# Ortho Effects in Organic Molecules on Electron Impact. Part 16. Novel Oxygen Transfers from the Nitro Group to Acetylenic Carbons in 2-Nitrodiphenylacetylenes

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Oxygen transfers to both acetylene carbons are noticed in parallel fragmentation pathways during the electron impact induced decompositions of 2-nitrodiphenylacetylene. The oxygen transfer to  $\beta$ -acetylenic carbon leads to the most abundant ion corresponding to benzoyl cation while transfer to the  $\alpha$ -acetylenic carbon affords less intense fragments corresponding to  $[M - OH]^+$ ,  $[M - CO]^{+\cdot}$  and  $[M - CO_2]^{+\cdot}$ . The proposed fragmentation pathways and ion structures are supported by high-resolution data, linked-scan spectra and chemical substitution.

## INTRODUCTION

A nitro group in the *ortho* position is a very powerful interacting function in aromatic compounds during mass spectral decompositions. It is capable of trans-ferring oxygens to the double bond,<sup>1-3</sup> hetero-atoms<sup>4,5</sup> and carbon<sup>6</sup> in the side chain of aromatic ortho-disubstituted compounds. The oxygen transfers from the nitro group to carbon-carbon and carbon-nitrogen double bonds are known to generate very abundant aroyl cations.<sup>1-3</sup> But transfer of oxygen to an acetylenic carbon has not been reported under electron impact (EI) while the thermolytic<sup>7,8</sup> and photolytic<sup>9</sup> isomerization of 2-nitrodiphenylacetylene (1) lead to 2-phenyl isatogen (compound 6) where the oxygen is transferred from the ortho nitro group to the acetylenic carbon atom. Hence it is considered interesting to study the mass spectral fragmentations of 2-nitro- diphenylacetylenes (compounds 1-5) to evaluate the possible occurrence of oxygen transfers from the nitro group to the acetylenic carbons under EI conditions.



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#### **RESULTS AND DISCUSSION**

The base peak in the mass spectrum of 2nitrodiphenylacetylene (1) is at m/z 105. The accurate mass of this fragment ion, as determined by highresolution technique, is 105.0338, which corresponds to an elemental composition of C<sub>7</sub>H<sub>5</sub>O. Based on this fact a benzoyl cation structure is assigned to this fragment at m/z 105. The formation of this fragment is envisaged to arise as a result of an oxygen transfer from the nitro group to the  $\beta$ -carbon of the acetylenic moiety leading to a cyclic intermediate a which then undergoes a simple fission, affording b at m/z 105 (Scheme 1). The proposed direct formation of b from the molecular ion is supported by the B/E linked-scan spectrum of the molecular ion and the  $B^2/E$  linked-scan spectrum of b. The benzovl cation structure assigned to b is confirmed by the fact that the collision-induced dissociation (CID) B/E linked-scan spectrum of b and that of the ion at m/z105 derived from benzoic acid are found to be identical (Fig. 1), showing the expected fragments characteristic of benzoyl cation. Further evidence for the transfer of oxygen from the nitro group to the  $\beta$ -acetylenic carbon during the formation of ion b is obtained from the corresponding shifts (Table 1)<sup>10,11</sup> in the m/z values of b of



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Figure 1. Collision-induced linked-scan spectra of ions at (a) m/z105 of 1, (b) m/z 105 of benzoic acid.

the substituted 2-nitrodiphenylacetylenes (compounds 3-5).

The other characteristic ions in the mass spectrum of 1 are due to  $[M - CO]^{+}$ ,  $[M - OH]^{+}$  and [M $-CO_2$ <sup>+</sup>. A common rearranged molecular ion c is proposed for the formation of these fragment ions. An oxygen transfer from the nitro group to the  $\alpha$ -acetylenic carbon followed by cyclization is visualized for the formation of c having the 2-phenyl isatogen radical cation structure (Scheme 2). Skeletal rearrangements in c initially triggered by the hydrogen transfer from the phenyl ring to nitrogen leads to another rearranged molecular ion d, which then undergoes two consecutive losses of CO to afford to  $[M - CO]^+$  ion d at m/z 195 and the  $[M - CO - CO]^+$  ion f at m/z 167, respectively (Scheme 2). The structures of e and f are assigned as being ionized acridone and ionized carbazole, based on the high-resolution data and the comparison of the B/E linked scans of e and f with those of the B/E linked scans of the molecular ions of the acridone and carbazole, respectively, taken as reference compounds (Fig. 2).

The [M - OH] ion noticed in the mass spectrum of 1 is envisaged to arise from a hydrogen transfer from the

Table 1. Partial mass spectra of compounds 1-6



Scheme 2



Figure 2. B/E linked-scan spectra of ions at (a) m/z 195 of 1, (b) M<sup>++</sup>, m/z 195 of acridone, (c) m/z 167 of 1, (d) M<sup>++</sup>, m/z 167 of carbazole.

			Relative abundance									
Compound 1	<sup>M+⁺</sup> 20	Arcُ <b>–</b> 0 ه 100	[M – CO]+' e 8	[M – CO – CO]+' f 28	[M – OH]+ <i>g</i> 40	[M – CO <sub>2</sub> ]+' <i>h</i> 14	Other ions					
							1	12	14	34	12	
	(223)	(105)	(195)	(167)	(206)	(179)	(193)	(177)	(165)	(151)	(146)	
2	100	``	· _ /	_		_	28	27	35	28	23	
	(223)						(193)	(177)	(165)	(151)	(150)	
3	14	100	3	3	24	3	14	13	9	18	18	
	(237)	(119)	(209)	(181)	(220)	(193)	(189)	(180)	(176)	(165)	(152)	
4	70	<b>1</b> 00	` 1 <sup>´</sup>	1	39	3	10	17	30	14	4	
	(253)	(135)	(225)	(197)	(236)	(209)	(193)	(164)	(163)	(152)	(146)	
5	<b>1</b> 6	100	9	8	23	7	20	23	10	11	16	
	(257)	(139)	(229)	(201)	(240)	(213)	(177)	(176)	(165)	(151)	(150)	
6	100	13	6	16	58	18	6	2	8	4	4	
	(223)	(105)	(195)	(167)	(206)	(179)	(177)	(165)	(151)	(140)	(139)	

m/z values correspond to  $^{35}$ Cl.



phenyl ring to the oxygen of the NO moiety in c followed by the ejection of  $\dot{O}H$ , leading to a cyclic fragment g at m/z 206 (Scheme 3). Another fragmentation of considerable interest is the loss of CO<sub>2</sub> from the molecular ion leading to  $[M - CO_2]^+$ . An oxygen migration from nitrogen to the carbonyl carbon in c accompanied by the expulsion of CO<sub>2</sub> is proposed for the formation of the  $[M - CO_2]^+$  ion h at m/z 179 (Scheme 4). The structures g and h were offered as reasonable possibilities for the intermediates involved in the fragmentations.

The mass spectrum of 2-phenyl isatogen (6) shows ions at m/z 195, 167, 206 and 179 of comparable abundances to those obtained from 2-nitrodiphenylacetylene (1). Hence the mechanism involving the oxygen transfer from the ortho nitro group to the  $\alpha$ -acetylenic carbon atom leading to the molecular ion of 2-phenyl isatogen as an intermediate for the formation of the ions e, f, gand h from 1 is justified. Furthermore the abundance of ion b at m/z 105 in the mass spectrum of 6 is reduced in importance compared to that of b in 1 (Table 1). This observation supports the view that the oxygen transfer from the nitro group to the  $\alpha$ -acetylenic carbon does not lead to b in 1. Therefore the proposed oxygen transfer from the nitro group to the  $\beta$ -acetylenic carbon leading to the rearranged molecular ion a, as an intermediate, for the formation of b in 1 is plausible.

All the proposed fragmentation pathways are characterized by the appropriate metstables as shown in the corresponding B/E linked-scan spectra. The proposed *ortho* interactions for the formation of ions b, e, f, g and h are also supported by the fact that these ions are



Scheme 4



totally absent in 4-nitrodiphenylacetylene (2) (Table 1). The other common fragments observed in 1 and 2 are shown in Scheme 5.

Hence it can be seen from this study that the oxygen transfer from the nitro group to the  $\beta$ -acetylenic carbon in 2-nitrodiphenylacetylene under EI conditions is more facile than that to the  $\alpha$ -acetylenic carbon, perhaps owing to a more favourable transition state, leading to the most abundant ion b in its spectrum.

#### **EXPERIMENTAL**

Compounds 1–5 were prepared from the appropriately substituted copper(I) phenylacetylide and corresponding iodonitrobenzene by refluxing for 10–12 h in dry pyridine solvent under a nitrogen atmosphere according to the general procedure reported in the literature.<sup>12,13</sup> Compound 6 was prepared by heating compound 1 in dry pyridine at 120 °C for 4 h under a nitrogen atmosphere as reported in the literature.<sup>8</sup>

All the compounds studied were recrystallized to constant melting point and their purity was checked by thin-layer chromatography. The structures were confirmed by nuclear magnetic resonance and infrared spectral data. The mass spectra were taken on Varian MAT CH-7 and Finnigan MAT 8230 mass spectrometers. The spectra were run at 70 eV with an emission current of 100  $\mu$ A. All the compounds were introduced into the mass spectrometer through the direct probe insertion at probe temperatures varying between 30 and 110 °C.

The linked-scan measurements  $(B/E \text{ and } B^2/E \text{ scans})$ were made on a Finnigan MAT 8230 mass spectrometer with PDP 11 data system at an ionization energy of 70 eV and an accelerating voltage of 3 kV. Accurate mass measurements were carried out at a resolution of 5000 with a Finnigan MAT 8230 mass spectrometer, and PFK was used as reference. The average deviation observed in these accurate mass measurements is  $\pm 0.0008$ . CID linked-scan spectra in the first field-free region were investigated using argon as collision gas with a VG Micromass 7070 H mass spectrometer.

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