Electron Impact Studies. Part CIV.[1] Cyclisation Reactions of Negative Ions. The o-$O_2NC_6H_4(CH{=}CH)_nCOR$ System

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Negative-ion mass spectra of compounds of the general type o-$O_2NC_6H_4(CH{=}CH)_nCOR$ (n = 1—3) show rearrangement peaks produced by novel cyclisation reactions occurring between the adjacent substituents. When n = 1, reactions proceed mainly through six- and seven-membered transition states, whereas for n = 2, six-centred states still predominate, but reactions also occur *via* five-membered transition states. Major fragment ions correspond to charged 1,2-dicarbonyl (n = 1), 2-ene-1,4-dicarbonyl (n = 2), and 2,4-diene-1,6-dicarbonyl (n = 3) systems. Rearrangement ions are *not* observed when the nitro-group is replaced by a carboxy-group.

ORGANIC compounds containing suitable electron-withdrawing groups yield pronounced molecular anions [2-4] produced by secondary electron capture.[5-7] We have reported the collision-induced [8-11] α-cleavage of the carbonyl groups in aryl-CO [12] and aryl-CH_2-CO [13] systems. When aryl = o-nitrophenyl, unimolecular reactions involving cyclisations of the charged nitro-group at carbonyl centres produce pronounced rearrangement ions.[12,13]

A logical extension of this work is to examine the behaviour of negative ions derived from molecules where double bond units have been placed between the o-nitrophenyl and carbonyl groups. In these circumstances, competition between nucleophilic (or radical) attack at the carbonyl and addition to the olefin may occur. This paper describes the result of such a study.

RESULTS AND DISCUSSION

The spectra of the compounds listed below were determined. Spectra of the unlabelled compounds are given in the Table; those of the ^2H- and ^{18}O-labelled derivatives were used to aid interpretation of fragmentation pathways. All fragmentations mentioned in the text have been substantiated by the observation of decompositions of the appropriate metastable ions in both field-free regions of the mass spectrometer.[11]

Apart from NO_2^- ions, all fragment ions in the spectra of (1), (4)—(7), and (10) are produced by rearrangement reactions.† The spectra of the labelled compounds (2), (3), (9), (16), and (17) suggest that the major ions are produced from those groups of atoms shown in *a* and *b*. The carboxylate anion $R^3CO_2^-$ (see *b*) is observed in abundances ranging from 7 to 33% of the base peak (see Table), and is probably produced by either anionic or radical attack of the nitro-group at the carbonyl centre through a seven-membered transition state (for radical attack see $c \longrightarrow d$). The benzoate anion is produced by a similar mechanism from the o-nitrophenyl benzoate molecular anion.[14]

Intensities (%) of mass spectral fragment ions

Compd.	$M^{-\bullet}$	$(M - HO\cdot)^-$	$(M - NO\cdot)^-$	$(M - R^3CO\cdot)^-$	$(M - CO_2H\cdot)^-$	$C_7H_4NO_2^-$	$(M - C_7H_5NO\cdot)^-$	$C_7H_5NO^-$	$R^3CO_2^-$	NO_2^-
(1)	100	4	27		6	6	17	3	12	50
(4)	100	3	4	4	3	10	15		7	22
(5)	100		16	3		6	9	1	14	38
(6)	100	2	4	8		8	10	1	23	26
(7)	100		5	3	2	2	46		30	13
(10)	100		2		2	2	33	1	33	24
(11)	100	3	3		3	77	92	11		31
(12)	100		3			34	22	13		21
(13)	71	3	2			30	100	8		11
(14)	88	1	2			39	100	8		18
(15)	82					51	100			31

The reactions depicted in *a* are best rationalised by attack of a nitro-oxygen at the carbon α to the carbonyl group through a six-membered transition state, followed by a retro-cleavage of the six-membered ring system. The former reaction has no prior analogy, but retro-processes of negative ions in the gas phase have been reported.[15] The formation of the non-decomposing α-dicarbonyl anion radical [16] [see $(M - C_7H_5NO\cdot)^-$ in

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† The spectra of the m- and p-derivatives have also been measured. They contain only $M^{-\bullet}$ $(M - NO\cdot)^-$, and NO_2^- ions. Collision excitation produced $(M - R^3CO\cdot)^-$ ions.

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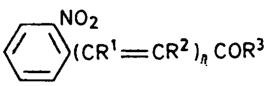
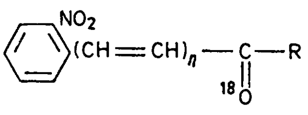
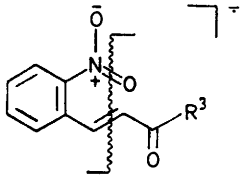


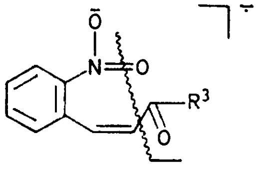
	R¹	R²	R³	*n*
(1)	H	H	H	1
(2)	D	H	H	1
(3)	H	H	D	1
(4)	H	Me	H	1
(5)	H	H	Me	1
(6)	H	Me	Me	1
(7)	H	H	Ph	1
(8)	D	H	Ph	1
(9)	H	D	Ph	1
(10)	H	H	*p*-MeC₆H₄	1
(11)	H	H	H	2
(12)	H	H	Me	2
(13)	H	H	Ph	2
(14)	H	H	*p*-MeC₆H₄	2
(15)	H	H	Me	3



	R	*n*
(16)	H	1
(17)	Ph	1
(18)	Ph	2

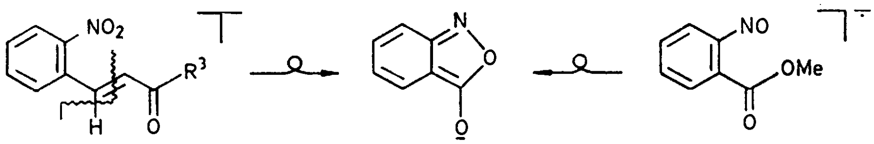


a

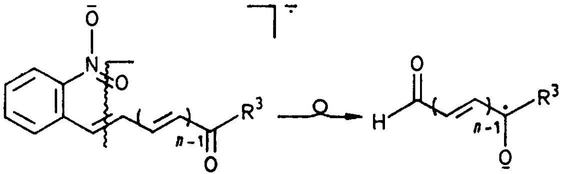


b

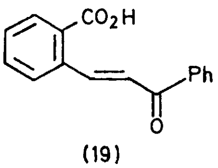
the Table; relative abundances 9—46%] is best represented as shown in *e* and *f*. The retro-cleavage may also produce an ion of low abundance where the charge is retained on the nitrogen-containing fragment [see *a*, also $C_7H_5NO^-$ (Table)].



g *h* *i*

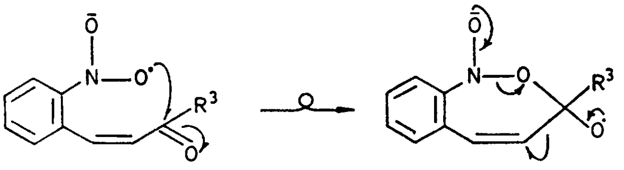


j *k*

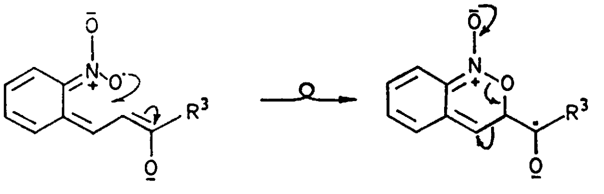


(19)

Other rearrangement ions of small abundance are shown in the Table. One of these, $C_7H_4NO_2^-$, is produced by the loss shown in *g*. The structure of this ion corresponds to *h*, an ion investigated in an earlier study.[13] The ion *h* may also be produced unambiguously by loss of MeO• from the methyl *o*-nitrosobenzoate molecular anion *i*. The $C_7H_4NO_2^-$ ions from the unlabelled compounds **(1)**, **(4)**—**(7)**, **(10)** [also **(12)**—**(15)** (see below)], and *i* eliminate both CO and CO_2[13] with kinetic energy releases at half height[17] (using *V* 3 600 V) in the ranges 48—57 and 21—28 meV respectively, thus establishing the structural correspondence of the ions.



c *d*



e *f*

When the number of olefinic bonds is increased to 2 [**(11)**—**(14)**] and 3 [**(15)**], the spectra are dominated by the dicarbonyl anion radicals *k*, produced as shown in *j*. The ion *h* is also prominent, but again, although the atoms involved in its genesis are the same as those shown in *g*, the overall mechanism is not known. The rearrangement reactions shown in *a* and *b* are not observed if the *o*-nitro group is replaced by an *o*-carboxy-unit. The spectrum of **(19)** shows only a molecular

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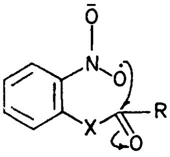
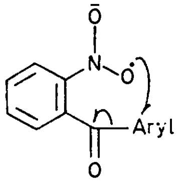
anion, and an $[M - CO_2]^-$ peak [5% of the base peak $(M^{-\cdot})$].

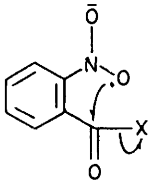
In conclusion, it is of interest to describe the type of transition state produced for negative ions during skeletal-rearrangement reactions occurring between *o*-nitro groups and carbonyl-containing systems. It should be stressed that no such generalisation can be made about the intimate mechanisms of such rearrangements, as these clearly depend upon the particular system under consideration.



l



m



n

The major reactions described in this paper proceed through six-centre states (*a*, *e*, and *j*) even though competing rearrangements going through five- (*g*) and seven-membered (*c*) transition states are observed in particular cases. Six-membered transition states are common for decompositions of similar systems, *e.g.* *l*; R = aryl or alkyl; X = CO,[12] CH_2,[13] and O,[14] and *m*,[18] but again, competing rearrangements of lesser importance, particularly those which utilise five-centre states, may be observed.[12,13] In general, negative ions derived from *o*-nitrophenyl-carbonyl systems will often undergo rearrangements through *suitable* six-membered transition states. A system which cannot attain such a state may also suffer rearrangement, *e.g.* the five-centre state *n* (where X = alkyl,[12] COR,[12] and OR [14]). Transition states in excess of seven have not been observed for skeletal-rearrangement reactions of negative ions in the gas phase.

EXPERIMENTAL

All spectra were measured at 70 eV, and a source pressure of 2×10^{-6} Torr, with an Hitachi–Perkin-Elmer RMU 7D mass spectrometer, modified as described previously.[11] Compounds were introduced into the ion source through an all-glass inlet system maintained at 150°. Fragmentations were substantiated by metastable focusing and the negative i.k.e. technique.[11] A description of equipment necessary for the measurement of kinetic energy release will be published elsewhere.[19]

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Light petroleum refers to the fraction of b.p. 40—60°.

The following compounds were prepared by reported procedures: (1),[20] (4),[21] (5),[22] (6),[21] (7),[23] (10),[24] (11),[25] (12),[26] and (13).[27]

5-(2-*Nitrophenyl*)-1-(4-*tolyl*)*pent*-2,4-*dien*-1-*one* (14).—To a mixture of *o*-nitrocinnamaldehyde (0.8 g) and *p*-methylacetophenone (0.8 g) in ethanol (25 cm^3) was added aqueous sodium hydroxide (10%) dropwise until the colour changed from yellow to dark brown. The mixture was then left at 20° for 8 h and the *product* (14) (0.7 g) was filtered off and crystallised from ethanol as yellow needles, m.p. 118—119° (60%) (Found: C, 73.9; H, 5.3; N, 4.4. $C_{18}H_{15}NO_3$ requires C, 73.7; H, 5.2; N, 4.8%).

8-(2-*Nitrophenyl*)*octa*-3,5,7-*trien*-2-*one* (15).—This was prepared from 5-(2-nitrophenyl)penta-2,4-dienal (11) and acetone by the method outlined above for (14). The *product* was crystallised from ethanol as yellow needles, m.p. 112—113° (70%) (Found: C, 69.0; H, 5.5; N, 5.5. $C_{14}H_{13}NO_3$ requires C, 69.1; H, 5.4; N, 5.8%).

2-(2-*Benzoylvinyl*)*benzoic Acid* (19).—A solution of (benzoylmethyl)triphenylphosphorane [28] (1.2 g) and *o*-phthalaldehydic acid (0.5 g) in dry benzene (50 cm^3), under nitrogen, was heated under reflux for 24 h. Removal of the solvent, followed by extraction of the residue with diethyl ether (2×50 cm^3), and removal of the ether solvent, gave the crude product, which was purified over Sorbsil using diethyl ether–light petroleum (1 : 4) as eluant. *Compound* (19) was crystallised from this solvent as needles, m.p. 140—141° (0.50 g, 61%) (Found: C, 76.6; H, 4.8. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%).

Labelled Compounds.—(A) ^{18}O-*Labelled Compounds*. (i) *o*-Nitro[^{18}O]cinnamaldehyde (16).—A solution of *o*-nitrocinnamaldehyde (50 mg) in dry dioxan (2 cm^3) containing $H_2{}^{18}O$ (^{18}O = 24.2%; 25 mg) and trifluoroacetic acid (1 drop) was stirred at 25° for 48 h. Removal of the solvent *in vacuo* yielded (16) (50 mg; ^{18}O = 12.0%) which was crystallised from ethanol as yellow needles, m.p. 126—127°.

(ii) 3-(*o*-Nitrophenyl)-1-phenylprop-2-en[^{18}O]one (17). Treatment of *o*-nitrocinnamoyl chloride (200 mg) with $H_2{}^{18}O$ (50 mg; ^{18}O = 24.2%) in dry dimethoxyethane (5 cm^3) gave the labelled *o*-nitrocinnamic acid (180 mg), which was reconverted to the labelled acid chloride (190 mg; ^{18}O = 12.1%) using oxalyl chloride. A Friedel–Crafts reaction [23] between the acid chloride and benzene yielded (17) (175 mg, 75%; ^{18}O = 12.1%) which was crystallised from ethanol as yellow needles, m.p. 124—125°.

(iii) 5-(2-Nitrophenyl)-1-phenylpenta-2,4-dien-1-[^{18}O]one (18). This was prepared by the method used for (17), from β-[2-nitrostyryl]acrylic acid, in 75% overall yield. Compound (18) was crystallised from ethanol as yellow needles, m.p. 140—141° (^{18}O = 12.2%).

(B) ^2H-*Labelled Compounds*. (i) 3-(2-Nitrophenyl)[3-^2H]prop-2-enal (2). [α-^2H]Benzaldehyde [29] (0.65 g; $^2H_1$ = 100%) and (formylmethyl)triphenylphosphorane [30] (2.0 g) in dry benzene (50 cm^3) were heated under reflux for 24 h. Removal of the solvent, followed by extraction of the residue with diethyl ether (2×10 cm^3) gave the labelled cinnamaldehyde (0.7 g, 53%), which was nitrated [20] to

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yield (2) (0.4 g, 45%), which was crystallised from ethanol as yellow needles, m.p. 126—127° ($^2H_1$ = 100%).

(ii) 3-(2-Nitrophenyl)[1-^{2}H]prop-2-enal (3). [α-^{2}H]-Cinnamaldehyde was prepared from the dithian by the same method [29] as that used for [α-^{2}H]benzaldehyde. Nitration [20] gave (3) (40%), which was crystallised from ethanol as yellow needles, m.p. 126—127° ($^2H_1$ = 100%).

(iii) 3-(2-Nitrophenyl)-1-phenyl[3-^{2}H]prop-2-en-1-one (8). [α-^{2}H]Benzaldehyde was converted [31] to the labelled cinnamic acid, which was nitrated by the same method [20] used for cinnamaldehyde, to yield the labelled *o*-nitrocinnamic acid in 72% yield. A Friedel–Crafts reaction [23] between the acid chloride and benzene yielded (8) (75%), which was crystallised from ethanol as pale yellow needles, m.p. 123—124° ($^2H_1$ = 100%).

(iv) 3-(2-Nitrophenyl)-1-phenyl[2-^{2}H]prop-2-en-1-one (9). Reaction [32] between [$^2H_3$]methyl phenyl ketone [33] and *o*-nitrobenzaldehyde gave (9) in 80% yield, which was crystallised from ethanol as pale yellow needles, m.p. 124—125° ($^2H_1$ = 68%).

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