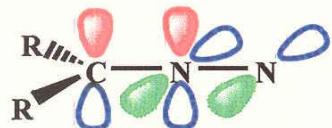


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## ELECTRON-IMPACT-INDUCED FRAGMENTATION OF CYCLIC 2-DIAZO-1,3-DIKETONES

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The electron-impact-induced fragmentation (the mass spectra, 15-70 eV) of cyclic 2-diazo-1,3-diketones (2-diazo-1,3-cyklohexadione, **Ia**; 2-diazo-4,4-dimethyl-1,3-cyklohexandione, **Ib**; 2-diazo-5,5-dimethyl-1,3-cyklohexandione, **Ic**; 2-diazo-4,6-dioxa-5,5-dimethyl-1,3-cyklohexandione, **Id**; 2-diazo-5-fenyl-1,3-cyklohexandione, **Ie**) was studied.<sup>1,2</sup> Used cyclic 2-diazo-1,3-diketones were synthetised by conventional methods.<sup>3</sup> The mass spectra were measured using Varian MAT 111 instrument with direct introduction of samples, with a source temperature of 120°C, energy of ionising electrons in the range 15-70 eV and 150 µA and sample reservoir laboratory temperature.

The elimination of diazogroup is typical reaction for fragmentation of diazocompounds<sup>4</sup> and diazoketones<sup>5,6</sup> after ionisation of molecules with electron impact. All investigated cyclic diazo-1,3-diketones show molecular ion with 0.7-86.4 % of relative abundance. A typical ions are [M]<sup>+</sup>, [M-N<sub>2</sub>]<sup>+</sup>, [M-N<sub>2</sub>-CO]<sup>+</sup>, [M-N<sub>2</sub>-CO-CH<sub>2</sub>]<sup>+</sup> and [M-N<sub>2</sub>-CO-CH<sub>3</sub>]<sup>+</sup>. The Wolff rearrangement was observed for all investigated cyclic diazo-1,3-diketones (without **Id**). The schemes of fragmentation of investigated cyclic diazo-1,3-diketones were proposed.

*Table 1.* The per cent from total ionic current (numerator) and relative abundance (%), denominator) of molecular ions and ionic fragments of cyclic diazo-1,3-diketones at 70 eV and 20 eV

| No.       | eV | [M] <sup>+</sup> | [M-N <sub>2</sub> ] <sup>+</sup> | [M-N <sub>2</sub> -CO] <sup>+</sup> | [M-N <sub>2</sub> -CO-CH <sub>2</sub> ] <sup>+</sup> | [M-N <sub>2</sub> -CO-CH <sub>3</sub> ] <sup>+</sup> |
|-----------|----|------------------|----------------------------------|-------------------------------------|--|--|
| <b>Ia</b> | 70 | 10,98/86,4       | 3,9/30,8                         | 0,99/7,8                            | 1,7/13,4   | -  |
|           | 20 | 15,75/37         | 11,02/26                         | 2,36/5,6                            | -  | -  |
| <b>Ib</b> | 70 | 5,94/29,1        | 2,71/13,3                        | 0,89/4,4                            | 0,78/3,8   | 12,24/60   |
|           | 20 | 2,67/13,5        | 8,53/43,2                        | 1,6/8,1                             | 1,53/6,8   | 19,73/100  |
| <b>Ic</b> | 70 | 2,18/13,4        | 3,9/24                           | 0,94/5,8                            | 1,4/8,6  | 2,6/16   |
|           | 20 | 6,82/42,1        | 14,79/91,2                       | 2,96/18,3                           | -  | 14,79/91,2   |
| <b>Id</b> | 70 | 2,58/5,1         | 0,28/0,5                         | -                                   | -  | -  |
|           | 20 | 3,85/8,4         | 9,78/21,4                        | -                                   | -  | -  |
| <b>Ie</b> | 70 | 0,21/0,7         | 3,07/31                          | 1,45/5                              | 0,37/1,3   | -  |
|           | 20 | 2,48/10,6        | 23,36/100                        | 10,36/44,4                          | 2,34/10  | -  |

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