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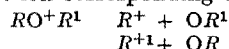
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Electron Impact and Molecular Dissociation Part IV

Considerable interest has been attached to the behaviour of ether compounds under electron bombardment and a comprehensive survey of the probable modes of fission of alkyl ethers¹ as well as analysis of specific re-arrangements have already been made². More recently BEYNON³ *et al.*, in the course of a wider survey, have observed the ready elimination of carbon monoxide from diphenyl ether. Little attention has, however, been paid to the possibility of identifying wholly aromatic ethers by their 'cracking-patterns' and this communication is intended to do this.

The aromatic ethers described here include compounds of the type diphenylether, naphthylphenylether, dinaphthylether, and 9-9¹ diphenanthrylether; the full list being included in the Table appended.

These aromatic compounds, in common with the other purely aromatic substances so far investigated, have the parent molecular ions as the most prominent in the spectrum. This is of considerable importance in determining the exact molecular weight of the compound. As already mentioned, there is a substantial fragment ion corresponding to the loss of carbon monoxide. This, in common with the oxygen compounds reported by BEYNON, requires that the elimination shall occur in such a way that the residue, the fragment ion, remains as a unit. Three other classes of aromatic compounds show a similar loss of carbon monoxide, the phenols, quinones, and ketones. The quinones are rather easily detected since the loss of carbon monoxide can and does occur twice over. Thus, for this series, there are abundant ions corresponding to the molecular weight, and the molecular weight less twenty-eight and fifty-six units respectively. The phenols are less easily differentiated from the ethers of corresponding molecular weight as each may eliminate only one carbon monoxide molecule and accordingly there is a parent molecular ion (P) and an abundant P-28 fragment ion. However, an aromatic ether has necessarily two aryl groups unlike a phenol. Accordingly the 'cracking pattern' of an ether will contain a fragment ion corresponding to one or other of the fissions



or the corresponding fissions with the charge on the other moiety.

Fortunately, with reservations to be detailed below, the production of aryl ions by such fissions is a rather probable process and ether spectra contain prominent fragment ions so derived.

In addition to the fragment ions so far mentioned, there are smaller but still significant ions representing the loss of one or two hydrogen atoms from the parent molecular ion. Such behaviour has previously been noticed in the electron-induced dissociations of aromatic hydrocarbons⁴ and have been used as part of the basis for distinguishing among various possible isomers in this series.

Whilst the determination of molecular weight and group thus seems a fairly simple process, the identification of the various possible isomeric aryl radical in the original

ether seems to be a problem of greater difficulty. So far, in the series presently reported, there seems little possibility of confusion amongst the various members. Even this series does, however, allow certain generalisation to be made.

(1) The probability of the loss of carbon monoxide and the appearance of the hydrocarbon residue as a single ion diminishes with the increasing molecular weight of the ether and the increasing complexity of the aryl group.

(2) The fission of the ether ion occurs in the way already described with the production of aryl ions in significant abundance, but with little formation of the corresponding aryloxy ion. In unsymmetrical compounds, this fission greatly favours the formation of the ion of the larger aryl radical as is shown in the fissions of the unsymmetrical phenyl ethers.

(3) In the unsymmetrical ethers two series are available, the three possible naphthyl ethers and *o*- and *p*-phenoxybiphenyl. In each case, the experimental evidence shows that distinctions amongst these series of isomers may be obtained by a consideration of the fragment ion P-1. The magnitude of this expressed as a percentage of the abundance of the parent molecular ion diminishes in the order $\beta:\beta^1$ dinaphthyl > $\alpha:\beta$ dinaphthyl > $\alpha:\alpha^1$ dinaphthyl and the corresponding function indicates that the order is *p*-phenoxy > *o*-phenoxy in the biphenyl series.

Experimental. The spectra were obtained in the usual way on a Metropolitan-Vickers Ltd. M. S. 2 Mass-Spectrometer employing a repeller potential of 2 K volts and magnetic scanning.

The appropriate ethers were obtained by the following methods. Diphenyl ether was reagent grade, purified by crystallisation. α -naphthyl phenyl, β -naphthyl phenyl, $\alpha:\alpha$ -dinaphthyl, $\alpha:\beta^1$ -dinaphthyl⁵, $\beta:\beta^1$ -dinaphthyl⁶, 9-phenanthryl phenyl⁷ and di-9-phenanthryl⁸ ethers were prepared by known methods. The phenoxybiphenyls were prepared by an adaptation of a known method⁹.

p-Phenoxybiphenyl. To a solution of 4.5 g sodium methoxide in 90 ml methanol was added 14.2 g *p*-hydroxybiphenyl and 6.0 g diphenyliodonium bromide¹⁰. After the mixture had been refluxed for 24 h, the ether soluble product was collected and distilled under reduced pressure. The solid distillate, recrystallised from benzene gave 1.37 g (48%) *p*-phenoxybiphenyl, m.pt. 136°C.

¹ F. W. McLafferty, *Anal. Chem.* **29**, 99 (1957).

² F. W. McLafferty, *Anal. Chem.* **31**, 2072 (1959).

³ J. H. BEYNON, G. R. LESTER, and A. E. WILLIAMS, *J. phys. Chem.* **63**, 1861 (1960).

⁴ R. I. REED, Third Int. Conf. on Coal Science, Falkenberg, April (1959).

⁵ F. ULLMAN and P. SPONAGEL, *Liebigs Ann.* **350**, 90 (1906).

⁶ M. E. BERGER, *C. R. Acad. Sci., Paris* **141**, 1027 (1905).

⁷ R. L. HUANG, *J. chem. Soc.* **1955**, 3295.

⁸ F. R. JAPP and A. FINDLAY, *J. chem. Soc.* **71**, 1115 (1897).

⁹ F. M. BERINGER, A. BRIERLEY, M. DREXLER, E. M. GINDLER, and C. C. LUMPKIN, *J. Amer. chem. Soc.* **75**, 2708 (1953).

¹⁰ F. M. BERINGER, M. DREXLER, E. M. GRINDLER, and C. C. LUMPKIN, *J. Amer. chem. Soc.* **75**, 2705 (1953).

M/e	$R \cdot O \cdot R^1$									
	9-Phenanthryl 9-Phenanthryl	9-Ph Phenyl	β -Naphthyl β -Naphthyl	β -Naphthyl α -Naphthyl	α -Naphthyl α -Naphthyl	4-biphenyl Phenyl	2-biphenyl Phenyl	β -Naphthyl Phenyl	α -Naphthyl Phenyl	Phenyl R Phenyl R ¹
370	<u>100</u>	—	—	—	—	—	—	—	—	—
369	55.1	—	—	—	—	—	—	—	—	—
368	13.7	—	—	—	—	—	—	—	—	—
342	<u>78.8</u>	—	—	—	—	—	—	—	—	—
341	16.5	—	—	—	—	—	—	—	—	—
270	—	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	—	—	—	—	—
269	—	—	80.5	77.0	69.4	—	—	—	—	—
268	—	—	24.6	16.9	25.3	—	—	—	—	—
246	—	—	—	—	—	<u>100</u>	<u>100</u>	—	—	—
245	—	—	—	—	—	64.5	50.3	—	—	—
244	—	—	—	—	—	16.6	30.7	—	—	—
242	—	<u>12.9</u>	<u>25.2</u>	<u>28.8</u>	<u>18.6</u>	—	—	—	—	—
241	—	20.6	22.3	17.8	15.7	—	—	—	—	—
220	—	—	—	—	—	—	—	<u>100</u>	<u>100</u>	—
219	—	—	—	—	—	—	—	61.1	62.5	—
218	—	—	—	—	—	<u>10.1</u>	7.8	22.3	20.3	—
217	—	—	—	—	—	5.3	8.0	—	—	—
192	—	—	—	—	—	—	—	<u>23.0</u>	<u>10.3</u>	—
191	—	—	—	—	—	—	—	30.7	19.5	—
177	8.3	63.8	—	—	—	—	—	—	—	—
170	—	—	—	—	—	—	—	—	—	100
169	—	—	—	—	—	—	—	—	—	73.8
168	—	—	—	—	—	—	—	—	—	37.0
165	18.3	35.1	—	—	—	—	—	—	—	—
153	—	—	—	—	—	43.8	38.4 ^a	—	—	—
151	—	—	—	—	—	—	—	—	—	—
142	—	—	—	—	—	—	—	—	—	39.3
141	—	—	—	—	—	44.4	10.9	—	—	60.7
140	—	—	—	—	—	—	—	—	—	15.5
127	—	—	39.6 ^a	38.4 ^a	28.4 ^a	—	—	15.3 ^a	11.7 ^a	—
126	—	—	—	19.2	14.8	—	—	—	—	—
117	—	—	—	—	—	—	—	—	—	7.0 ^b
115	—	—	—	—	—	12.6	9.5	—	—	17.1
94	—	—	—	—	—	—	—	—	—	6.8
89	—	—	—	—	—	—	—	—	—	6.0
88	—	—	—	—	—	—	—	—	—	—
78	—	—	—	—	—	—	—	—	—	—
77	—	—	—	—	—	9.4	10.2 ^a	—	—	72.7 ^a
76	—	—	—	—	—	—	—	—	—	—
65	—	—	—	—	—	—	—	—	—	14.5
63	—	—	—	—	—	—	—	—	—	8.5
51	—	—	—	—	—	—	—	—	—	75.2
50	—	—	—	—	—	—	—	—	—	16.2
39	—	—	—	—	—	—	—	—	—	33.3

Masses underlined 100 represent the abundance of the parent molecular ion. Underlined 25.2 the abundance of the parent minus 28 (P-28) ion. ^a This represents the abundance of one or other of the possible aryl ions from the ether. ^b Represents a metastable ion.

o-Phenoxybiphenyl. The same method was used, but light petroleum b. pt. 60°–80°C was used to recrystallise the ether. This gave 0.91 g *o*-phenoxybiphenyl (35%) m.pt. 37°C.

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J. M. WILSON

Chemistry Department, The University, Glasgow, February 15, 1960.

Zusammenfassung

Es wird über die ionischen Hauptbruchstücke in den Massenspektren von zehn Diaryläthern berichtet. Die Intensitäten können zur Identifizierung dieser Verbindungen dienen.

The Structure of Cassamine and Erythrophlamine¹

The crystalline alkaloids cassamine (C₂₅H₃₉O₅N) and erythrophlamine (C₂₅H₃₉O₆N), isolated² from *Erythrophleum guineense* G. Don, are known³ to be β -dimethylamino-ethanol esters of two unsaturated acids named respectively cassamic acid (C₂₁H₃₀O₅) and erythrophlamic acid (C₂₁H₃₀O₆). Cassamic acid contains one double bond $\alpha\beta$ to the carboxyl group, one keto and one methoxyl group. Erythrophlamic acid, in addition to the same functional groups, also carries a hydroxyl group. In both acids the nature of one oxygen atom, the carbon skeleton and the position of the functional groups remained to be determined⁴.

¹ 16th Communication on Erythrophleum Alkaloids. 15th Comm.: B. G. ENGEL, *Helv. chim. Acta* **42**, 1127 (1959).

² B. G. ENGEL and R. TONDEUR, *Exper.* **4**, 430 (1948); *Helv. chim. Acta* **32**, 2364 (1949).

³ B. G. ENGEL, R. TONDEUR, and L. RUZICKA, *Rec. Trav. chim. Pays-Bas* **69**, 396 (1950).

⁴ The numbering used is that common to steroids and triterpenes.