylacetate nitro derivatives [3,4]. The above phenomenon can be reasonably explained as an enhanced conjugation between the C=O and $N(CH_3)_2$ groups resulting in the amplification of the inductive electron-withdrawing influence of the $CON(CH_3)_2$ moiety on the NO_2 groups attached to the *meta*-position of the diphenylmethyl system. The

Table 4
FT-IR data for the isomeric mononitro and dinitro derivatives of *N,N*-dimethyldiphenylacetamide

GC peak No. (Fig. 1)	Position of NO_2 groups on the benzene rings	$\tilde{\nu}$ (cm^{-1})		
		ν(C=O)	ν_{as} (NO_2)	ν_s (NO_2)
2	*Ortho-*	1677	1532	1355
3	*Meta-*	1679	1548	1352
4	*Para-*	1679	1531	1351
5	*Ortho,ortho′-*	1678	1536	1353
6	*Ortho,meta′-*	1677	1548	1353
7	*Ortho,para′-*	1679	1537	1351

final effect of these electronic interactions is the increase of the $\tilde{\nu}_{as}$ (NO_2) vibrational wave number due to a significant deconjugation between the benzene ring and the nitro group in the *meta*-position.

On the basis of obtained GC–FT-IR data analysis it follows that GC peaks 3 and 6 can be reliably assigned to the isomers connected with the *meta*-nitro substitution in the *N,N*-dimethyldiphenylacetamide system. On the other hand, the GC–FT-IR data did not provide a satisfactory tool for the identification of the *para*- and *ortho*-nitro substitution in the systems studied here.

The FT-IR spectra via GC for **8**, **9** and **10** could not be recorded due to absorption band broadening and high background noise in the IR spectrum in connection with lower volatility and higher polarity of these compounds [9].

3.3. MS

The EI mass spectra obtained at 70 eV ionization energy both from the parent amide **1** and its mononitro **2**, **3** and **4** and dinitro derivatives **5–10** were characterized by the dominant fragment ion at 72 u (Me_2NCO), which was the observed base peak in all instances except for **1** (Figs. 3 and 4), for which an ion at 168 u (formally Ph_2CH_2) was the evidence for a migration of a hydrogen atom from the methyl groups to the diphenylmethyl moiety prior to fragmentation. The *ortho* derivatives **2**, **5**, **6** and **7** all showed a remarkable loss of a nitro group from the parent ion, which was absent in other cases.

Although many ion compositions as well as some decompositions did not admit alternatives, the reconstructed patterns shown in all the figures were not supported by high resolution measurements and metastable ions. The few ion structures shown are speculative, but based on similar rearrangement reported in the literature [10].

The base peak at 167 u for the hydrocarbon ion $C_{13}H_{11}^+$, showed both decay to the ion at 165 u by two sequential hydrogen losses and the expulsion of a methyl group high energy rearrangement-fragmentations which were largely suppressed in the EI spectrum at 20 eV. The introduction of nitro groups caused the sharp decrease of the parent ions, which were detectable in most cases only at much higher amplifications of the higher mass part of the spectra; it was often part of a cluster starting at 330 u for M+H ions deriving from H transfer from the walls of the ion source, a phenomenon frequently present in the EI mass spectra of nitro derivatives, which may undergo deep reductions in some instances. The fragmentation pattern was most varied with the mononitro derivatives **2–4** at 20 eV: for the *ortho*-isomer the base peak was at 195 u a deep rearrangement ion most likely deriving from the parent ion. The *meta*-nitro derivative **3** underwent a facile expulsion of NO from the parent ion to yield the rearrangement peak at 254 u. Evidence for one or two rearranged structures for the ions at 195 and 196 u in the *ortho*-isomer mass spectrum was offered by the ions at 167 u of unequivocal composition (195−CO), 168 u (196−CO) and 179 u (195−O). A weak ion at 105 u (C_7H_5O) gives further support to these rearranged structures, which were observed in the *ortho*-nitrodiphenylmethane spectrum [11]. The overall pattern of fragments in the spectrum of *para*-isomer **4** was quite different from that of the order two mononitro isomers. The expected fragmentations of nitro aromatics were to be found scattered through the spectra of all these nitro derivatives. Contrary to what is to be found in 20 eV spectra of **5–7** bearing an *ortho*-nitro group, which showed a sizable number of fragment ions up to 283 u only, great enhancements allowed to uncover fragments beyond 72 u, formed from the parent ions of **8–10**: a characteristic peak at 272 u, formed from the sequential losses of NO and $CONMe_2$ from the parent ions was a constant prominent feature.

In GC–CH_4-CI–MS of mixtures containing **1** and its mononitration products **2–4** as well as dinitration products **5–10**, some GC peak flattening was observed, but it did not interfere with resolution. GC peak areas ratios were comparable with those observed in GC–EI-MS at 70 eV. Still, for strictly quantitative work on nitration mixtures, GC–FID responses from peaks separated on our high-resolution columns were found to be in excellent agreement with very accurate quantitative measurements of isomer ratios by ^{1}H-nuclear magnetic resonance (NMR) [1,2] based on the integral values of the several α-H peaks in the range of 4–6 ppm, which, on the other hand, showed some overlappings under the instrumental conditions of our observa-

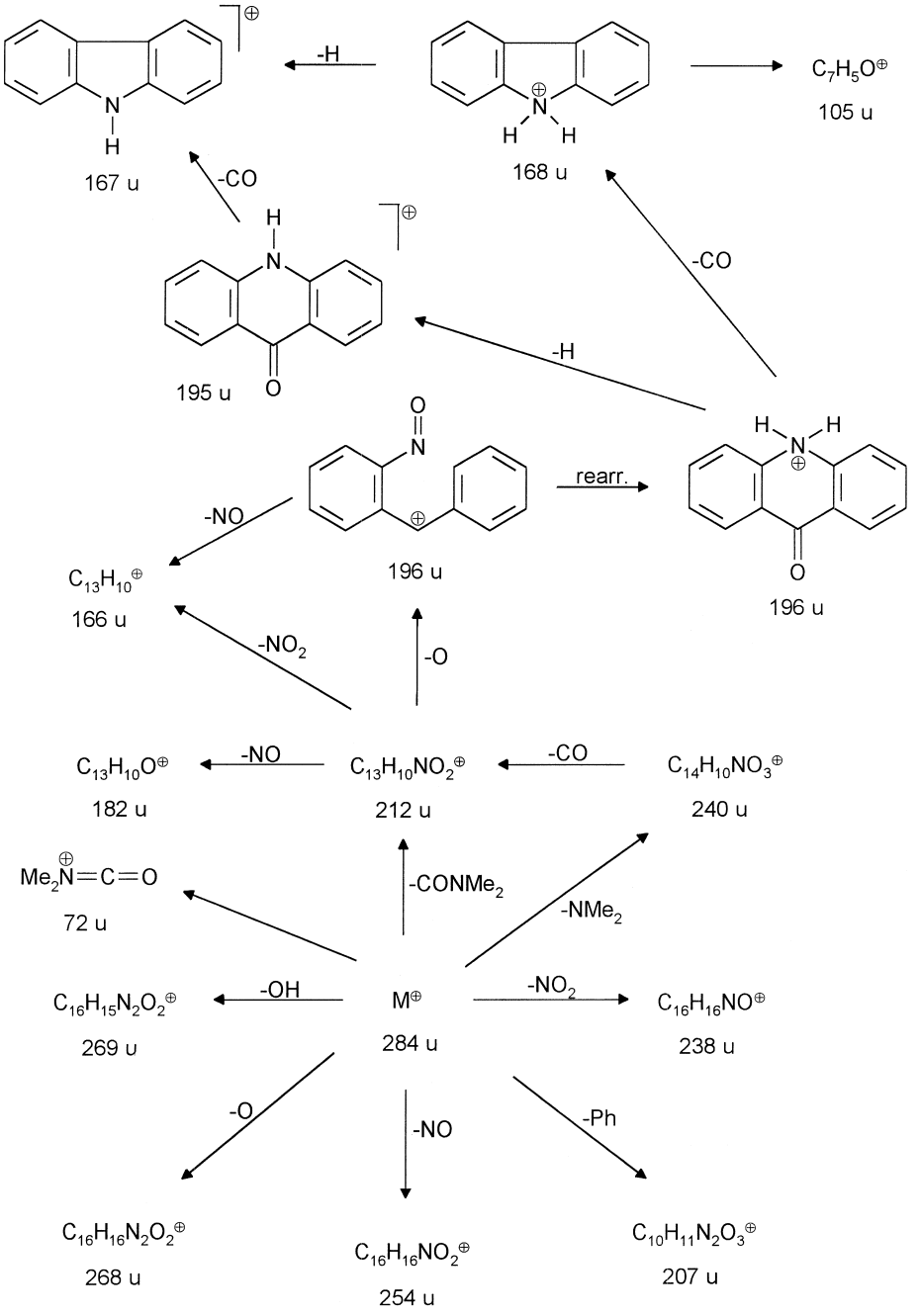


Fig. 3. Fragmentations of the positive parent ions of the mononitro derivatives **2–4**.

tions. Pretty much according to expectation, **1**, the mononitro derivatives **2–4** and the dinitro derivatives **8–10** yielded simplified mass spectra (Fig. 5) dominated by their quasi molecular ions MH^+ at 240, 285 and 330 u, respectively. A peak at 46 u for the ion $H_2NMe_2^+$ was conspicuous for all the mononitro

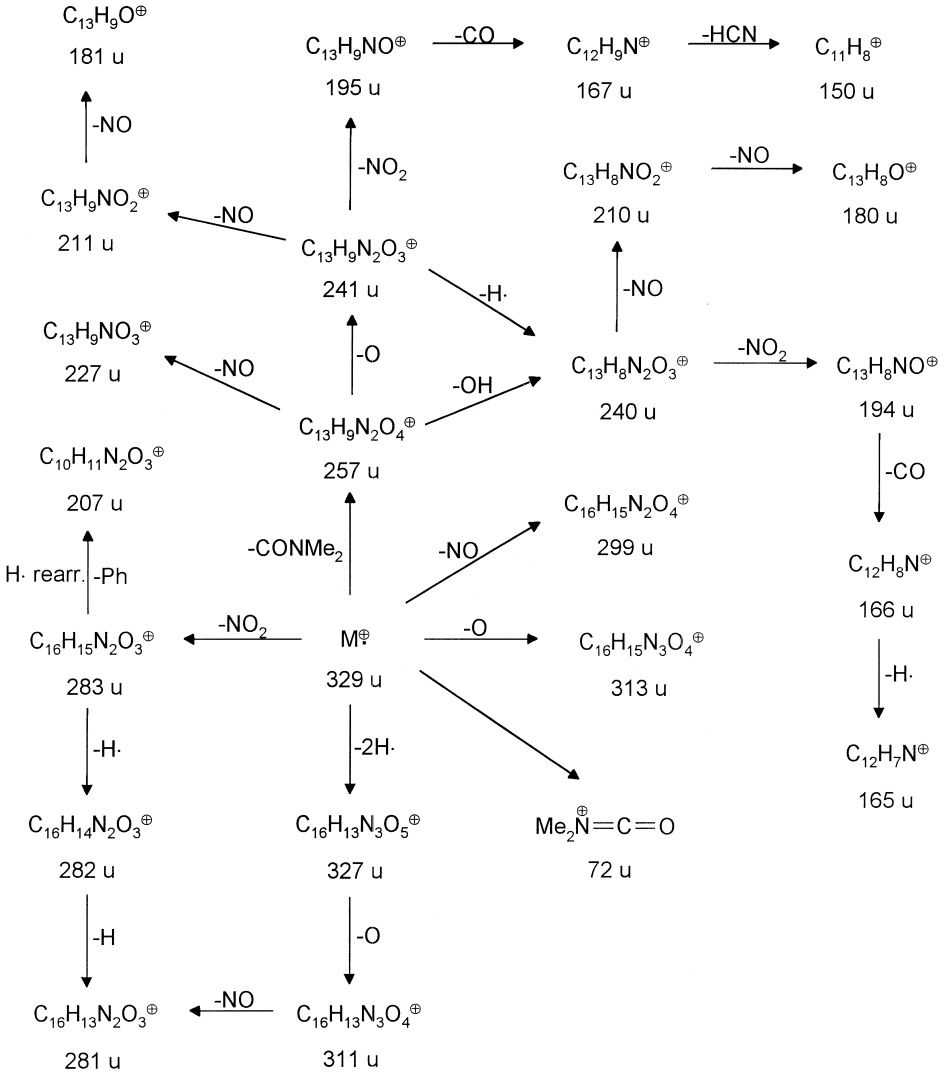


Fig. 4. Fragmentations of the positive parent ions of dinitro derivatives **5**–**10**.

derivatives **2**–**4** and also present in the spectra of **5**–**7**. The ion **11** at 46 u was identified as the dimethylammonium ion produced by the protonation of the molecule **12,** produced in the CI process shown in Fig. 6.

The evidence for the nature of the 46 u ion **11** came from the absence of such an ion from the CI-MS spectra of nitro derivatives from diphenylmethane [10]. A tiny, but definitively above background level, peak at 46 u also appeared in the spectrum of **1**. The complementary ion M-$NHMe_2$ at 240 u could be observed for **2–4**.

Rather surprisingly, the isomers **8–10** yielded CH_4-CI spectra, where the intensity of the MH^+ ion was low, fragments were extensive and the intense base peak appeared at 270 u (MH^+-NO-NO). This behavior may allow one to infer that the loss of NO in all the other nitro derivatives occurred prevalently from *meta*- and *para*-nitro groups.

Sharp GC peaks were obtained from negative ion

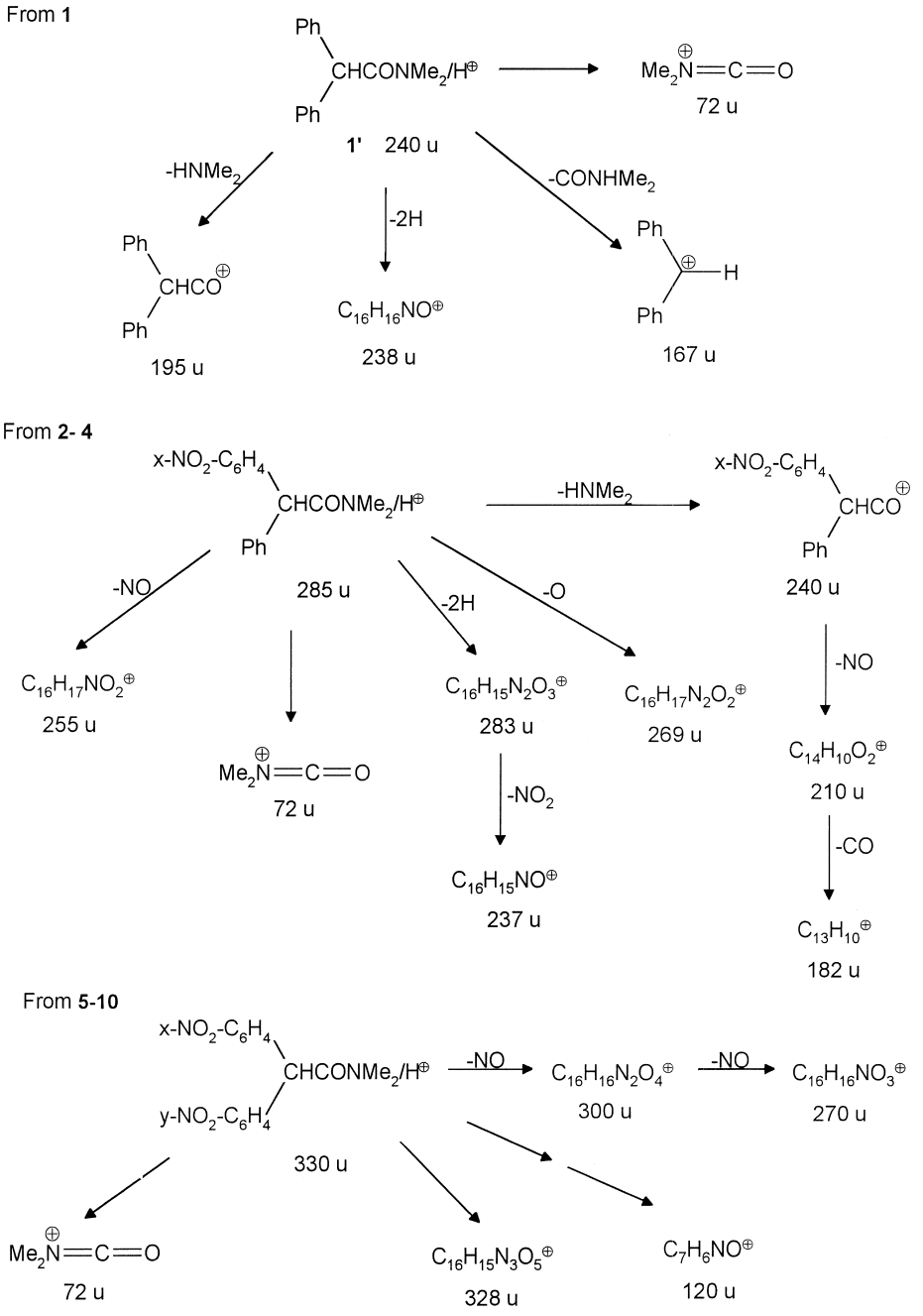


Fig. 5. Behavior of CH_4-CI quasimolecular positive ions from **1–10**. All types of fragmentations were collected under one subheading, although they might not be common to all isomers.

GC–MS: GC peak integral ratios were in rather close agreement with those of GC–EI-MS at 70 eV.

A weak signal was detectable for the parent compound **1** at 167 u (Ph_2CH^-), but all nitro derivatives exhibited an intense peak for their parent ions. Reductive dinitration yielded in all cases the

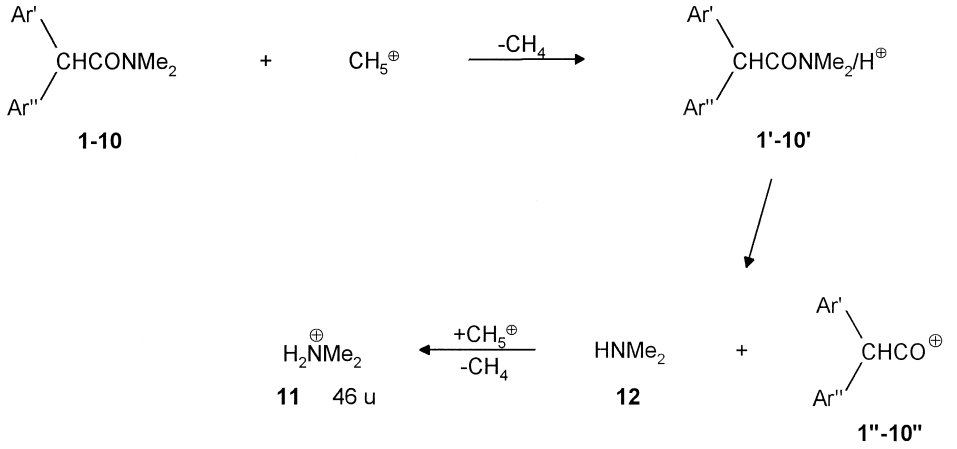


Fig. 6. CI-MS induced processes on amides **1–10**.

ion NO_2^- at 46 u, which was the more intense, the closer was (were) the nitro group(s) to the aryl connecting carbon center. A few more or less intense fragmentations of the parent negative ions were observed. There was a tendency towards the expulsion of the amide function as a radical which increased sharply with *meta*- and *para*-substitution(s) reaching its apex with the parent ion of **10**, but practically missing in **5–7**. Sequential losses of OH, NO and CO were conspicuous for **6** and **7**, which exhibited an intense ion at 239 u, corresponding to the fast loss of a nitro group and the amide function from the parent ions.

In this work we were not especially concerned with quantitative measurements, but a few passing remarks seem useful. The quantitative response in

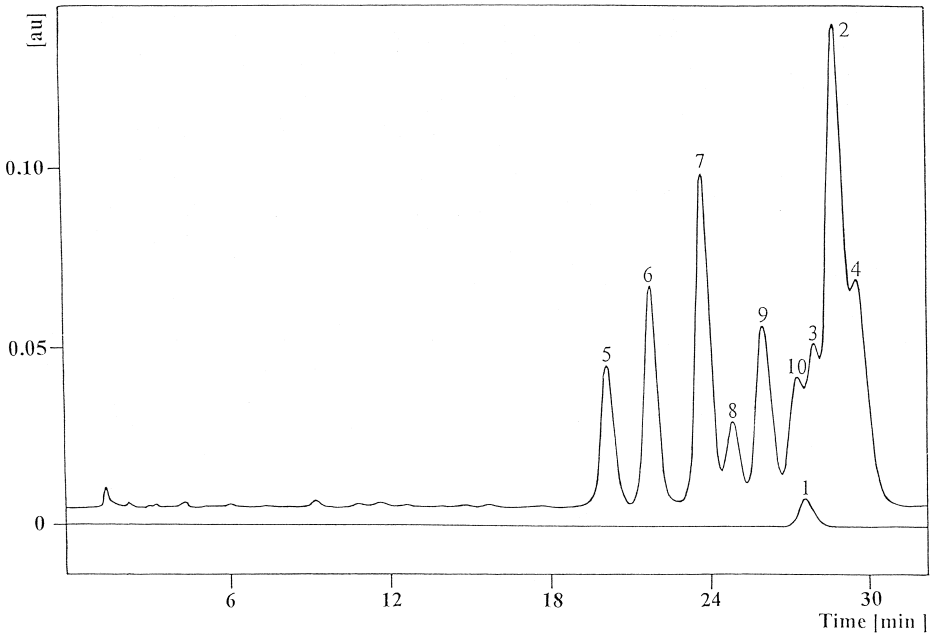


Fig. 7. HPLC–DAD chromatogram of the products from the nitration of *N,N*-dimethyldiphenylacetamide and parent compound obtained at 267 nm. Peak identification as in Table 2.

the negative ions spectra strongly depended both on the number of nitro groups present in each molecule, but also on their position in the rings. Peak widening in the CI spectra both prevented accurate and reliable quantitative measurements and showed a decrease in sensitivity.

3.4. HPLC

N,*N*-dimethyldiphenylacetamide (**1**) and its mononitro **2**–**4** and dinitro derivatives **5**–**10** are expected be solids with low volatility. We have therefore first attempted to separate the components from nitration mixtures by HPLC using a reversed-phase column. A typical chromatogram is shown in Fig. 7. The HPLC retention order of nitration products is different from that of GC. The more nitrated products being more polar were those eluted initially, whereas the last ones were the mononitro derivatives. However, the parent compound **1** is eluted with the *para,para′*-dinitro derivative **10**. Also the separation order of mononitro derivatives is different. For identification of HPLC peaks, prepared standards, as well as HPLC prepared peaks identified by GC were used. The minor peaks detected by DAD in the front of chromatogram were found to be by-products of different nature.

A distinctly better resolution of components from nitration of dimethyldiphenylacetamide obtained by GC in comparison with HPLC is mainly due to the different selectivity of both separation systems. The separation factor for the last and first eluted nitro derivatives for HPLC is $\alpha = 1.5$ at 21°C, and for GC is $\alpha = 10.3$ at 200°C.

Table 5
Procedural keys to identification of individual nitro derivatives of **1**[a]

Compound	M_r	Location of nitro group(s)	Comments
Ortho-	NI-MS CI-MS	70-MS, NI-MS	70-MS and NI-MS distinctive from **3** and **4**
Meta-	NI-MS CI-MS	FT-IR	IR: distinctive from **2** and **4**
Para-	NI-MS CI-MS	20-MS, 70-MS	EI-MS: the peak at 254 u is intensive for **4**, quite small for **3**
Ortho,ortho′-	NI-MS CI-MS	NI-MS	NI-MS: the peak at 239 u is a low intensity and is distinctive from **6** and **7**
Ortho,meta′-	NI-MS CI-MS	FT-IR	IR: distinctive from **5** and **7**
Ortho,para′-	NI-MS CI-MS		IR: the υ_{as} (NO_2) is different from that of **6**
Meta,meta′-	NI-MS		20-MS: looking separately at the ions in the region 207–299, intense peaks are present only in the mass spectrum of **8**. CI-MS: does not show the MH ion: distinctive from **5**–**7**
Meta,para′-	NI-MS		NI-MS: the ion at 46 u is definitively more intense than that at 270 u: the contrary is observed for **9** CI-MS: see **8**
Para,para′-	NI-MS		NI-MS: see **9** CI-MS: see **8**

[a] NI-MS=Negative ion mass spectrometry, CI-MS=chemical ionization mass spectrometry, 20-MS and 70-MS=electron impact spectra obtained at 20 and 70 eV ionization energy, respectively.

4. Conclusion

Whereas this work has reached the aim of a definitive structure identification of all the components of nitration mixtures of **1**, we have also obtained a wealth of GC, FT-IR and MS data on all of them, which will allow their recognition as individual compounds in mixtures from other origins. Table 5 shows the main combinations of hyphenated analytical procedures for any individual compound and when it appeared of interest, properties useful to choose from isomers, which appeared very similar and for which, of course, authentic specimens were not at hand. The GC separation was found to be more suitable for the separation of nitration products due to its substantially higher selectivity compared to reversed-phase HPLC separation. HPLC analysis, on the other hand, confirmed that polynitration products ($n>2$) did not form during nitration under our conditions.

Acknowledgements

This work was carried out with partial support from funds for inter-university cooperation between Comenius University (Bratislava, Slovak Republic) and University of Udine (Italy). More support came from VEGA funds (No. 1/6108/99 to L.S.), the Italian Research Council (CNR grants 1996–1999 to A.G.G.) and MURST (1997–1999 to G.V. and A.G.G.) and from Dow Europe in the form of a postdoctoral grant (to M.M.M.).

References

[1] P. Strazzolini, A.G. Giumanini, G. Verardo, Bull. Chem. Soc. Japan 69 (1996) 2943.
[2] P. Strazzolini, A.G. Giumanini, A. Runcio, M. Scuccato, J. Org. Chem. 63 (1998) 952.
[3] L. Soják, A. Perjéssy, R. Kubinec, A.G. Giumanini, P. Strazzolini, J. Chromatogr. A 665 (1994) 169.
[4] L. Soják, A. Perjéssy, R. Kubinec, A.G. Giumanini, P. Strazzolini, J. Chromatogr. A 695 (1995) 57.
[5] L. Soják, A. Perjéssy, R. Kubinec, A.G. Giumanini, Chem. Papers 52 (1998) 34.
[6] A. Sturaro, G. Parvoli, R. Rella, L. Doretti, J. Chromatogr. A 688 (1994) 211.
[7] J. Kríž, M. Popl, J. Mostecký, J. Chromatogr. 97 (1974) 3.
[8] L. Soják, M.S. Vigdergauz, J. Chromatogr. 148 (1978) 159.
[9] J.F. Schneider, J.C. Demirgian, J.C. Stickler, J. Chromatogr. Sci. 24 (1986) 330.
[10] H. Budzikiewicz, C. Djerassi, D.H. Williams, in: Mass Spectrometry of Organic Compounds, Holden-Day, San Francisco, CA, 1967, pp. 515–520.
[11] H. Budzikiewicz, J. Rullkoelter, H.M. Schiebel, Org. Mass Spectrom. 6 (1972) 251.