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Decarbonylation of two α-diketones: 1,2-Bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione

M. Judith Percino*, Víctor Manuel Chapela, Omar Urzúa, Héctor Toribio

Centro de Química, Instituto de Ciencias, Universidad Autónoma de Puebla, Complejo de Ciencias,
ICUAP, Edif. 76, 22 Sur y San, Claudio, C.P. 72570, Puebla, Mexico

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Abstract

EI mass fragmentation of the 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione radical cations gave rise to a sequence of unexpected composite ion peaks. The molecular ion *m*/*z* 240 gives mass measurements of metastable ions at *m*/*z* 212 and 184 and the molecular ion *m*/*z* 226 gave peaks at *m*/*z* 198 and 170 resulting from the successive loss of two fragments of 28 mass units each, corresponding to CO. These fragmentations yield the products $[CH_3C_5H_3NCOC_5H_3NCH_3]^+$, $[(CH_3C_5H_3N)_2]^+$ and $[C_5H_4NCOC_5H_3NCH_3]^+$, $C_5H_4NC_5H_3NCH_3]^+$, respectively, as confirmed by mass determination identification of the precursor ions and decomposition product ions. In addition, the prominent ions $[CH_3C_5H_3NC{=}O]^+$, $[O{=}CNH_3C_5CH_3]^+$, $[C_5H_3NC{=}O]^+$ and $[O{=}CNH_3C_5CH_3]^+$, arising from cleavage of the C—C bond, were detected in similar abundance ratios for both fragments and the corresponding secondary fragments, which can be attributed to the dissociation of several ionized α-diketones. The ionized homologue α-diketone 1,2-dipyridyldione also exhibited a decarbonylation channel yielding the molecular ion *m*/*z* 212, and before losing CO gave peaks at *m*/*z* 184 and 156. The fragmentation of 1,2-diphenylethane-1,2-dione did not exhibit the same behavior. The results confirm that the green co-crystal obtained is a co-compound formed of 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione.

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Keywords: α-Diketones; EI mass spectra; Decarbonylation; 1,2-Bis(6-methylpyridin-2-yl)ethane-1,2-dione; 1-(Pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione co-crystal

1. Introduction

α-Diketones, $R^1C({=}O)C({=}O)R^2$, dissociate promptly upon electron ionization via direct C–C bond cleavage to generate high levels of the corresponding $R^1C({=}O)^+$ and $R^2C({=}O)^+$ acylium ions. This cleavage seems to indicate a loosely bonded structure for the molecular ions, with the major formation of the two acylium ions indicating an interesting electron-bonded diacylium ion dimer structure [1] for ionized α-diketones (Fig. 1). A typical α-diketone example was reported by Meurer et al. [1]. They showed the formation of two acylium ions from 2,3-pentanedione in the 70 eV EI mass spectrum by cleavage of the C–C bond. These were at *m*/*z* 52 $[C_2H_5CO]^+$ and *m*/*z* 43 $[CH_3CO]^+$, with an abundance ratio between the acylium ions of 1:3. In addition, secondary fragments of $[C_2H_5]^+$ at *m*/*z* 29 and $[CH_3]^+$ at *m*/*z* 15 occurred on losing CO. The same authors reported similar behavior for several α-diketones, such as 3,4-hexanedione, 1-(4-chlorophenyl)-2-phenylethan-1,2-dione, 2-oxobutyric acid, *m*-nitro-1-phenyl-1,2-propanedione, methyl pyruvate, and 1-phenyl-1,2-propanedione. From their theoretical study, they predicted which acylium ion would dominate from dissociation of a loosely bonded one-electron dimer. On the other hand, Wang and Holmes recently reported [2] that fragmentation of the 2,3-pentanedione radical cation gave rise to an unexpected composite metastable ion peak at *m*/*z* 72. The radical cation is a result of isobaric losses of CO and C_2H_4. The fragmentation process yielded $[CH_3C(O)CH_2CH_3]^\bullet$ and $[CH_3C(OH)C{=}C{=}O]^\bullet$. The latter ion was explained by a McLafferty rearrangement [3] of the molecular ion, leading to C_2H_4 loss. The same

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[*] Corresponding author at: 1215-San Dario Avenue Suite G 48-126, Laredo, TX 78040, USA. Tel.: +52 222 2295500x7285; fax: +52 222 2295551 (Mexico).
E-mail address: jpercino@siu.buap.mx (M.J. Percino).

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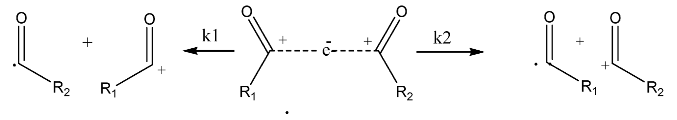


Fig. 1. Formation of the two acylium ions indicating an electron-bonded diacylium ion dimer structure [1] for α-diketones.

fragmentation was also observed for $CH_3CH_2COCOCH_2CH_3$, $CH_3CH_2COCOCH_3$, $CH_3COCOCH_3$ and CH_3COCH_3.

In the present work we report results from electron impact ionization (EI) positive-ion mass spectra of a co-crystal of two compounds, 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione, as well as 2,2′-pyridil, which showed composite ion peaks of *m/z* 212, 184, *m/z* 198, 170, and *m/z* 184, 156, respectively, resulting from the successive loss of two fragments of 28 mass units corresponding to CO. The results are compared with the EI fragmentation of 1,2-diphenylethane-1,2-dione (benzil).

2. Experimental

2.1. Materials and method

EI mass spectra were acquired in the positive ion mode, recorded at an ion source temperature of 300 °C and electron beam energy of 70 eV, on a JEOL SX-102 mass spectrometer.

The two compounds 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione were co-crystallized with cyclohexane [4]. The compounds were obtained by condensation of stoichiometric amounts of 2-pyridincarboxaldehyde and (6-methyl-pyridine-2-yl)methanol without a catalyst in a solvent-free reaction at 140 °C. 2,2′-Pyridil was purchased from Aldrich and benzil from UIC Inc. Both compounds were used without further purification.

3. Results and discussion

The EI mass spectra of 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione are shown in Fig. 2. Mutual mass spectra of the two compounds showed molecular ions at *m/z* 240 and 226, corresponding to the molecular masses expected for each compound. The EI spectrum in Fig. 2 shows four unpredicted composite peaks; two at *m/z* 212 and 198 with an intensity corresponding to ∼10% of that of the base peak for each compound are due to the loss of 28 mass units (CO). The fragmentation peaks corresponding to $[CH_3C_5H_3NCOC_5H_3NCH_3]^+$ and $[C_5H_4NCOC_5H_3NCH_3]^+$ were identified by mass determination of the precursor ions and the decomposition product ions shown in Schemes 1 and 2. In Schemes 1 and 2 the composite peaks corresponding to *m/z* 184 and *m/z* 170, which are >10% of the intensity of the base peak, yield compositions of $[(CH_3C_5H_3N)_2]^+$ and $[C_5H_4NC_5H_3NCH_3]^+$, respectively, with each fragment resulting from the loss of 28 mass units. These results were unexpected, since, based on the structure of 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione, theoretical studies of similar pyridine-substituted α-diketones performed by Rogachev et al. [5], and identification of EI mass fragments of organic compounds [6,7] homolytic bond cleavage to form two acylium ions is more probable, which usually account for the base peak. From the estimated C–C bond energy between the carbonyl group in these α-diketones [5], values of 66.61, 64.79 and 65.63 kcal/mol can be predicted for homolytic bond cleavage for compounds with nitrogen atoms in the *para*-, *ortho*- and *meta*-positions, respectively. In general, the probability of cleavage of a particular bond is related to both its chemical lability and the thermodynamic stability of the fragments that are formed [3]. EI mass spectra showed significant peaks arising from cleavage of the C–C bond as expected for 1,2-bis(6-

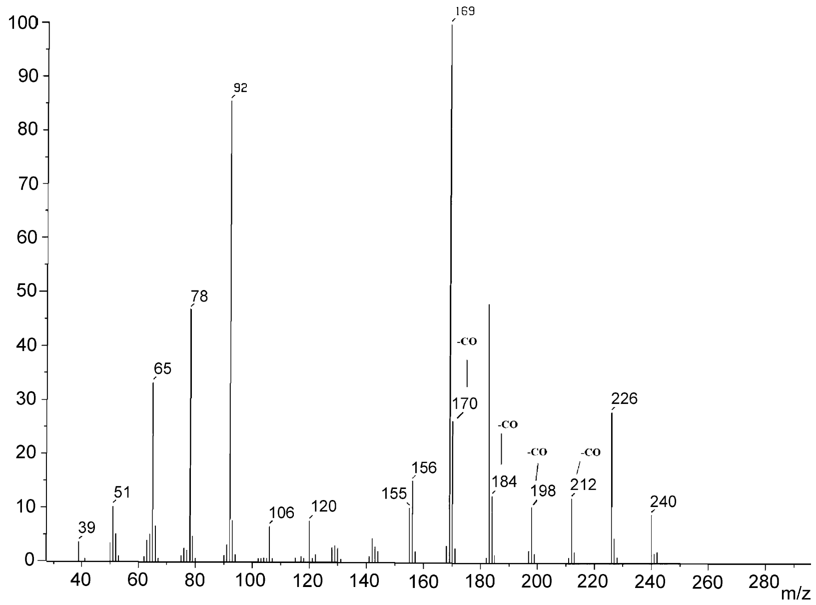
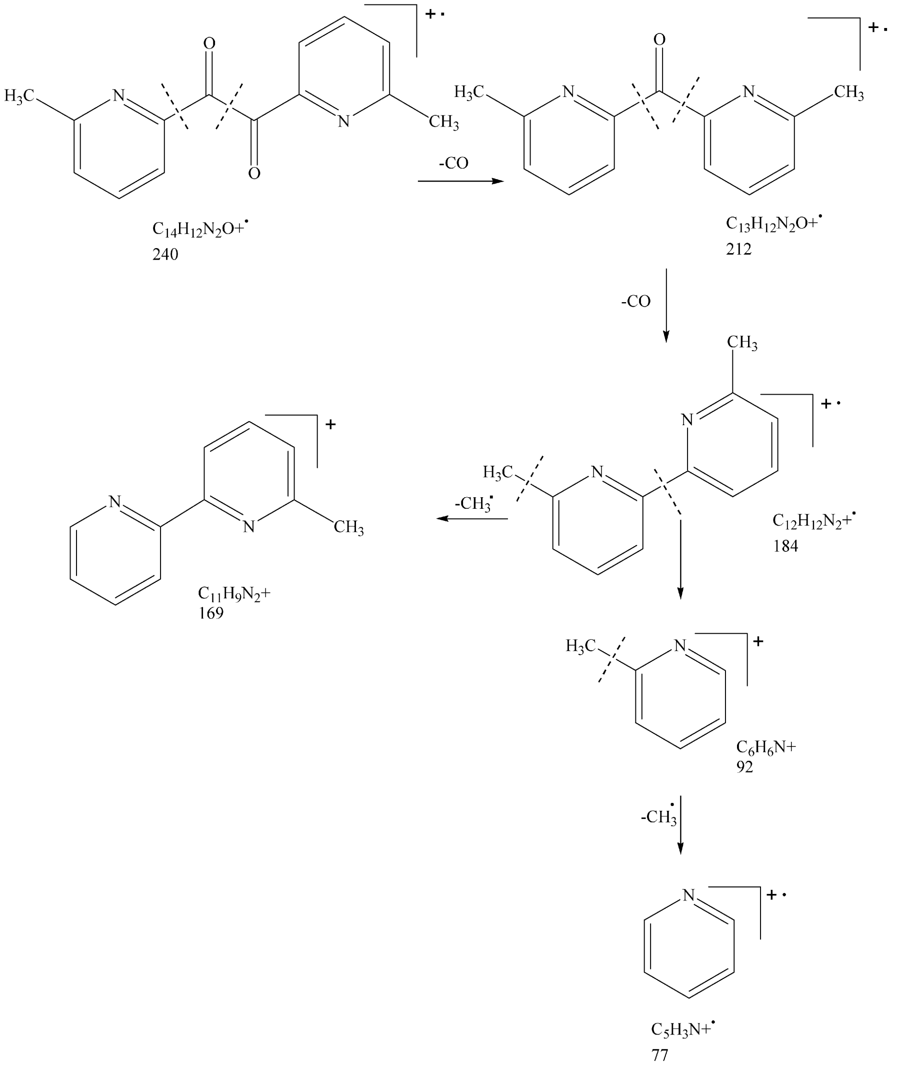


Fig. 2. EI simultaneous mass spectra of 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione.



Scheme 1. Proposed fragmentation pathway for 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione.

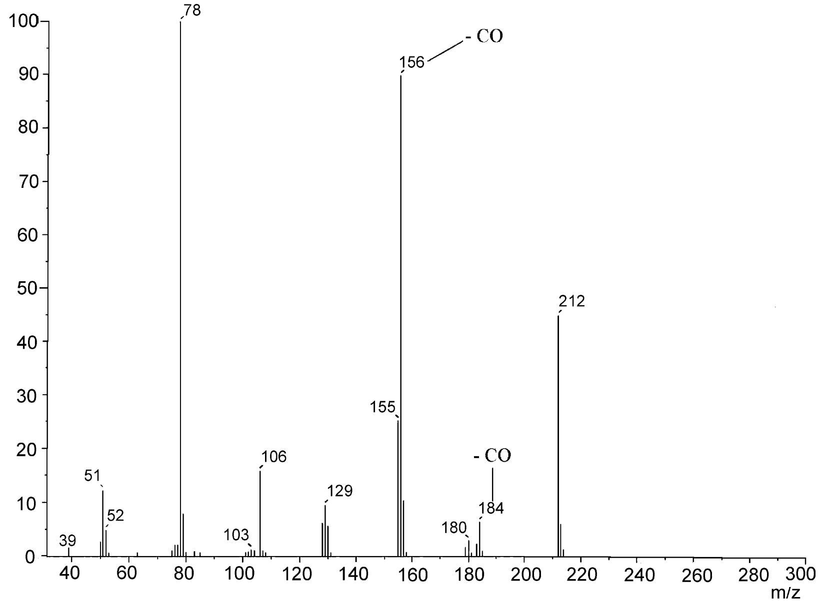
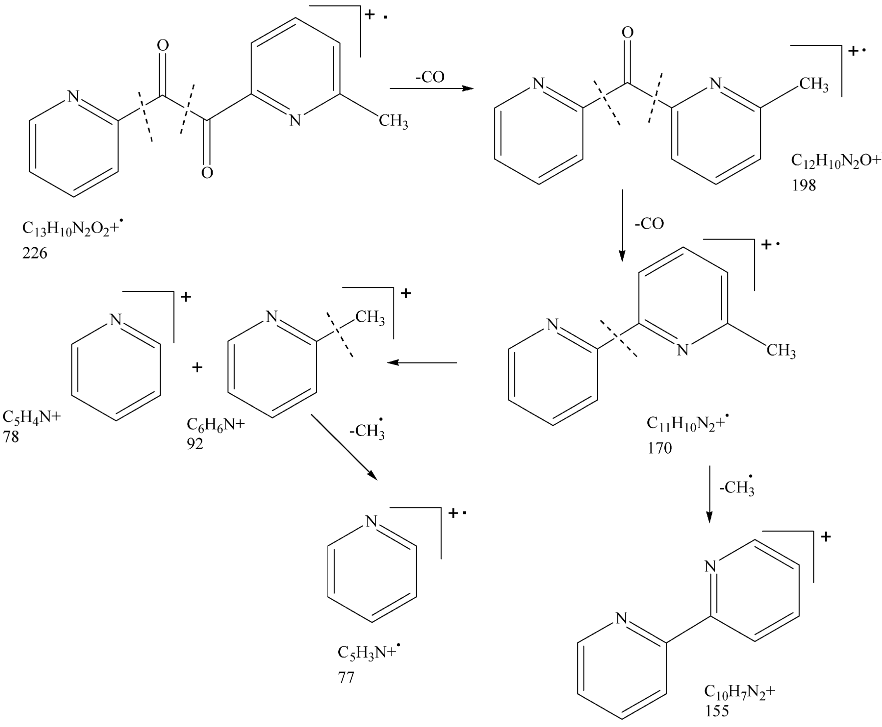
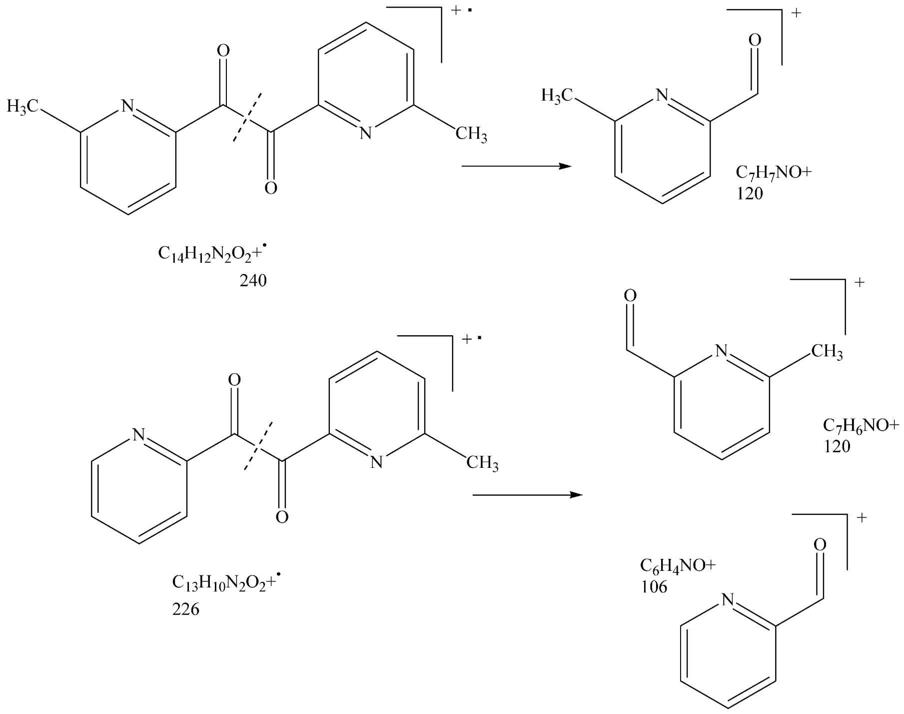


Fig. 3. EI mass spectrum of 2,2′-pyridil.

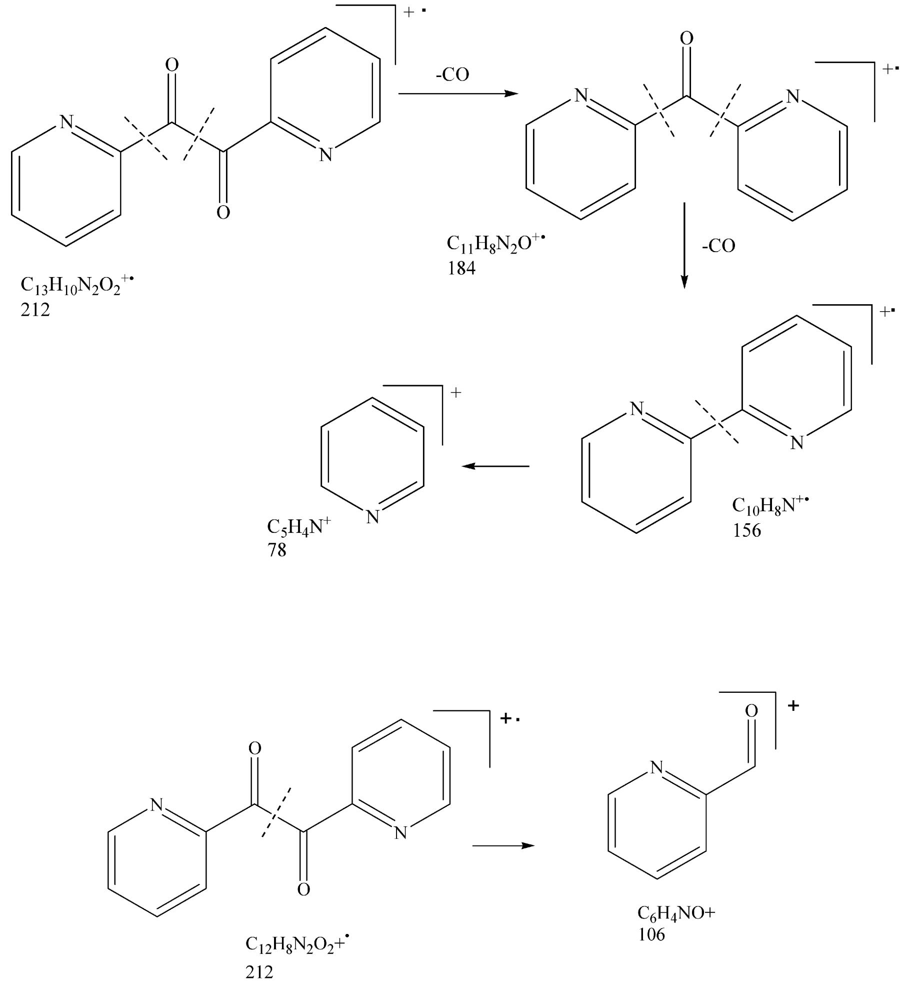


Scheme 2. Proposed fragmentation pathway for 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione.

methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione, yielding fragments at *m/z* 120 $[CH_3C_5H_3NC{=}O]^+$, *m/z* 106 $[C_5H_3NC{=}O]^+$ and *m/z* 120 $[O{=}CNH_3C_5CH_3]^+$ (Scheme 3). Wang and Holmes recently reported [2] small decomposition peaks for the decarbonylation of the ionized α-diketones 2,3-pentanedione, 2,3-butanedione and 3,4-hexanedione explained by the loss of 28 mass units and McLafferty rearrangement. Another example reported by Trikoupis et al. [8] involves spontaneous rearrangement of the initially generated molecular ions of conventional structures to



Scheme 3. Fragmentation products from cleavage of the C—C bond for 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione.



Scheme 4. Proposed fragmentation and product from cleavage of the C—C bond of 2,2′-pyridil.

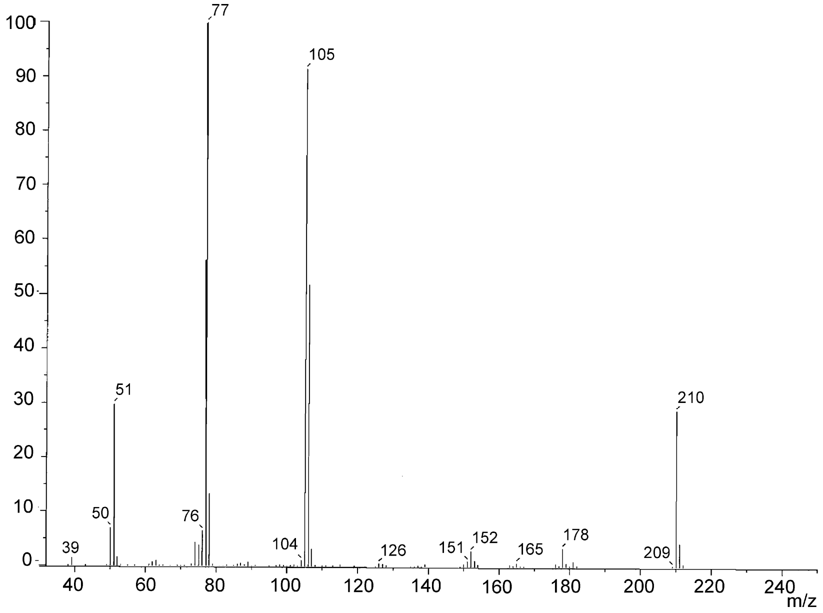
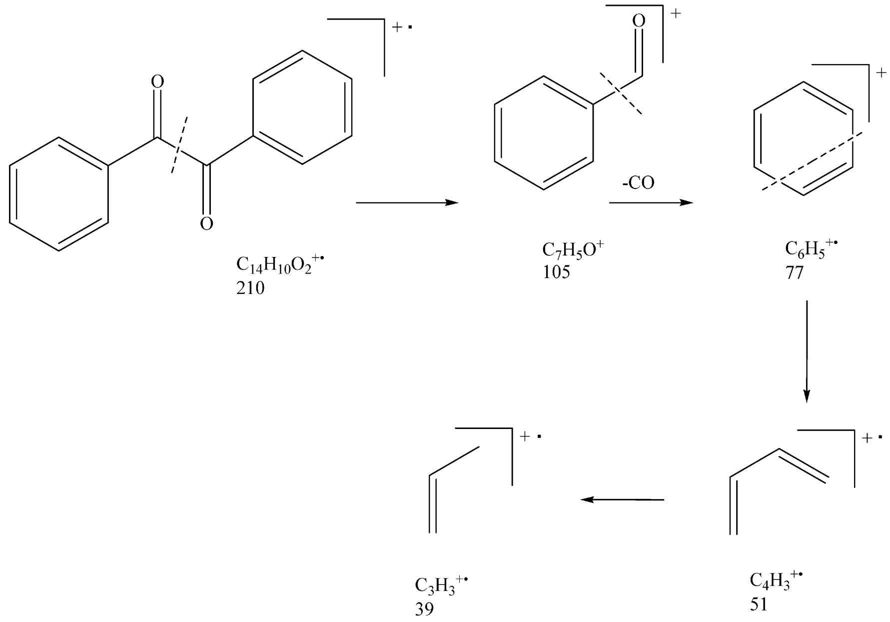


Fig. 4. EI mass spectrum of benzil.



Scheme 5. Proposed fragmentation products from cleavage of the C—C bond of benzil.

more stable species characterized by a long one-electron C–C bond, such as the molecular ion of $[CH_3C(=O)C(=O)OCH_3]^+$. Dimethyl oxalate (DMO) shows interesting intramolecular dissociation chemistry involving competition between the loss of CH_3 and CO_2 and the loss of $CH_3O–C=O$ ions.

EI spectra were measured for the homologous α-diketone 1,2-dipyridyldione (2,2′-pyridil) to verify this behavior, as shown in Fig. 3. 2,2′-Pyridil exhibits a decarbonylation channel similar to the title compounds, i.e., the molecular ion at *m*/*z* 212 loses CO to yield a peak at *m*/*z* 184 corresponding to a fragment composition of $[C_5H_4NCONC_5H_4]^+$ and loses another CO to yield the fragment $[C_5H_4NNC_5H_4]^+$ at *m*/*z* 156. Interpretation of the other peaks observed leads to confirmation of the fragments shown in Scheme 4. The EI spectrum of benzil shown in Fig. 4 was compared with the NIST library of mass spectra. The composition of the fragments is not equivalent to the pyridine-α-diketones. In fact, benzil only showed cleavage of the C–C bond to yield two symmetrical $[C_6H_5CO]^+$ acylium ions (Fig. 4), reflected in a peak at *m*/*z* 105 with >90% of the intensity of the base peak at *m*/*z* 77, which can be attributed to fragmentation of the acylium ion to yield $[C_5H_4]^+$ and CO (Scheme 5). The contrasting EI mass fragmentation behavior for benzil is interesting because it highlights the characteristic structure of compounds containing pyridine rings, which confers the extra stability required for the rearrangement reaction.

The results are also important because they confirm that the green crystals obtained contain two co-existing novel compounds: 1,2-bis(6-methylpyridin-2-yl)ethane-1,2-dione and 1-(pyridin-2-yl)-2-(6-methylpyridin-2-yl)ethane-1,2-dione.

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