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# Identification of the isomers from mono- and dinitration of phenyl- and diphenylacetic acids by gas chromatography with Fourier transform infrared and mass spectrometric detection

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## Abstract

The problem of the identification of the isomers from mono- and dinitration of diphenylacetic acid prior to their individual separation was investigated by studying the corresponding methyl esters by capillary gas chromatography with Fourier transform infrared detection with the aid of data obtained by gas chromatography–mass spectrometry (GC–MS) in the positive-ion mode. The isomer assignments were essentially made by extrapolation of the observations of the IR stretching vibrations of both the nitro group and the benzene ring in the methyl esters of mononitrophenylacetic acid isomers. Heteronuclear nitro substitution of diphenylacetic acid was confirmed by GC–MS. The occurrence of products of dinitration on the same benzene ring, if any, was below the observable limits in the mixtures studied.

## 1. Introduction

In the course of synthetic work [1] aimed at the preparation of the mono- and dinitrophenylacetic and diphenylacetic acids, we encountered the problem of the identification of the isomers produced in both the mono- and the dinitration procedures. Most of the likely isomers not only are commercially unavailable, but also are not known in the literature or their syntheses are cumbersome. No chromatographic or spectral data for most of these compounds

have been published. A simple and rapid procedure for their identification was extremely desirable. The investigated dinitration mixtures presented the problems of identification of the position and attachment of the nitro groups to one or two benzene rings. Mass spectrometry alone is generally unable to distinguish between ring-substituted isomers [2], especially between *meta* and *para* isomers.

This paper describes the investigation of this problem by combining the high separation power of capillary gas chromatography (cGC) with the highly informative detection of the eluates by both Fourier transform infrared (FT-IR) spectrometry and electron impact ionization mass spectrometry (MS).

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## 2. Experimental

### 2.1. Materials

The chemicals used were of 99% purity from Aldrich (Milwaukee, WI, USA).

Nitro compound mixtures came from different reaction batches; they were usually obtained by direct nitration of phenylacetic and diphenylacetic acid or their methyl esters under different experimental conditions [1]. 2-Nitrodiphenylacetic acid and its methyl ester was also nitrated according to procedures leading mainly to either 2,2'- or 2,4'-dinitro products. The authentic original substrate 2,2'-dinitrodiphenylacetic acid was obtained by crystallization from the mononitration reaction mixture of 2-nitrophenylacetic acid. 4,4'-Dinitrodiphenylacetic acid was obtained from the dinitration of diphenylacetic acid with pure  $\text{HNO}_3$ . Free nitro and dinitro acid mixtures were methylated with dry ethereal diazomethane to obtain the corresponding methyl esters before admission to the injection port of the GC apparatus.

### 2.2. GC-FT-IR and GC-MS measurements

GC separations were carried out on a capillary column (50 m  $\times$  320  $\mu\text{m}$  I.D. coated with OV-1 as stationary phase (0.33  $\mu\text{m}$  film thickness). The capillary column was prepared as described previously [3]. The carrier gas was helium at an inlet pressure 0.15 MPa. The column temperature was programmed with an isothermal period at 150°C for 2 min, then increased at 10°C  $\text{min}^{-1}$  to 300°C with an isothermal period at 300°C for 5 min. For detection of the separated peaks, flame ionization (FID), FT-IR and MS detection were applied.

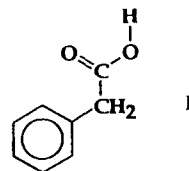
A Finnigan (Bremen, Germany) Model 1020 mass spectrometer equipped with an automated data collection system was used to record electron impact positive-ion mass spectra at 70-eV electron energy. The separated GC peaks were monitored by MS many times during the elution to ensure homogeneity of the eluted material. Peaks from reactions under different conditions were compared for identity by both GC and MS.

Whenever possible, mass spectra of GC peaks were compared with those of authentic specimens that were recorded both via the GC system and via the direct inlet port.

A Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph with an HP Model 5965 A IR detector was used to obtain FT-IR spectra.

## 3. Results and discussion

As the identification of isomeric products obtained by nitration of phenyl- and diphenylacetic acid has not previously been investigated by using FT-IR spectrometry, we present below more detailed information about the spectral and structural assignment. To simplify the identification of products of dinitration we first studied the products of the mononitration of phenylacetic acid (I).



The chromatogram of the mixture of mononitrophenylacetic methyl esters is shown in Fig. 1. The peak identifications and the FT-IR data measured for the methyl esters of the products of mononitration of phenylacetic acid (I) are given in Table 1.

As the GC-FT-IR system employed could not be used for the identification the region of CH out-of-plane wagging vibrations of the benzene ring (900–650  $\text{cm}^{-1}$ ), we applied the well resolved absorption bands belonging mainly to the stretching vibrations of both the  $\text{NO}_2$  group and the benzene ring. The *ortho*, *meta* and *para* isomers from the mononitration of phenylacetic acid can be assigned on the basis of the FT-IR spectra of their methyl esters as follows. The carbonyl stretching frequency [ $\nu(\text{C}=\text{O})$ ] of the  $\text{COOCH}_3$  group hardly undergoes any changes

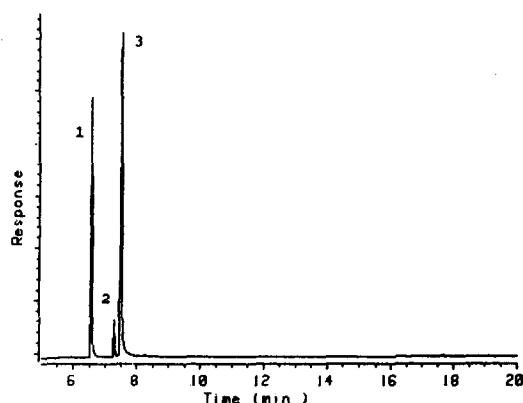


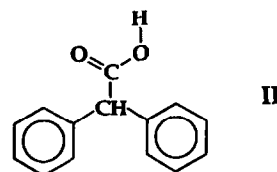
Fig. 1. Chromatogram of the mixture of mononitrophenylacetic acid methyl esters. Peak identifications as in Table 1.

on passing from isomer to isomer. Nearly the same is true regarding the symmetrical stretching frequency of the  $\text{NO}_2$  group [ $\nu_s(\text{NO}_2)$ ]. However, the structurally sensitive IR property of the mononitrated molecule is the asymmetric stretching vibration of the nitro group [ $\nu_{as}(\text{NO}_2)$ ] [4,5].

For the *para*-substituted isomer (with respect to the electron-releasing property of the  $-\text{CH}_2\text{COOCH}_3$  moiety), the lowest value is observed for  $\nu_{as}(\text{NO}_2)$ , which is caused by the efficient conjugation of the  $\text{NO}_2$  group with the aromatic  $\pi$ -electron system. For the *ortho*-substituted compound a higher frequency band of  $\nu_{as}(\text{NO}_2)$  was found because of deconjugation due the steric effect between the  $\text{NO}_2$  group and the  $-\text{CH}_2\text{COOCH}_3$  chain of the molecule. For the *meta* isomer the conjugation between the  $\text{NO}_2$  group and the aromatic ring should be weakened and consequently the  $\nu_{as}(\text{NO}_2)$  ab-

sorption appeared at the highest frequency ( $1548 \text{ cm}^{-1}$ ), which is  $12 \text{ cm}^{-1}$  higher than the  $\nu_{as}(\text{NO}_2)$  absorption of the well conjugated *para* isomer. In addition, for the *para*-substituted derivative an additional sharp absorption band was observed at *ca.*  $1600 \text{ cm}^{-1}$ , which belongs to the stretching vibration mode of the aromatic ring [ $\nu(\text{arom.})$ ] and usually characterizes the *para* position of the substituent group.

The second step in the study of the dinitration was to investigate the products of mononitration of diphenylacetic acid (II).



The chromatogram of the products from the nitration of diphenylacetic acid methyl esters is shown in Fig. 2. The peak identifications and the FT-IR data measured for these isomers are given in Table 2. The FT-IR spectral behaviour of the mononitro derivatives of the methyl esters of diphenylacetic acid in the region of the  $\text{NO}_2$  stretching vibration frequencies is close to that of the mononitro derivatives of the methyl ester of phenylacetic acid. However, for all the nitrated methyl esters of diphenylacetic acid we observed a shift of  $7 \text{ cm}^{-1}$  to lower frequencies in the bands belonging to the  $\nu(\text{C}=\text{O})$  of the ester moiety, which is caused by the electron-donating effect of the additional benzene ring.

On the basis of the above empirical investigations, we were able to identify the six isomeric products obtained by the dinitration of diphenylacetic acid.

Table I  
GC and FT-IR data for methyl esters of the products of the mononitration of phenylacetic acid (I)

| GC peak No. (Fig. 1) | Retention time (min) | Position of $\text{NO}_2$ group on benzene ring | $\nu(\text{C}=\text{O})$ ( $\text{cm}^{-1}$ ) | $\nu_{as}(\text{NO}_2)$ ( $\text{cm}^{-1}$ ) | $\nu_s(\text{NO}_2)$ ( $\text{cm}^{-1}$ ) | $\nu(\text{arom.})$ ( $\text{cm}^{-1}$ ) |
|----------------------|----------------------|---|---|--|---|--|
| 1                    | 6.57                 | <i>ortho</i>                                    | 1764  | 1544   | 1353                                      | —  |
| 2                    | 7.27                 | <i>meta</i>                                     | 1763  | 1548   | 1354                                      | —  |
| 3                    | 7.52                 | <i>para</i>                                     | 1763  | 1536   | 1350                                      | 1602                                     |

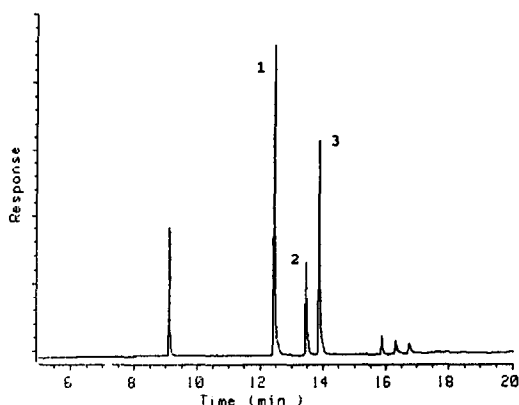


Fig. 2. chromatogram of methyl esters of products from the nitration of diphenylacetic acid. Peak identifications as in Table 2.

MS was used to confirm that the main products of the dinitration of diphenylacetic acid are heteronuclear dinitro derivatives. The common feature of mono- and dinitro derivatives of diphenylacetic acid (**II**) was the presence of the ion at  $m/z$  167, which was found to correspond to  $C_{12}H_9N$  by high-resolution MS and is believed to have the structure of the carbazole parent ion. For the mononitro derivatives this ion was accompanied by its protonated species  $C_{12}H_{10}N^+$ . By and large, the molecular ion is always absent in mononitro derivatives and in all dinitro derivatives containing at least one nitro group in the *ortho* position. Owing to steric effects, the parent ions and their fragments are more exposed by extensive cleavage: the mass spectra of *ortho* derivatives were substantially more complex than those not having nitro groups in this location. The presence of the carbomethoxy group was always evidenced by the ion at  $m/z$  59

and most often by an ion obtained by the loss of 59 u from the parent ion.

When we performed the nitration of 2-nitrodiphenylacetic acid, the GC profile showed only minor amounts of two products, the mass spectra of which could be reconciled with those of some dinitro derivatives, which could only be homonuclearly dinitrated products containing at least one nitro group in the *ortho* position. These spectra showed peaks in the upper mass region which were not present in any of the heteronuclearly dinitrated products.

The chromatogram of the dinitration products of diphenylacetic acid methyl esters is shown in Fig. 3. The peak identifications and the FT-IR data measured for the methyl esters of the products of heteronuclear dinitration of diphenylacetic acid and their assignments are given in Table 3. As both the *para*, *para* and *ortho*, *ortho* isomers (*i.e.*, the methyl esters of 4,4'- and 2,2'-dinitrodiphenylacetic acid) were

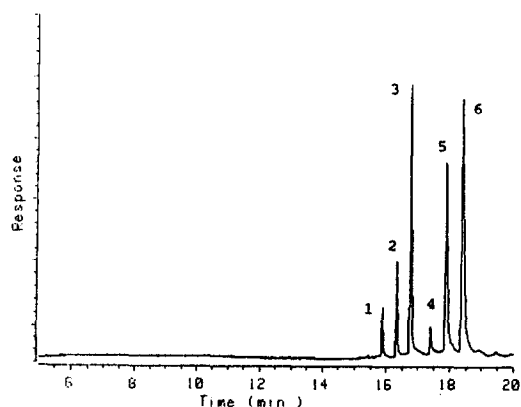


Fig. 3. Chromatogram of methyl esters of the dinitration products of diphenylacetic acid. Peak identifications as in Table 3.

Table 2  
GC and FT-IR data for methyl esters of the products of the mononitration of diphenylacetic acid (**II**)

| GC peak No. (Fig. 2) | Retention time (min) | Position of NO <sub>2</sub> group on benzene ring | $\nu(C=O)$ (cm <sup>-1</sup> ) | $\nu_{as}(NO_2)$ (cm <sup>-1</sup> ) | $\nu_s(NO_2)$ (cm <sup>-1</sup> ) | $\nu(\text{arom.})$ (cm <sup>-1</sup> ) |
|----------------------|----------------------|---|--------------------------------|--------------------------------------|-----------------------------------|---|
| 1                    | 12.45                | <i>ortho</i>                                      | 1756                           | 1543                                 | 1355                              | —                                       |
| 2                    | 13.46                | <i>meta</i>                                       | 1757                           | 1547                                 | 1353                              | —                                       |
| 3                    | 13.88                | <i>para</i>                                       | 1757                           | 1537                                 | 1350                              | 1600                                    |

Table 3  
GC and FT-IR data for methyl esters of the products of the heteronuclear dinitration of diphenylacetic acid (II)

| GC peak No.<br>(Fig. 3) | Retention time<br>(min) | Position of NO <sub>2</sub> groups<br>on benzene rings | $\nu(\text{C}=\text{O})$<br>(cm <sup>-1</sup> ) | $\nu_{\text{as}}(\text{NO}_2)$<br>(cm <sup>-1</sup> ) | $\nu_{\text{s}}(\text{NO}_2)$<br>(cm <sup>-1</sup> ) | $\nu(\text{arom.})$<br>(cm <sup>-1</sup> ) |
|-------------------------|-------------------------|--|---|---|--|--|
| 1                       | 15.87                   | <i>ortho,ortho</i>                                     | 1757  | 1545  | 1353   | ca. 1605                                   |
| 2                       | 16.32                   | <i>ortho,meta</i>                                      | 1758  | 1546  | 1354   | –  |
| 3                       | 16.75                   | <i>ortho,para</i>                                      | 1758  | 1543  | 1351   | 1603                                       |
| 4                       | 17.36                   | <i>meta,meta</i>                                       | 1759  | 1548  | 1352   | –  |
| 5                       | 17.85                   | <i>meta,para</i>                                       | 1759  | 1547  | 1351   | 1604                                       |
| 6                       | 18.35                   | <i>para,para</i>                                       | 1758  | 1543  | 1349   | 1600                                       |

also isolated and identified as pure compounds, their spectral data were used as reference values for the assignment of further isomers. In the FT-IR spectra of all isomers containing at least one *para*-substituted benzene ring the previously discussed  $\nu(\text{arom.})$  band was observed at ca. 1600 cm<sup>-1</sup> as the characteristic feature of *para* substitution. This phenomenon was used to distinguish the isomers belonging to the three GC peaks from others. With *ortho,ortho* substitution there is an exception: the additional  $\nu(\text{arom.})$  band at ca. 1605 cm<sup>-1</sup> is also present in the spectra owing the *ortho* effect of both NO<sub>2</sub> groups. To distinguish the isomers containing *meta*-substituted nuclei, again the criterion of the upward shift of the  $\nu_{\text{as}}(\text{NO}_2)$  absorption caused by the deconjugation effect was employed.

It follows from the comparison of retentions in Figs. 2 and 3 and from the corresponding FT-IR spectra that the last three small peaks at retention times of 15.86, 16.31 and 16.75 min in the nitration products of diphenylacetic acid in Fig. 2 are identical with peaks 1, 2 and 3, respectively in Fig. 3, *i.e.*, *ortho,ortho*-, *ortho,meta*- and *ortho,para*-dinitro derivatives, respectively, of diphenylacetic acid.

#### 4. Conclusions

This work has shown conclusively that the combination of GC with FT-IR and MS detec-

tion allows the successful identification of all the isomers from the nitration and dinitration of mono- and diphenylacetic acid. It is possible that the essential features of this method could be applied to the identification of nitration mixtures from similar substrates.

#### 5. Acknowledgements

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