OMS Letters

Dear Sir

Mass Spectral Studies, of 7,9-di-*tert*-butyl-1-oxaspiro[4.5] deca-6,9-diene-2,8-dione

I wish to report here the electron impact (EI) mass spectrum of 7,9-di-*tert*-butyl-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione (Fig. 1). This compound forms in the injection port of a gas chromatograph from the 3-(3,5-di-*tert*-butyl-1-hydroxy-4-oxo-2,5-cyclohexadien-1-yl)propionic acid, (1).



I first detected this compound in a river water downstream from a chemical plant¹ and tentatively identified it as 2,6-di*tert*-butyl-parabenzoquinone methide-acetic acid (3) or 2,6-di*tert*-butyl-4-hydroxycinnamic acid (4). The molecular formula of compound 3 ($C_{17}H_{24}O_3$) was correct since it was determined by high resolution mass spectrometry.



I have synthesized 3 and found out upon its analysis by gas chromatography/mass spectrometry that 3 is thermally unstable and it degrades in the injection port of the gas chromatograph to the corresponding styrene (5). The mass spectrum of 3 obtained by direct probe mass spectrometry exhibited a strong molecular ion $(m/z \ 276)$ and did not match at all the mass spectrum of my unknown compound. Thus, I concluded that my unknown could not be 3.



The structure for 4 seems to be more likely and it is in agreement with some other experimental data which I have reported previously.² However, if the compound with molecular formula $C_{17}H_{24}O_3$ is indeed an acid, I would have expected a similar chromatographic behaviour with 3 and the 3(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid (5).

Recently, I have obtained both 1 and 2 and found that the mass spectrum of my unknown matched perfectly the mass spectrum of 2, which is given in Fig. 1.

The fragmentation pathway of 2 by EI is shown in Scheme 1. The structures assigned to the various fragment ions were derived from the high resolution mass spectrometric data which are given in Table 1. The base peak in the mass spectrum shown in Fig. 1 is the tertiary carbonium ion at m/z 57 which indicates that substituted γ -lactones of this type tend to cleave at the phenyl ring. The next most intense peak is the ion at m/z 205 which forms from the ion m/z 261 by elimination of C₄H₈. Abundant ions associated with loss of CO₂ were observed at m/z 232. Once the lactone ring is opened, the fragment ion at m/z 232 will either lose a methyl radical from one of the *tert*-butyl groups to give the ion at m/z 217 or



Figure 1. Electron impact mass spectrum of compound 2.

Received 22 April 1987 Accepted 11 May 1987



Scheme 1. Electron impact fragmentation pathway for compound 2.

ethylene from the original lactone chain to give the fragment at m/z 175. The fragment ion at m/z 177 forms from the ion at m/z 205 by loss of CO, and the fragment ion at m/z 189 forms from the ion at m/z 217 by elimination of ethylene.

The EI mass spectrum was obtained on a Finnigan 4510B GC/MS system interfaced with a Nova 4X computer. The column was a 30 m×0.25 mm i.d. fused silica capillary column (DB-5, J and W Scientific, Folsom, California) programmed from 40 °C (initial hold 4 min) to 300 °C at 8 °C min⁻¹. Injector temperature was 250 °C. The mass spectrometer was operated in the electron impact mode at a nominal of 70 eV with the ionizer temperature set at 190 °C. The mass spectrometer was scanned from 45 to 350 at a rate of 1 s per decade. High resolution (20 000) mass spectrometer with photographic plate detection. The photographic plates were read on an automatic densitometer operated on line to an IBM 1800 computer.

Acknowledgement. I would like to thank Michael McMillan of the University of California, Berkeley, California for providing compounds 1 and 2.

Yours

VIORICA LOPEZ-AVILA, Acurex Corporation, Environmental Systems Division, 485 Clyde Avenue, P.O. Box 7044, Mountain View, California 94039, U.S.A.

References

- V. Lopez-Avila, 'Organic Compounds in an Industrial Waste Water: A Case Study of their Environmental Impact,' Ph.D. Thesis, Massachusetts Institute of Technology (1979).
- V. Lopez-Avila and R. A. Hites, *Environmental Sci. Technol.* 15, 1386 (1981).