On the Stability, Detection, and Isolation of 9-Anthrone. Reply to the Communication by Stuart, Majeski, and Ohnesorge

By LENNART EBERSON* and VERNON D. PARKER

(*Division of Organic Chemistry, Chemical Center, University of Lund, Lund, Sweden*)

Summary Dimerisation of 9-anthrone was observed under g.l.c. analysis conditions while no reaction was detected during attempted air-oxidation.

THE report from this laboratory[1] concluding that 9-anthrone is not the initial product of anodic oxidation of anthracene in acetonitrile containing ethanol has been questioned.[2] It was claimed that 9-anthrone was detected in large quantities during the anodic oxidation of anthracene by g.l.c. analysis and that it is converted into another compound when a solution of it in acetonitrile is exposed to air.

Without going into detail about data that will soon be published,[3] it will suffice to say that over fifty coulometric experiments under various conditions of water concentration and differing supporting electrolytes, verify the results given in the preliminary communication.[1] In this, an experiment was described in which oxygen was bubbled through a solution of 9-anthrone in acetonitrile for 30 min. from which the compound was recovered unchanged.[1] However, Stuart, Majeski, and Ohnesorge[2] claim that exposing a solution of 9-anthrone in acetonitrile to air for 4 hr. converts it into another, unspecified, compound. This conclusion was based on the disappearance of the fluorescence spectrum. Our attempts to repeat this observation have been entirely unsuccessful. The fluorescence of a 1 mM-solution of 9-anthrone in acetonitrile was measured before and after air had been bubbled through the solution for 5 hr. and the solution allowed to stand for an additional 15 hr. exposed to air; no significant change was observed. Removal of the solvent showed that the aerated sample was identical to the original one (i.r.,† n.m.r., m.p.).

Using the same g.l.c. conditions as those previously reported[4] but with the column outlet coupled with a mass spectrometer, we find that 9-anthrone is transformed to a mixture of 9,9′-bianthryl (3·5%) and bianthronylidene (96·5%) during chromatographic analysis with an injection temperature of 350° (see Table), the amount of material

G.l.c. data for 9-anthrone and related compounds

Compound		Column temp.	Retention time,[a] (min.)
9-Anthrone	.. ..	235°	19·5 and 33·0
Bianthrone	.. ..	235°	33·0
9,9′-Bianthryl	.. ..	235°	19·5
Bianthronylidene	..	235°	33·2
Anthraquinone	.. ..	235°	0·75[b]
Anthraquinone	.. ..	200°	2·0[b]
Anthracene	.. ..	235°	0·5
Anthracene	.. ..	160°	4·0

[a] 5% SE-30 column, 2 m by ⅛ in., injection temp. 350°.

[b] At 310°, where g.l.c. analysis of anthraquinone was previously conducted,[2] anthraquinone was eluted in the solvent (tetrahydrofuran) peak.

---

† By i.r. spectral analysis of standard mixtures of 9-anthrone and bianthrone, the limit of detection of bianthrone in 9-anthrone was found to be less than 1%.

passing through the column corresponding to about 40% of the anthrone injected. The relative and total amounts of the two eluted products were found to be dependent on the column and injection port temperatures. Under the same conditions as used for 9-anthrone, bianthrone was converted almost quantitatively into bianthronylidene. Thus, g.l.c. analysis is not suitable for the detection of 9-anthrone in electrolysis mixtures unless conditions can be found which allow it to pass through the chromatograph unchanged.

The results presented here and before[1] clearly show that 9-anthrone is sufficiently stable to be isolated without difficulty from electrolysis mixtures. We conclude that any 9-anthrone formed during the anodic oxidation of anthracene would survive the work-up conditions and would be readily detectable (by i.r. analysis) if present to the extent of 1% or greater of the total product mixture.

(*Received, May* 18*th*, 1970; *Com.* 759.)

[1] V. D. Parker, *Chem. Comm.*, 1969, 1131.

[2] E. J. Majeski, J. D. Stuart, and W. E. Ohnesorge, *Chem. Comm.*, 1970, 353.

[3] V. D. Parker, *Acta Chem. Scand.*, 1970, **27**, in the press.

[4] E. J. Majeski, J. D. Stuart, and W. E. Ohnesorge, *J. Amer. Chem. Soc.*, 1968, **90**, 633.