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MONSANTO CHEMICALS LIMITED

TO DR. W.E. KOERNER. DATE 11/5/62 REF. jch/sfd:

FROM J.C. Hawkes. AT Ruabon SUBJECT QUATERPHENYL ANALYIS

cc: Dr. J.W. Barrett.
Dr. R.A. Baxter.
Mr. H.L. Hubbard.
Dr. C.E. Anagnostopoulos.

I delayed replying to your memo of April 16th, as further work on the gas chromatographic analysis of isomeric quaterphenyls was in progress. I now have photostat copies of suitable chromatograms, and these are enclosed.

Owing to the current non-availability of 1,2,3-triphenyl benzene and 1,2,4-triphenyl benzene, we do not know whether complete resolution of isomeric quaterphenyls can be achieved. From chromatograms obtained to date, however, it would appear that there is a reasonable probability of complete resolution, particularly if programmed temperature operation is used.

At the start of this work, o,o- and p,p-quaterphenyl were the only two reference compounds available. These, however, were the most and least sterically hindered molecules of the series, and it was presumed that they would represent the limits between which other isomers would be eluted from a chromatographic column. Peaks in the gas chromatograms of reaction mixtures, appearing between these limits, were assigned according to their apparent steric hindrance (by using molecular models). In order to obtain more definite information of the order of elution, without resorting to prolonged synthetic methods, the three isomeric terphenyls were phenylated by free radical substitution, using benzene sulphonyl chloride. The quaterphenyl composition of the products was then assumed to depend upon the original terphenyl, and by examination of the three chromatograms and a process of elimination, some confirmation of the initial peak assignments was made. Four of the isomers have since been obtained in pure form, and has further confirmed the chromatogram peak assignments. The order of elution is now as follows:-

1. o,o-quaterphenyl
2. o,m-quaterphenyl
3. o,p-quaterphenyl
4. 1,3,5-triphenyl benzene

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5. m,m-quaterphenyl
6. m,p-quaterphenyl (this is yet to be confirmed by elution of the pure material)
7. p,p-quaterphenyl

On steric grounds, we would expect 1,2,3-triphenyl benzene to be eluted shortly after o,o-quaterphenyl and considerably before o,m-quaterphenyl. We would also expect 1,2,4-triphenyl benzene to be eluted between o,m- and o,p-quaterphenyl, or shortly after o,p-quaterphenyl.

The chromatograph which we constructed for this work is equipped with a Pye micro-ionisation detector and high temperature injection system. As the maximum operating temperature of the detector is 225°C., it was decided to use small bore (3/32") columns containing packings of low stationary phase content. Packings using Silicon Oil (MS 200) showed little solubility for quaterphenyls, and provided the columns were of high plate number, reasonable resolution was obtained with chromatograms of short duration (not greater than 30 mins.). Asphalt used at concentrations of 1-2% by weight of packing gave good selectivity for quaterphenyls, but also resulted in long retention times with shallow peaks. Reduction of stationary phase concentration to below 1% gave no improvement on account of the increasing part played by the column support (Chromosorb or Embacel). The selectivity of Asphalt looked promising enough to make further examination worthwhile, and glass bead packings were used in order to reduce the effect of column support. Fairly good resolution of quaterphenyls was obtained, as is illustrated in the attached chromatograms. Asphalt has also been used to coat capillary columns of 20-30' length with promising results, and this work is being continued both for quaterphenyl analysis and for other high boiling aromatic mixtures. It has been found, however, that an Asphalt coated capillary column should not be allowed to cool, as subsequent melting of Asphalt following crystallisation in the column results in breakdown of the film to droplets.

If we make any striking advances in the use of these columns, I will let you know.

Kind regards.

J.C. HAWKES.

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