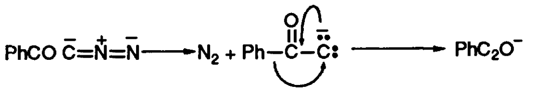
Anionic Rearrangement in the Gas Phase. The Negative Ion Wolff Rearrangement

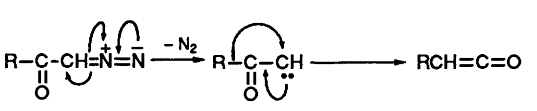
Albert T. Lebedev,[a] **Roger N. Hayes**[b] **and John H. Bowie**[c]
[a] *Department of Chemistry, Lomonosov University of Moscow, Moscow, 119899, USSR*
[b] *Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0362, USA*
[c] *Department of Organic Chemistry, The University of Adelaide, South Australia, 5001*

Product ion studies indicate that the collision-induced loss of N_2 from deprotonated aryl diazomethyl ketones yields an ion formed by Wolff rearrangement, *e.g.*



We have reported a number of negative ion rearrangements in the gas phase which have mechanisms similar to some reactions which occur in solution.[1] In particular we have described rearrangement reactions for a number of deprotonated organonitrogen systems, *e.g.*, the Lossen rearrangement[2] and the negative ion Beckmann rearrangement.[3]

$$RCOCl + CH_2N_2 \longrightarrow RCOCHN_2 \xrightarrow[Ag_2O]{H_2O} RCH_2CO_2H \qquad (1)$$



(2)

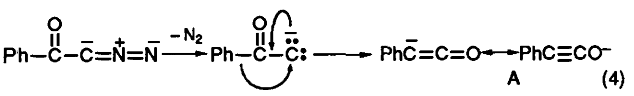
The condensed phase Arndt–Eistert synthesis is thought to involve a carbene rearrangement; here an acyl halide is converted into a carboxylic acid containing one additional carbon.[4] The overall reaction sequence is shown in eqn. (1). The rearrangement occurs in the second step of the reaction, in which the diazomethyl ketone is transformed into a ketene derivative with concomitant elimination of N_2. This process is called the Wolff rearrangement[5] [see *e.g.*, eqn. (2)]. Similar types of rearrangement have been proposed to explain the mass spectral fragmentations of some molecular radical cations of diazoketones.[6–8]

This paper addresses the question: does a Wolff type rearrangement occur when deprotonated diazoketones are subjected to collisional activation in a mass spectrometer?

Results and Discussion

The collision-induced mass spectra (MS/MS) of some deprotonated aryldiazoketones are recorded in Table 1, while that of $(PhCOCDN_2–D)^-$ is illustrated in Fig. 1. Phenyl diazomethyl ketone is typical in this series. It deprotonates specifically at the methine position, and its major fragmentations are losses of $H^{\bullet}$ and N_2. The loss of $(N_2 + CHO^{\bullet})$ and the formation of HC_2O^- are minor in comparison (see Fig. 1). Loss of $H^{\bullet}$ may be rationalised as shown in eqn. (3). The loss of N_2 yields the base peak of Fig. 1. This is a facile process having both unimolecular and collision induced components (see legend to Fig. 1). If the loss of N_2 is followed or accompanied by the Wolff rearrangement, the product ion should be PhC_2O^- [A, eqn. (4)]. We have prepared authentic PhC_2O^- by the unambiguous route[9] outlined in eqn. (5) and its collision activation and charge reversal mass spectra are identical with the collisional activation (Fig. 2) and charge reversal (Table 2) tandem MS/MS/MS data for *m*/*z* 117 (Fig. 1). Thus we conclude that the major fragmentation of $PhCOCN_2$ proceeds *via* the Wolff rearrangement outlined in eqn. (4).*

$$PhCO\bar{C}N_2 \longrightarrow (C_6H_4)^{\bullet}CO\bar{C}N_2 + H^{\bullet} \qquad (3)$$



(4)

$$Ph\bar{C}HCO_2Et \longrightarrow [(PhCH{=}C{=}O)EtO^-] \longrightarrow PhC_2O^- + EtOH \qquad (5)$$

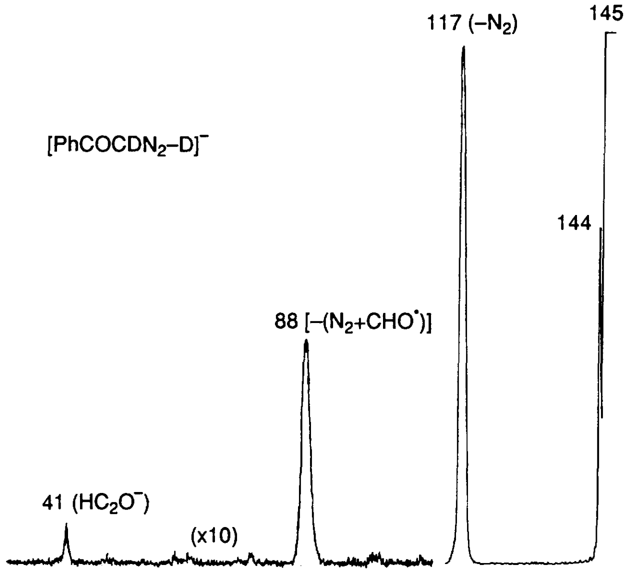


Fig. 1 Collisional Activation Mass Spectrum (MS/MS) of the $(PhCOCDN_2–D)^-$ ion. VG ZAB 2HF instrument. Collision gas helium; 10% decrease in main beam signal. Decompositions occur both inside and outside the collision cell when a voltage of 1000 V is applied to the cell. A peak shifted from its normal value is produced by a collision process occurring in the cell, whereas an unshifted peak is due to processes occurring outside the cell. The unshifted peak is a combination of unimolecular and collision inducted processes (the latter due to leakage of gas from the cell). Results are [*m*/*z* (unshifted–shifted components)]: 144 (10:90), 117 (40:60), 88 (10:90) and 41 (20:80). The presence of a major unshifted component for *m*/*z* 117 indicates that the Wolff rearrangement occurs unimolecularly as well as on collisional activation.

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* The major fragmentation of PhC_2O^- involves loss of $CHO^{\bullet}$ to form $C_7H_4^{\bullet -}$ (see Fig. 2). Corresponding $-(N_2 + CHO^{\bullet})$ species are observed for all deprotonated aryl diazomethyl ketones (Fig. 1, Table 1). A stable cyclic C_7H_4 radical anion seems unlikely; perhaps the ion is a linear species, *e.g.* $HC{\equiv}C{-}CH{=}C{=}CH{-}C{\equiv}CH^{\bullet -}$.

Table 1 Collisional activation mass spectra of deprotonated aryl diazomethyl ketones

Parent ion: p-R–C_6H_4–CO–CHN_2–H R	(m/z)	Spectrum [m/z (loss) relative abundance]
H	145	144 (H•) 70, 117 (N_2) 100, 88 (N_2 + CHO•) 5, 41 ($C_6H_4N_2$) 1.
Me	159	158 (H•) 33, 144 (Me•) 1, 131 (N_2) 100, 116 (N_2 + Me•) 1, 102 (N_2 + CHO•) 3, 41 ($C_7H_6N_2$) 1
F	163	162 (H•) 87, 135 (N_2) 100, 116 (N_2 + F•) 4, 106 (N_2 + CHO•) 5
Cl	179 (Cl^{35})	178 (H•) 73, 151 (N_2) 100, 143 (HCl) 1, 122 (N_2 + CHO•) 3, 115 (N_2 + HCl), 35 ($C_8H_4N_2O$) 2
Br	223 (Br^{79})	222 (H•) 30, 195 (N_2) 100, 166 (N_2 + CHO•) 3, 143 (HBr) 16, 115 (N_2 + HBr) 2, 79 ($C_8H_4N_2O$) 18
MeO	175	114 (H•) 15, 160 (Me) 3, 147 (N_2) 4, 146 (29) 12, 132 (N_2 + Me•) 100, 117 (N_2 + CH_2O) 3, 104 (71) 6
NO_2	190	189 (H•) 8, 162 (N_2) 100, 143 (HNO_2) 8, 133 (N_2 + CHO•) 16, 116 (N_2 + NP_2•) 10, 104 (86) 3

Table 2 Charge reversal (positive ion)[a] MS/MS/MS data for m/z 117 (from $PhCO\bar{C}N_2$) and authentic PhC_2O^-

Parent ion (m/z)	Daughter ion [m/z (loss)]	CR MS/MS/MS data [m/z (relative abundance)]
$PhCO\bar{C}N_2$ (145)	117 ($-N_2$)	98 (7), 89 (54), 86 (37), 77 (17), 74 (44), 62 (100), 61 (97), 51 (36), 50 (40), 39 (28), 37 (22), 26 (4)
$Ph\bar{C}HCO_2Et$ (163)	PhC_2O^- (117, −EtOH)[b]	98 (5), 89 (65), 86 (34), 77 (15), 74 (38), 62 (100), 61 (92), 51 (22), 50 (36), 39 (25), 37 (24), 26 (2)

[a] Charge-reversal (CR) spectra are obtained by collision-induced charge stripping of the negative ion to the corresponding decomposing positive ion.[9] [b] In this case the CR MS/MS/MS spectrum was weak and noisy—the recorded spectrum is CR MS/MS data for m/z 117 formed in the source (of the VG ZAB 2HF instrument).

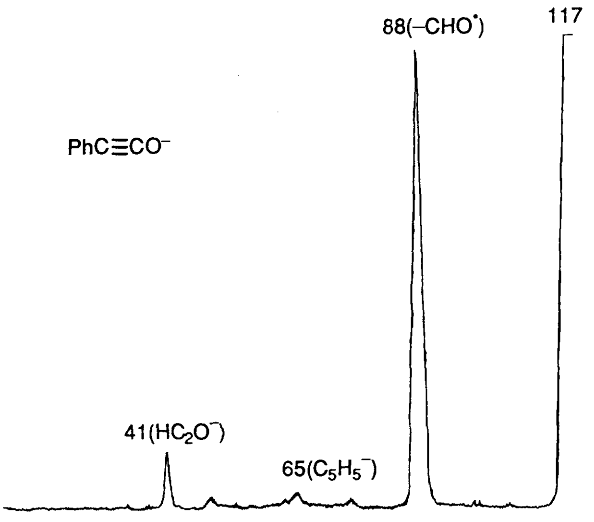
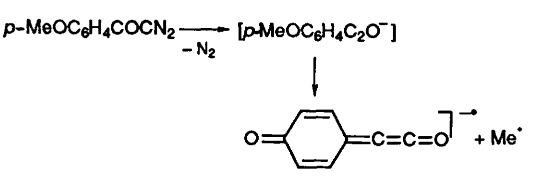


Fig. 2 Collisional Activation Mass Spectrum (MS/MS/MS) of the m/z 117 daughter ion shown in Fig. 1. MS 50 TA instrument—see Experimental section for specific details. The CA MS/MS/MS data for authentic PhC_2O^- [prepared as shown in eqn. (5)] are identical with those shown in this spectrum. Charge reversal (positive ion) spectra are recorded in Table 2.

The major fragmentations of most of the parent ions shown in Table 1 are similar to those already outlined for $PhCO\bar{C}N_2$. Some minor processes are observed for p-$RC_6H_4CO\bar{C}N_2$ species including losses of RH (R = Cl, Br and NO_2), (N_2 + R•) (R = Me, F and NO_2), and (N_2 + RH) (R = Cl and Br). The spectrum that deviates most from the norm is that of p-$MeOC_6H_4CO\bar{C}N_2$. Here, the loss of N_2 is minor, and the base peak is produced by loss of (N_2 + Me•). We propose that this occurs *via* a Wolff intermediate which then eliminates a methyl radical to form the stabilized anion radical shown in eqn. (6). In summary, we conclude that the collision induced loss of N_2 from deprotonated aryl diazomethyl ketones produces an ion ArC_2O^- formed by the negative ion Wolff rearrangement outlined in eqn. (4).



(6)

Experimental

Collisional activation mass spectra (MS/MS) and charge reversal (positive ion) mass spectra[10] were recorded using a VG ZAB 2HF mass spectrometer operating in the negative chemical-ionization mode.[11] Operating procedures have been reported.[2] Deprotonation of all neutrals was effected using NH_2^- (from NH_3); solids were introduced through the direct probe with no direct heating (the source was maintained at 150 °C), and helium was used as collision gas at a pressure (2×10^{-7} mmHg) sufficient to reduce the main beam signal by 10%.

Consecutive collision induced dissociation spectra (MS/MS/MS) and charge reversal MS/MS/MS data[10] were measured with a Kratos MS 50 TA instrument.[12] Operating details have been reported.[2] Deprotonating agent MeO^- (from MeONO[13]); collision gas in both cells—helium, pressure 2×10^{-6} mmHg—decrease in main beam signal 30%.

All the aryl diazomethyl ketones are known and were prepared by standard procedures, *viz.* p-$RC_6H_4COCHN_2$; R = H,[14] Me,[15] F,[16] Cl,[15] Br,[16] MeO[14] and NO_2.[17]

The labelled compound $PhCOCDN_2$ was prepared by allowing $PhCOCHN_2$ (5 mg) to stand in MeOD (1 cm^3) under nitrogen, for 3 h (D_1 = 95%).

Acknowledgements

One of us (A. T. L) acknowledges the award of a fellowship awarded under the auspices of the Australia/USSR Academic Exchange Scheme. J. H. B. and R. N. H., respectively, acknowledge the support of the Australian Research Council and the Midwest Center for Mass Spectrometry, an NSF Instrumental Facility.

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Paper 1/00768H
Received 18*th February* 1991
Accepted 8*th April* 1991