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THE OXIDATION OF AROMATIC AMINES BY PERACETIC ACID (1)

J.W.Gorrod

Dept. of Pharmacy. Chelsea College of Science
and Technology, (University of London), London, S.W.3.

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The failure of Gutmann(2) to isolate 2-nitrosofluorene and 4-nitrosobiphenyl from the reaction of hydrogen peroxide with 2-aminofluorene and 4-aminobiphenyl dissolved in glacial acetic acid, cast considerable doubt on the general usefulness of this simple technique described by Holmes & Bayer(3). In addition, as this method had previously been used by Uehleke(4,5) to synthesise the above-mentioned nitroso compounds for use as reference compounds in a study of the metabolism of 2-aminofluorene and 4-aminobiphenyl, it appeared that the compounds which he had isolated were of unknown structure and correspondingly the structure of the metabolites which he detected were also suspect.

During the course of some experiments on the site of hydroxylation of aromatic amines(6), it was found that C-nitroso compounds, synthesised by the oxidation of the corresponding hydroxylamines with potassium ferricyanide could be detected as single discrete peaks using gas liquid chromatography.

This method has been used to investigate the formation of nitroso compounds in the reaction procedure described by Holmes & Bayer.

Experimental

Aniline, 1-naphthylamine, 2-naphthylamine, 4-aminobiphenyl and 2-aminofluorene (0.001 mole) were separately dissolved in glacial acetic acid (4 mls) and treated with hydrogen peroxide 30% (0.01 mole). The reactions were allowed to proceed at 20° and at various times aliquots (0.5 ml) were removed, diluted with water (3 mls) and the solution extracted with ether (1 ml).

The ether extract (1μl) was examined on a Perkin-Elmer F11 gas chromatograph equipped with a $\frac{1}{4}$" glass column, two metres in length. The liquid phase was 2.5% Silicone gum rubber E301 supported on AW-DMCS chromosorb G 80-100 mesh. The retention times of the amines and corresponding nitro and nitroso compounds are recorded in the Table.

TABLE 1

Retention Times of Some Aromatic Amines and Corresponding Nitro and Nitroso Compounds

Nitrosobenzene	1 min 15 secs
Aniline	1 min 40 secs
Nitrobenzene	3 min 0 secs
1-nitrosonaphthalene	1 min 30 secs
1-aminonaphthalene	1 min 50 secs
1-nitronaphthalene	2 min 10 secs
2-nitrosonaphthalene	1 min 30 secs
2-aminonaphthalene	1 min 55 secs
2-nitronaphthalene	2 min 25 secs
2-nitrosobiphenyl	1 min 40 secs*
2-aminobiphenyl	2 min 0 secs
2-nitrobiphenyl	2 min 40 secs
4-nitrosobiphenyl	2 min 20 secs
4-aminobiphenyl	3 min 5 secs
4-nitrobiphenyl	4 min 10 secs
2-nitrosofluorene	4 min 50 secs
2-aminofluorene	5 min 50 secs
2-nitrofluorene	8 min 40 secs

The oven temperature was 190° for all experiments except nitrosobenzene, aniline, and nitrobenzene when it was 100°. The nitrogen flow rate was 45 cc/min.

* Compound detected in oxidation of 2-aminobiphenyl and presumed to be 2-nitrosobiphenyl.

Results

The results obtained indicated that in all the cases studied with the exception of 2-naphthylamine a compound was formed which had chromatographic properties identical to the synthetic nitroso compounds.

A comparison of the peak heights of the injected material indicated that the optimum time for the formation of the highest yield of the nitroso compounds varied considerably for each amine studied.

For example, the yields of nitroso benzene from aniline diminished after three hours, whereas 1-naphthylamine required about seven hours, 2-aminofluorene sixteen hours and 4-aminobiphenyl thirty hours to produce the maximum peak heights.

After these times a compound having the same retention times as the corresponding nitro compound was formed and increasing the reaction time only increased the yield of the nitro compound. 2-Aminonaphthalene produced neither 2-nitrosonaphthalene or 2-nitronaphthalene. When 2-aminobiphenyl was oxidised in this system only trace amounts of a substance having a shorter retention time than the parent amine was detected and after three hours 2-nitrobiphenyl was formed in large amounts.

These findings do not in any way invalidate the findings of the previous workers(2,4,5) as the exact reaction conditions, i.e. temperature, time or concentration were not described.

The detection of the nitro compounds is in accord with the findings of Gutmann(2), the azo and azoxy compounds could not be chromatographed using the system described. The detection of 2-nitrosofluorene and 4-nitrosobiphenyl is in agreement with the observation of Uehleke(4,5). It is suggested that the differences observed by these authors can be accounted for by differences in reaction temperature, time and concentrations.

References

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