

was reduced to about 50 ml by rotary evaporation and cooled in a refrigerator. The white crystalline product was recrystallized from carbon tetrachloride, m.p. 47–48°C.

The NMR spectrum of I was examined in benzene solution. A small amount of TMS was added and used as internal standard and lock signal source. The NMR tube was thoroughly degassed and sealed under vacuum.

The spectra were run at ambient temperature (ca. 30°C) on a JEOL-C-60H spectrometer. Line positions were obtained by averaging the results of four scans at 54 Hz sweep width. Computations were performed on an IBM/50H computer. The graphical output was obtained using a Calcomp Plotter.

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## Skeletal Rearrangements in the Mass Spectrometric Fragmentation Pattern of Phenylcarbamic Acid Anhydrides\*

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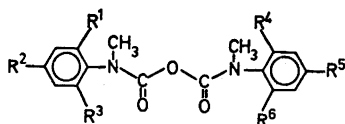
In a preliminary communication we described the first discovery of a stable phenylcarbamic acid anhydride, isolated as a by-product during the synthesis of some carbanilates.<sup>1</sup> Later, a useful method of synthesis of this new class of compounds was developed and a plausible mechanism for their formation was reported.<sup>2</sup> Continuing the studies of the phenylcarbamic acid anhydrides we have now recorded and evaluated the mass spectra of compounds I–VI (Table 1).

The high (70 eV) and low (9 eV) energy spectral data are collected in Table 2. The proposed general fragmentation pattern, supported by appropriate metastable ions, is outlined in Scheme 1. Some interesting peaks corresponding to ions formed by skeletal rearrangements will be discussed in detail.

All spectra of the compounds studied display a peak corresponding to a fragment deriving from the molecular ion, after expulsion of CO<sub>2</sub>. The relative importance of this process increases at lower eV (cf. Table 2) suggesting that the reaction involved has a low frequency factor,<sup>3</sup> which is characteristic for rearrangements. The reaction seems to be substituent dependent (cf. Table 2), being most pronounced in the breakdown pattern of the *p*-methoxy derivative III. This M–CO<sub>2</sub> fragmentation belongs to a general type of skeletal rearrangements, which is quite common in mass spectrometry.<sup>4,5</sup> However, formation of a new carbon-nitrogen bond, as in the present case, is not commonly observed and, to our knowledge, skeletal rearrangements with loss of CO<sub>2</sub> from the molecular ion have not earlier been noted for anhydrides.

\* Carbamic acid anhydrides Part III; Part I and II see Refs. 1 and 2.

Table 1. Phenylcarbamic acid anhydride.



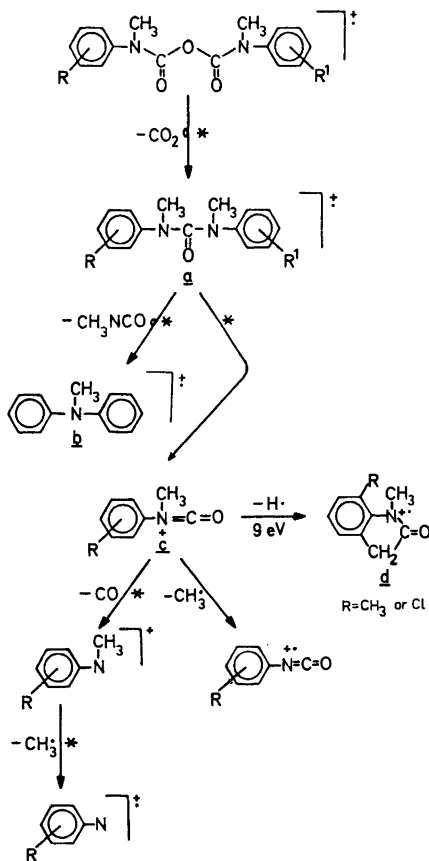
Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>
I	H	H	H	H	H	H
II	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H
III	H	OCH <sub>3</sub>	H	H	OCH <sub>3</sub>	H
IV	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>
V	CH <sub>3</sub>	H	Cl	CH <sub>3</sub>	H	Cl
VI	CH <sub>3</sub>	H	Cl	H	OCH <sub>3</sub>	H

Table 2. Mass spectral peaks of phenylcarbamic acid anhydrides.

Compound	<i>m/e</i> (rel.int. %) <sup>a</sup>
I (70 eV)	284(1), 240(6) <sup>b</sup> , 183(3) <sup>c</sup> , 135(8), 134(100), 119(4), 107(5), 106(50), 105(5), 86(4), 77(64).
I (9 eV)	284(2), 241(3), 240(21), 239(3), 183(8), 135(10), 134(100), 106(47), 77(12).
II (70 eV)	312(0.1), 268(0.1), 253(0.2), 148(100), 121(6), 120(28), 92(5), 91(42), 65(16).
II (9 eV)	312(7), 268(23), 253(6), 162(8), 148(100).
III (70 eV)	344(4), 300(19), 165(8), 164(59), 149(8), 137(12), 136(100), 122(4), 121(12), 120(7), 107(9), 92(7), 77(9).
III (9 eV)	344(10), 300(100), 177(6), 165(4), 164(11), 137(15), 121(9).
IV (70 eV)	341(2), 340(6), 296(2), 175(3), 162(100), 161(36), 135(6), 134(24), 133(5), 121(5), 120(7), 119(4), 117(5), 116(3), 106(7), 105(63), 91(15), 79(20), 77(19).
IV (9 eV)	341(12), 340(61), 297(4), 296(16), 162(38), 161(100), 118(12), 105(15).
V (70 eV)	382(2), 380(6), 336(2), 303(3), 301(9), 184(33), 182(100), 167(7), 154(26), 141(7), 134(7), 125(6), 117(6), 91(16), 89(9), 77(11).
V (9 eV)	382(10), 381(8), 380(28), 336(3), 303(9), 301(28), 184(22), 183(39), 182(50), 181(100), 152(6).
VI (70 eV)	362(2), 320(5), 318(13), 284(4), 283(18), 184(30), 182(100), 154(4), 136(4), 134(3), 78(3).
VI (9 eV)	364(10), 362(27), 320(27), 318(37), 302(17), 301(38), 284(11), 283(58), 195(37), 184(22), 183(22), 182(52), 141(48), 137(100), 107(87), 106(53), 77(50).

<sup>a</sup> Peaks in italics correspond to the ions formed in the skeletal rearrangement (M-CO<sub>2</sub>).  
<sup>b</sup> C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O. <sup>c</sup> C<sub>13</sub>H<sub>13</sub>N.

A peak in the spectra of compound I corresponds to  $C_{13}H_{13}N$  (*b*) as found by exact mass measurements (Table 2). A metastable peak at  $m/e$  202.8 verifies that fragment *b* originates from species *a* (cf. Scheme 1), indicating that the reaction



Scheme 1. General fragmentation pattern of phenylcarbamic acid anhydrides. Compounds I–VI.

proceeds through an aryl transfer, with simultaneous loss of  $CH_3NCO$ . This is a

skeletal rearrangement of the same type as the one mentioned above, implying formation of a new carbon-nitrogen bond with ejection of a neutral molecule from a radical ion. However, the rearrangement is remarkable with respect to the nature of the moiety lost<sup>4,5</sup> ( $CH_3CNO$ ). The reason why the loss of methyl isocyanate from *a* only occurs in the fragmentation of compound I is not fully understood, but might be connected with the substitution pattern of the aromatic rings.

At 70 eV, the spectra of all the compounds except III exhibit the base peak corresponding to the phenyl isocyanate moiety *c*. In the low eV spectra of compounds IV and V species *d* becomes the major fragment. It is important to note that these compounds have two substituents in the *ortho*-positions, at least one of them being a methyl group. This fact, together with the increased importance of the process at low eV, indicates that the formation of *d* occurs through a cyclization reaction of *c* with loss of a hydrogen atom.

**Experimental.** Compounds I–VI have been synthesized as described.<sup>2</sup> The mass spectra were recorded on an AEI, MS-30 mass spectrometer using the direct probe technique. The ionizing energy was kept at 9 or 70 eV, the temperature of the ion source being maintained at 200°C. High resolution spectra were obtained using an Atlas SM 1 mass spectrometer in the laboratory of Dr. R. Ryhage. The results were within 4 ppm of the calculated values.

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