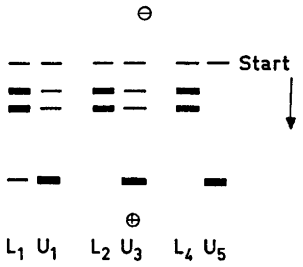

Fig. 4. The electrophoretic pattern of acid phosphatase after polyacrylamide gel electrophoresis. Samples were taken from the phase systems of Fig. 3. L and U correspond to lower and upper phase of the phase systems, respectively. The indices refer to the phase systems of Fig. 3.

nent in phase system 4. The results obtained by electrophoresis shown in Fig. 4, agree with the CCD pattern shown in Fig. 2.

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Substituent Dependent Mass Spectrometric Fragmentation of Monosubstituted Phenyl Propargyl Ethers

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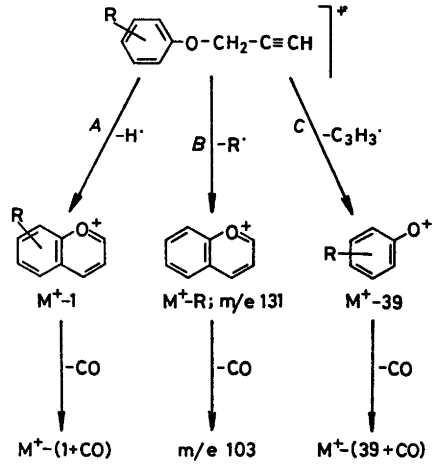
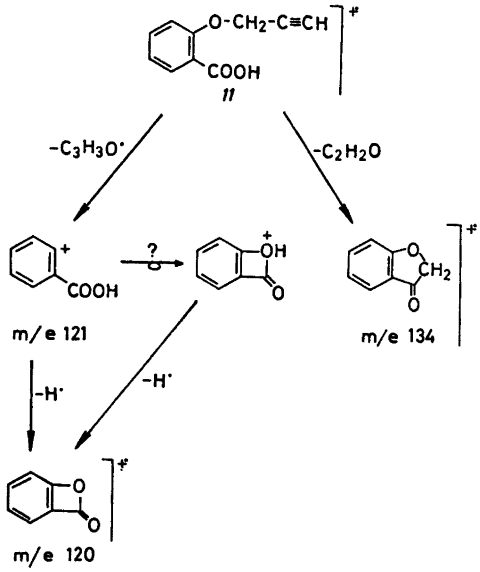
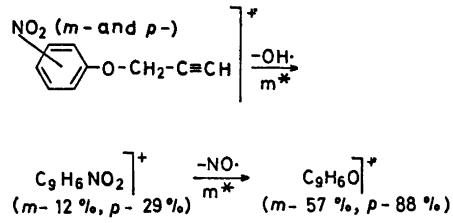
N-Propargylaniline moieties generated by electron impact fragmentation from several different types of molecular ions undergo an intramolecular cyclization to the corresponding quinoline ion.[1] It is reasonable to assume that phenyl propargyl ethers may rearrange in a similar manner giving rise to stable chromanonium ions (*cf.* Scheme 1, routes *A* and *B*). However, from a structural point of view, it is evident that this type of compounds should also be able to decompose by an ether cleavage at an activated benzylic or propargylic[2] site (route *C* in Scheme 1). We have studied a series of monosubstituted phenyl propargyl ethers (compounds *1–15*) and found that their fragmentation patterns follow the proposed routes as outlined in Scheme 1. The relative abundance of the peaks associated with these fragmentations are collected in Table 1. The spectra of compounds *11* and *13* exhibit prominent peaks corresponding to ions formed by fission of the aryl-oxygen bond, a behaviour that may be explained on the basis of an *ortho* effect,[3] which process is exemplified in Scheme 2. Compound *11* also fragments by an unusual route involving a



Scheme 1.



Scheme 2.



Scheme 3.

complex rearrangement with expulsion of a C_2H_2O fragment (*cf.* Scheme 2). The *m*- and *p*-isomers of the nitro derivatives (compounds *14* and *15*) behave in an unexpected manner with consecutive loss of OH and NO as outlined in Scheme 3. This fragmentation is consistent with the metastable peaks found in the mass spectra of *14* and *15* and with the results of high resolution measurements on crucial fragments. No analogous reactions seem to have been reported in the literature.[4] It is evident from the data in Table 1 that the dominating mode of fragmentation for the phenyl propargyl ethers is governed by the electronic properties of the substituent. The unsubstituted derivative *1* as well as those with a strongly electron attracting group (compounds *11*–*15*) completely lack fragments arising from fission at the propargylic bond (route *C* in Scheme 1) whereas this cleavage dominates the fragmentation pattern of the compounds having an electron donating group in *ortho* or *para* position (compounds *2*, *4*, *5*, *7*). Thus there is also a considerable difference in the mass spectrometrical behaviour between position isomers, since the corresponding *meta* isomers (compounds *3* and *6*) break down mainly by routes *A* and *B*.

Table 1. Mass spectra of compounds *1*–*15*. Relative abundance of selected peaks.

Compound No.	R	M+	M+−1	M+−(1+CO)	M+−39	M+−(39+CO)	M+−R	M+−(R+CO)	M+−C_3H_3O
1	H	52	100	48	—	—	—	—	20
2	*o*-CH_3	48	45	43	93	45	50	12	24
3	*m*-CH_3	50	78	50	19	48	100	20	50
4	*p*-CH_3	56	45	33[a]	100	67	50	12	15
5	*o*-CH_3O	54	4	—	100	65	3	—	—
6	*m*-CH_3O	72	100	5	—	18	19	8	—
7	*p*-CH_3O	50	6	—	100	13	—	—	—
8	*o*-Cl	88	78	18	13	76	100	63	—
9	*m*-Cl	16	25	—	—	16	100	31	3
10	*p*-Cl	71	16	16	67	80	100	53	6
11[b]	*o*-COOH	11	11	22	—	—	65[a]	29[a]	84
12	*p*-COOH	25	16	7	—	4	100	25	4
13[c]	*o*-NO_2	24	5	4	—	—	26	14	98
14[d]	*m*-NO_2	14	4	6	—	—	30	27	—
15[e]	*p*-NO_2	29	29	13	—	—	79	50	4

[a] Fragment examined by high resolution measurement. [b] *m/e* 120 100 %, *m/e* 134 74 %. [c] *m/e* 63 100 %, *m/e* 122 98 %. [d] *m/e* 64 100 %, *m/e* 63 90 %. [e] *m/e* 63 100 %, *m/e* 77 94 %.

Substituent dependent fragmentation is a well-known phenomenon and different explanations involving both qualitative and quantitative aspects have been presented.[4] It seems adequate to explain our results on the basis of the charge localization theory,[5] since this is a widely accepted concept in the interpretation of organic mass spectral data. The phenyl propargyl ethers contain two principal centra where the charge may be localized. Electron withdrawing groups facilitate the localization on the aromatic ring, favouring loss of the substituent and formation of the stable *m/e* 131 ion.[6] On the other hand, electron donating groups in *ortho* and *para* positions favour the ether oxygen as a site of the charge, which triggers the ether cleavage.

Experimental. General. Mass spectra were recorded on an AEI MS 30 mass spectrometer at 70 eV. The temperature of the ion source was kept at 250 °C. High resolution measurements on crucial fragments were performed at the laboratory of Dr. R. Ryhage, Karolinska Institutet, Stockholm, using an Atlas SM 1 instrument. Stable isotope studies with deuterium labelling of the acetylenic hydrogen[3] are in agreement with the data presented. PMR and IR spectra were routinely recorded and found to be in accordance with the proposed structures. Melting points were determined in open capillary glass tubes in an electrically heated metal block and are uncorrected. Elemental analyses were performed at the laboratories of Dr. A. Bernhardt, Mülheim, West Germany.

Syntheses. Compounds *1*, *5–10*, *13–15*,[7] *3*,[8] *4*,[9] and *12*[10] were all prepared as described in the literature cited.

o-*Tolyl propargyl ether.* This substance (compound *2*) was prepared from *o*-cresol, 10.8 g (0.10 mol), propargyl bromide, 11.9 g (0.10 mol), and anhydrous K_2CO_3, 16.6 g (0.12 mol) in refluxing acetone (40 ml) according to a general method.[7] The product was purified by distillation *in vacuo*, b.p. 52–53 °C (0.4 mmHg). Yield 10.2 g (69 %), n_D^{25} 1.5330. (Calc. for $C_{10}H_{10}O$: C 82.16; H 6.90. Found: C 82.23; H 7.01).

Methyl o-*propargyloxybenzoate.* Methyl salicylate, 15.2 g (0.10 mol), dissolved in 50 ml of dry methanol was added to 100 ml of a 1 M sodium methoxide solution followed by propargyl bromide, 11.9 g (0.10 mol) in one portion. The mixture was refluxed for 10 h and then cooled in an ice-bath. To the reaction mixture was added 1 M HCl to make it faintly acidic whereupon the solvent was evaporated. The residue was taken up in 200 ml of ether, and the ethereal solution was washed consecutively with 3 × 50 ml of 1 M NaOH, 100 ml of 0.5 M H_2SO_4, and 100 ml of water. The crude product obtained after removal of solvent from the dried ($MgSO_4$) ether solution was fractionated *in vacuo*, b.p. 109–110 °C (1 mmHg). Yield 10.0 g (52 %), n_D^{25} 1.5440. (Calc. for $C_{11}H_{10}O_3$: C 69.47; H 5.30. Found: C 69.29; H 5.33).

o-*Propargyloxybenzoic acid.* (Compound *11*). Methyl *o*-propargyloxybenzoate, 4.8 g (0.025 mol), was warmed with 40 ml of 1 M NaOH at 70 °C for 1 h. The reaction mixture was cooled in an ice-bath and then acidified. The yellowish crystalline precipitate was filtered off, and refluxed with decolourizing charcoal in 25 ml of 50 % ethanol. After two recrystallizations from 50 % ethanol, 3.6 g (82 %) of product, m.p. 88–89 °C, was obtained. (Calc. for $C_{10}H_8O_3$: C 68.18; H 4.58. Found: C 68.29; H 4.64).

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