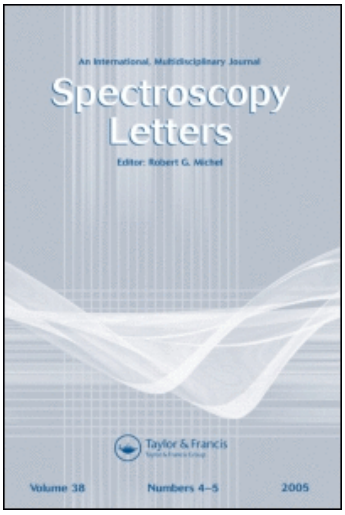

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

GC-MS Study of Gif-Oxidation System. GC-MS Contribution to Elucidation of Gif-Oxidation Mechanism on the Formation of Bipyridines and Coupled Pyridines

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To cite this Article Barton, D. H. R. , Boivin, J. , Schwartzentruber, K. , Ozballk, N. , Gaudin, D. and Jankowski, K.(1987) 'GC-MS Study of Gif-Oxidation System. GC-MS Contribution to Elucidation of Gif-Oxidation Mechanism on the Formation of Bipyridines and Coupled Pyridines', Spectroscopy Letters, 20: 12, 963 — 981
To link to this Article: DOI: 10.1080/00387018708081602
URL: http://dx.doi.org/10.1080/00387018708081602

SPECTROSCOPY LETTERS, 20(12), 963-981 (1987)

GC-MS STUDY OF GIF-OXIDATION SYSTEM.

GC-MS CONTRIBUTION TO ELUCIDATION OF GIF-OXIDATION MECHANISM ON THE FORMATION OF BIPYRIDINES AND COUPLED PYRIDINES

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Abstract

The mechanism for the Gif system of selective oxidation of hydrocarbons has been studied using the GC-MS technique. Several observations reported here concerning bipyridines, pyridine--hydrocarbon coupling products and oxidation products themselves contribute to the elaboration of the proposed mechanism.

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Introduction

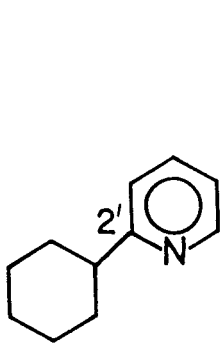
Mechanistic studies of the Gif-oxidation system have been based on extremely diverse spectrometric material (1-4). In these studies the GC-MS has played an important role. The determination of the structure of main oxidation products, as well as the investigation of secondary and reagent originated products, equally important for mechanistic considerations, have been performed using this technique. In this latter area, the study of bi- or higher polymeric pyridines and of pyridine or bipyridine coupled to hydrocarbons and/or their oxidation products, some of them being on the trace concentration level, leads to several interesting observations.

We would like to report here two GC-MS studies of

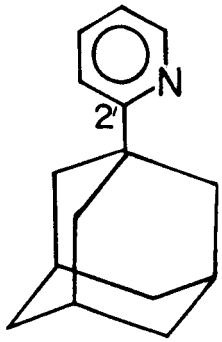
1. bipyridines obtained during the Gif-oxidation, and
2. crossover experiments (protio-deuterio) on hydrocarbon oxidation compounds and the compounds resulting from coupling to pyridine.

Bipyridine Studies

The oxidation of cyclic hydrocarbons with the Gif-oxidation system (1) (iron catalyst, oxygen-zinc, organic acid and solvent) leads to alcohols and ketones. An intriguing selectivity for this oxidation was observed. For example, in the case of adamantane, oxidation on the secondary carbon to give the ketone has been observed together with an equal amount of the coupling product between the tert-adamantyl radical and pyridine. The preceding study (3,4) has showed that although several organic acids may replace the acetic acid, the pyridine is absolutely necessary for the Gif-system oxidation to occur. The oxidation of adamantane's methylene leads to both alcohol and ketone (which is by



2'-, 4'-, 3'-



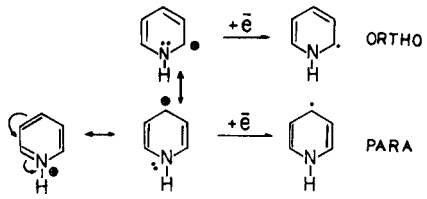
2'-, 4'-

far the main product). The presence of several isomeric bipyridines, mass 156, in this reaction was observed and the formation of 2,2'-, 4,4'- and 2,4'- bipyridines under these conditions can be rationalised by the following scheme (Scheme 1, 2).

The presence of meta (3 or 3') related bipyridines, which cannot be explained by the above-mentioned mechanism, is a crucial point in a search for a mechanistic overview of the reaction. For instance, the meta bonded bipyridines or their derivatives could be explained by following mechanism (Scheme 3, 4).

The radical coupling between meta carbons leads to 3,3'-bipyridine. Or, in the presence of previously formed and stabilised 2- and 4-pyridyl radicals, the formation of 3,2'- or 3,4'-bipyridines takes place via radical or ionic mechanism.

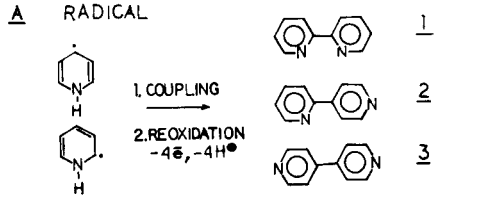
The GC of the products of the oxidation of adamantane by the Gif IV system mixture displays the presence of several bipyridines. Apart from the highly retained and easily identified



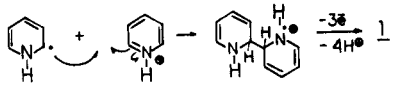
RADICAL COUPLING

SCHEME 1

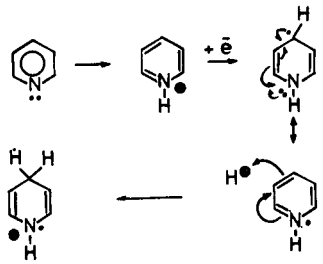
FORMATION OF 1,2 AND 3



B RADICAL-PROTONATED PYRIDINE COUPLING
e.g. 1



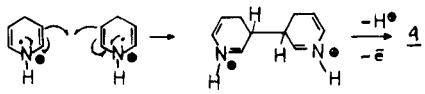
SCHEME 2



FORMATION OF 4,5 AND 6

SCHEME 3

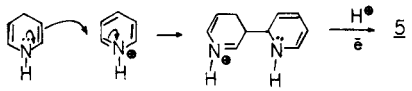
A META RADICAL COUPLING



AS WELL AS 5 AND 6

B META IONIC COUPLING (FOR 5 AND 6 ONLY)

e.g.



FORMATION OF 4, 5 AND 6

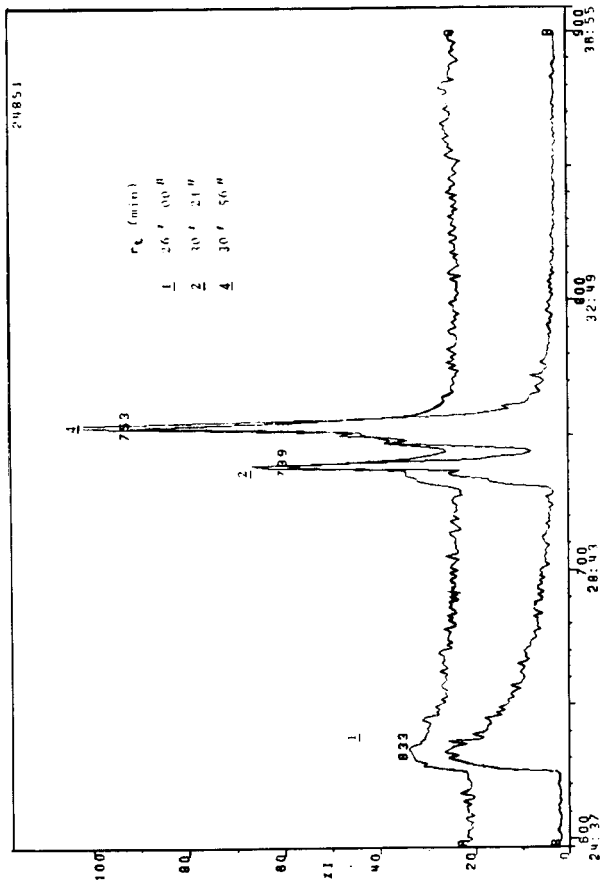
SCHEME 4

TABLE 1

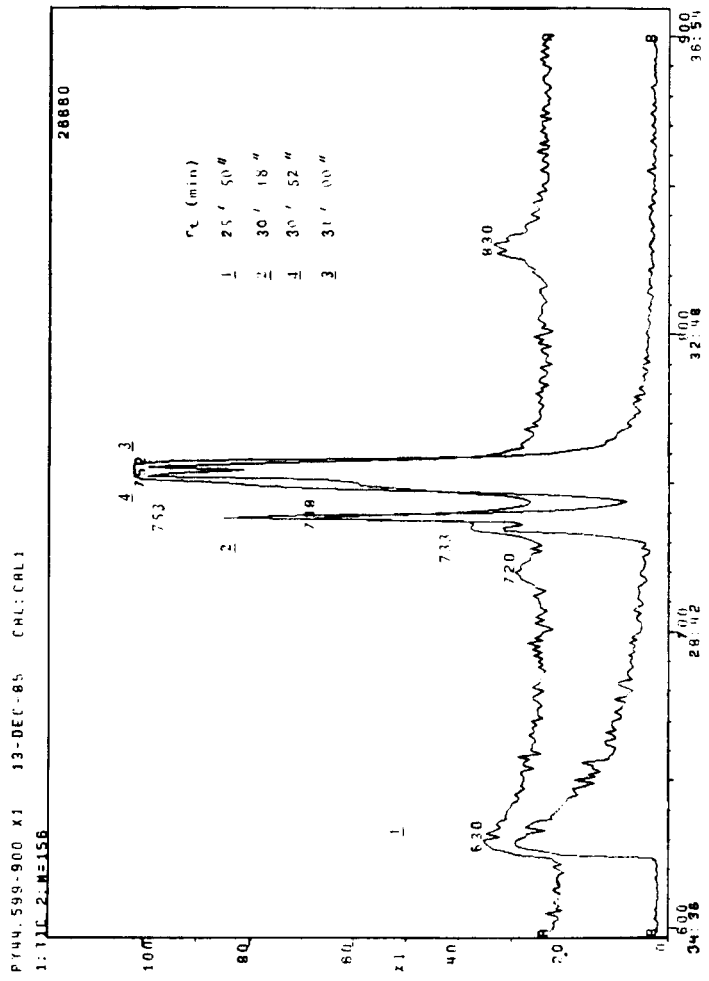
Bipyridines (r_t)

		m/z	1 2,2'	5 2,3'	2* 2,4'	3 4,4'	4 3,3'	6 3,4'
HPLC	d_o		32.0	18.8	20.2	17.5	18.8	15.0
			1.58	0.93	1.00	0.87	0.93	0.74
GC-MS	d_o	156	630	720	737	753	747	756
			0.85	0.97	1.00	1.02	1.015	1.025
(CPSIL 5)	d_4	160			728	743		747
					1.00	1.02		1.03
	d_8	164			718	733		743
					1.00	1.02		1.035

* r_t of 20.2 min for 2,4'-bipyridine-d_o has been normalised to 1.00 ($r_t d_o > r_t d_4 > r_t d_8$)

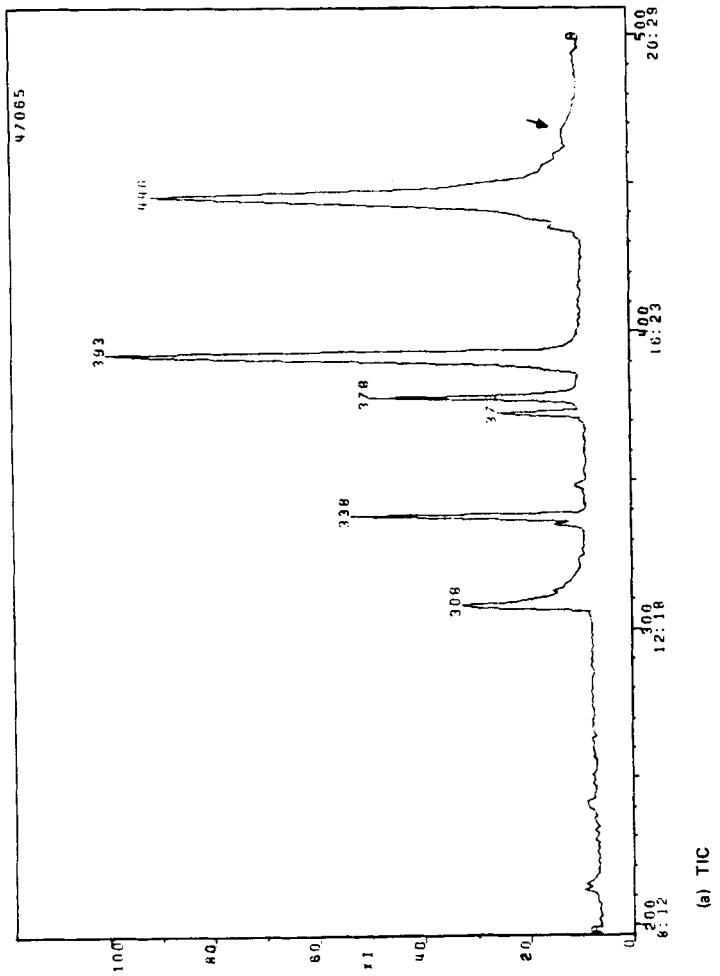


(a) Identification of 2,2'-, 2,4'-, 3,3'- and 4,4'-bipyridines

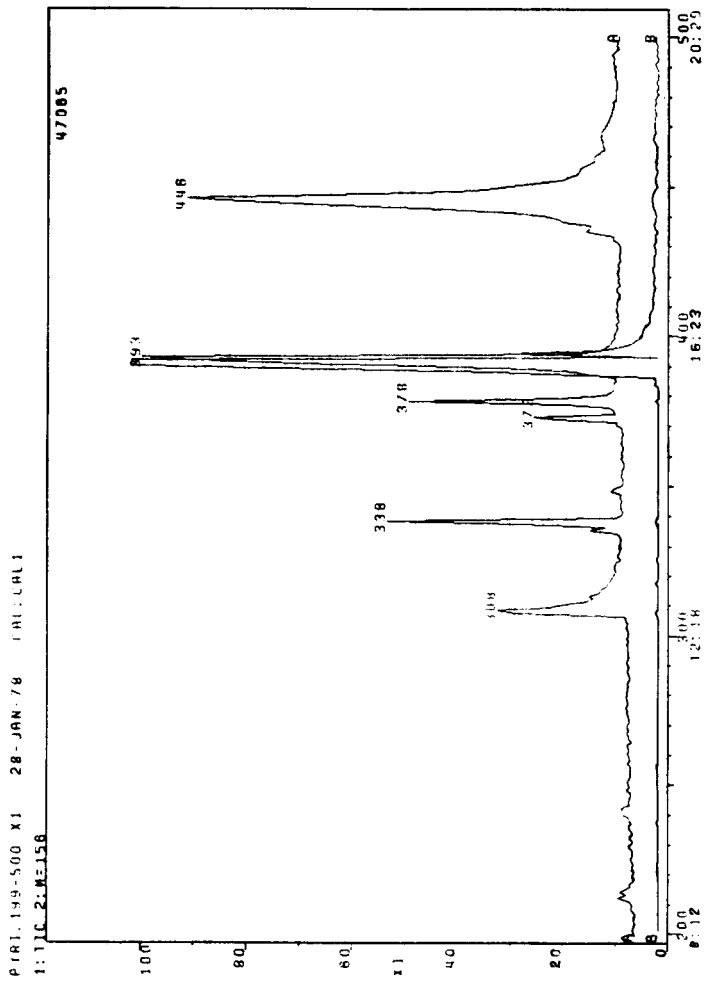


(b) Identificaion of 2,2'-, 2,4'- and 3,3'-bipyridines

Fig. 1
- Bipyridine fraction



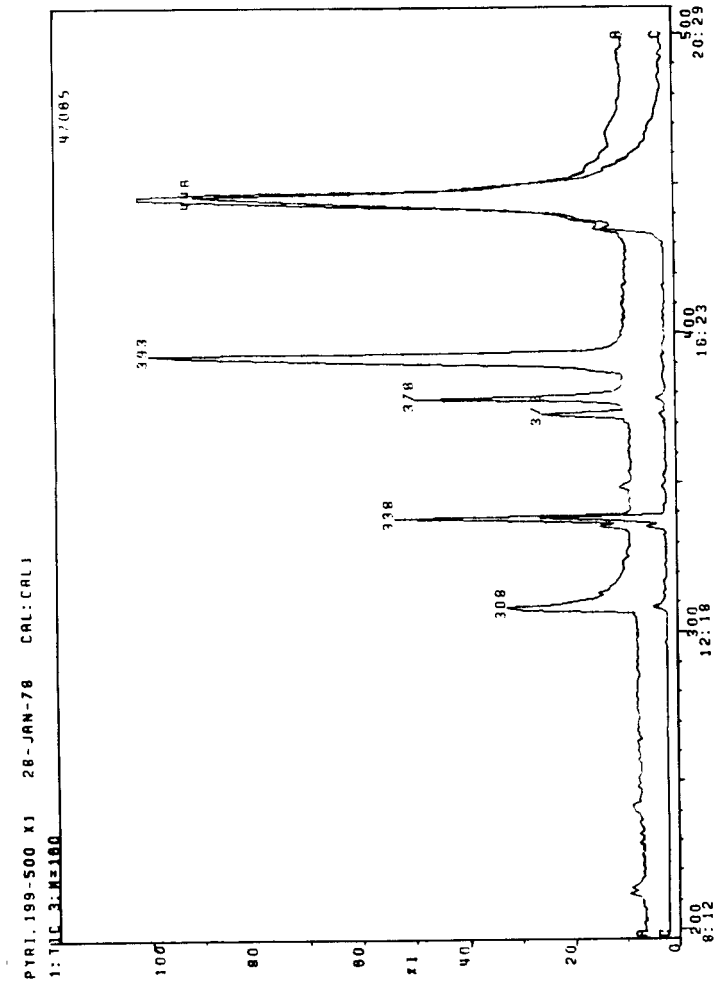
(a) TIC



(b) Mass chrom m/z 156

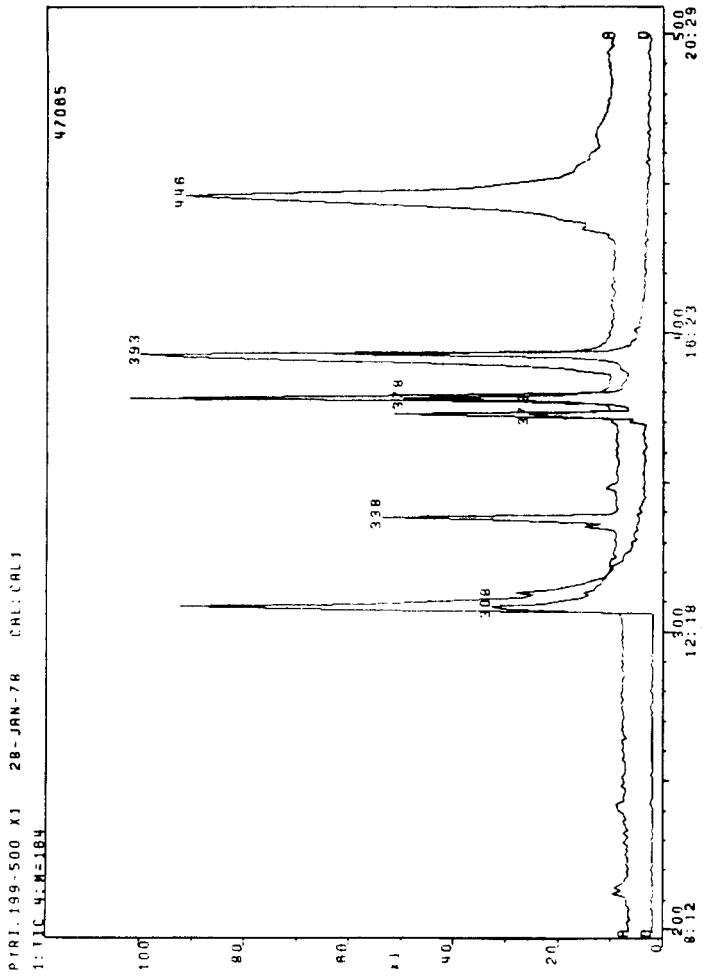
(bipyridines - d_0)

Fig. 2 Oxidation of hydrocarbons
- Bipyridine and coupled
Bipyridine fracion



(c) Mass chrom m/z 160

(bipyridines - d_4)



(d) Mass chrom m/z 164

(bipyridines - d_8)

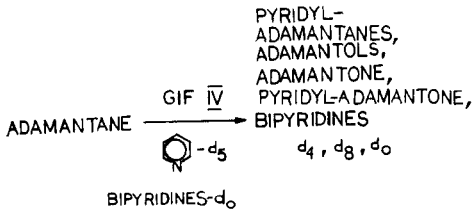
2,2'-bipyridine (1) and the 2,4'- and 4,4'-bipyridines ((2) and (3) respectively) the presence of meta coupled bipyridines was observed (Table 1) and identified by comparison to available standards. The quantities of meta coupled bipyridines are small and their occurrence should be related to activation of this position of the heterocycle as proposed in Scheme 3. The origin of the meta radical-cation is uncertain. The complex Gif-oxidation system could react with the pyridine and then allow the reduced pyridine radical-cation to dimerise (e.g. 3,3') or to react with the ortho or para radical-cations (Scheme 1) to form two remaining bipyridines (2,3' and 3,4'). In order to investigate this mechanism, some cross-over experiments (deuterio-protio) have been performed (Fig. 1a, 1b).

The Gif-oxidation performed in deuterated pyridine leads to six isomeric bipyridines of masses 164 which retention time r_t can be compared to the corresponding protio analogs (smaller r_t has been observed for corresponding deuterio bipyridines (Table 1) (Fig. 2a-d).

A similar reaction in an equimolar mixture of pyridine $-d_0$ and pyridine $-d_5$ also leads to six mixed bipyridine products having four deuteriums and masses of m/z 160.

The Gif-oxidation of adamantane performed in perdeuterated pyridine as solvent in the presence of a protio bipyridine fraction 1-3 (or some individual bipyridines 1-3) does lead to GC-detectable amount of the mixed protio-deuterio bipyridines (Scheme 5).

This does not mean that the meta activation is related to the presence of bipyridines which could be formed in a parallel manner because the mixed protio-deuterio meta bipyridines have not been observed. The meta bipyridines are minor products in



SCHEME 5

this reaction. The reversibility of the bipyridine-pyridine system, however, has been confirmed.

Crossover Experiments

It has also been shown that the Gif oxidation reaction performed in a 50:50 mixture of pyridine-d_0 and d_5 clearly displays the presence of a series of bipyridines-d_8, d_4 and d_0, as well as the coupling of these bipyridines and original pyridines to the hydrocarbon (or its oxidation products).

One more crossover reaction has been performed on a series of protio or perdeuterated cycloalkane. When reacted in the Gif-oxidation system the GC-MS clearly displays both deuterated and protio oxidation products as well as the pyridine coupling products to both cycloalkanes when mixed 50:50 (Table 2).

For instance the oxidation of equimolar quantity of cyclohexanes d_0 and d_{12} with Gif Oxidation System IV leads to nicely separated cyclohexanones d_{10} and d_0 as well as cyclohexanols d_{11} and d_0. The TIC run for this reaction, presented in Ref. 5 and Table 2, shows the utility of GC-MS in such a crossover study.

The pyridine coupled to oxidized cycloalkane products have been easily identified using the GC-MS technique. The search for

TABLE 2

Cyclohexane Oxidation

Cyclohexane	1-ol	1-one
d_0	1.00*	0.60
d_{12}	0.96	0.57

* r_t of 3.14 min has been normalised to 1.00.

secondary oxidation products reveals the presence of several pyridine coupled to cyclohexane compounds which were easily identified using GC-MS. For instance, when equimolar quantities of cyclohexane d_0 and d_{12} are oxidised, three isomeric (masses 161-d_0 and 172-d_{11} respectively) pyridyl cyclohexanes are observed (Table 3) in both series (d_{11} or d_0).

The same reaction run in the presence of pyridine -d_5 leads to the perdeuterated coupling products of masses 176 (d_{11} + d_4) or using cyclohexane -d_0 in pyridine -d_5 of masses 165 (d_0 + d_4). In all above-mentioned series, the major products are the 2′-pyridyl cyclohexane followed by 4′-pyridyl and traces of 3′-pyridyl. All three of them however do not exceed 3% of total pyridyl radical containing compounds.

A similar experiment has been designed for adamantane oxidation leading to two distinctive pyridyl adamantanes: 2′-pyridyl 1-adamantane and 4′-pyridyl 1-adamantane in a ratio of 2:1 (Table 4). Several minor isomeric coupling products are present however their identification is difficult because of the lack of model compounds. All cross reactions described above, when

TABLE 3

Pyridyl cyclohexanes

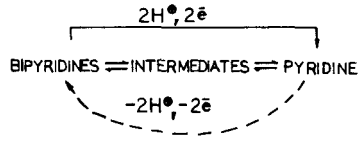
Cyclohexane	Pyridine	m/z	r_t (%)* 2'-	4'-	3'-
d_0	d_0	161	0.71 (1.6)	1.00 (0.6)	1.02 (0.05)
d_{12}	d_0	172	0.71 (1.2)	1.00 (0.4)	1.02 (0.03)
d_{12}	d_5	176	0.72 (1.1)	1.00 (0.3)	1.03 (0.02)
d_0	d_5	165	0.70 (1.0)	1.00 (0.3)	1.02 (0.01)

* r_t of 4'-pyridyl cyclohexane -d_0 19.1 min has been normalised to 1.00, % of total oxidation products.

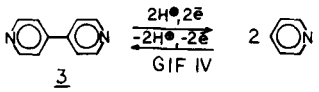
TABLE 4

	Pyridyl adamantane (r_t)		
(m/z)	2'-	4'-*	3'-(?)
d_o (213)	453	415	462
	1.09	1.00	1.11
d_4 (217)	1.08	1.00	1.105
	451	416	460

* r_t of 1-(4'-pyridyl)-adamantane has been normalised to 1.00 (2'- and 4'-compounds have totalised 95% of pyridyl adamantanes).



e.g.



3

SCHEME 6

deuterated and nondeuterated compounds are used, display an extremely good sensitivity for detection of these products via GC-MS and provide us with qualitative and quantitative data concerning cycloalkane oxidation products and, in a very spectacular way, the bipyridines.

The oxidation of adamantane in pyridine-d_5 in the presence of bipyridine-d_o 3 (4,4') does lead to three essential mixed bipyridines-d_4 (4,4', 2,4' and 2,2'). This result means that under the Gif-IV oxidation conditions the reversible bipyridine-pyridine reaction is effectively performed. The presence of two other major d_o pyridines 2 and 3 has also been observed (Scheme 2, 6). However, the GC detection of bipyridine 1 which has always been laborious (the large base peak on both columns used) was not confirmed.

In all this work, the GC-MS experiments have been performed using EI ionisation and capillary columns. The use of methane CI instead of more popular EI ionisation technique leads to less sensitive detection of bipyridines and that of their coupled pro-

ducts in spite of their well-defined basic character. The situation is similar when ammonia CI is applied.

The series of experiments described here clearly show the potential and practical utility of the GC-MS for mechanistic studies. An important number of details to Barton's (5) proposal for the Gif-oxidation system mechanism have been ascertained using GC-MS technique.

Experimental

General techniques of purification as well as work-up procedures and oxidation method are the same as in Reference 1. The Gif IV system oxidation typical procedure is as in Reference 4.

Mass spectrometric experiments were performed using a Riber R-1010 quadrupole mass spectrometer (Nermag, France) or with a VG 70-70E spectrometer (VG, UK) both in the positive ionisation mode. Spectra were recorded and calculated on a PDP 8M computer coupled to these spectrometers. Typical GC-MS analytical conditions were for E.I.: 70 eV, direct probe temperature 70 - 200°C, Carbowax 57 CB or OV-17 capillary columns (25 m x 0.22 mm OD), temperature programme 70 - 200°C, 5°/min and for C.I.: source temperature 200 - 220°C, the 5 mm filament (tungsten wire 60 µm, 9 turns) was heated from 300 - 800°C in 40s (current programmed from 200 - 600 mA, 10 mA s^{-1}). The source was indirectly heated by a filament (variation of ±10°C) for this reason the direct probe was removed at the end of the programme. The pressure of reagent gases (CH_4 or NH_3), measured at the secondary vacuum gauge, was 10^{-4} Torr. A constant alimentation of buffer gas (He) was maintained. For reagent gases the initial pressure was ca. 3 Torr and the mean electron energy was maintained at 80 eV. The reagent gases ammonia and methane were obtained from Air Liquide

(Alpha Gaz, France). An aliquot (1.0 ml) was treated according to procedure described in Reference 4 (basic fraction extracted with ether then analysed by GC-MS).

Acknowledgements

We wish to thank the CEN de Saclay for use of their facilities, the FESR Council (U de M) for generous support of this work and Henri Virelizier for technical help and helpful discussions.

References

1. Part 1 - D.H.R. Barton, R.S. Hay-Motherwell and W.B. Motherwell, J. Chem. Soc. Perkin Trans. I, 445 (1983).

Part 2 - D.H.R. Barton, A.K. Gokturk, J. Morzycki and W.B. Motherwell, J. Chem. Soc. Perkin Trans. I, 583 (1985).

Part 4 - D.H.R. Barton, J. Boivin, M. Gastiger, J. Morzycki, R.S. Hay-Motherwell, W.B. Motherwell, N. Ozbalik and K.M. Schwartzentruber, J. Chem. Soc. Perkin Trans. I, 947 (1986).

Part 6 - D.H.R. Barton, J. Boivin and C.H. Hill, J. Chem. Soc. Perkin Trans. I, 1797 (1986).

Part 7 - D.H.R. Barton, J. Boivin, D. Crich and C.H. Hill, J. Chem. Soc. Perkin Trans. I, 1805 (1986).

- D.H.R. Barton, J. Boivin, N. Ozbalik, K.M. Schwartzentruber and K. Jankowski Tetrahedron Letters, 447 (1985).

- D.H.R. Barton, M.J. Gastiger and W.B. Motherwell, J.C.S. Chem. Comm., 731 (1983).

- D.H.R. Barton, M.J. Gastiger and W.B. Motherwell, J.C.S. Chem. Comm., 41 (1983).

- D.H.R. Barton, J. Boivin, N. Ozbalik and K.M. Schwartzentruber, Tetrahedron Letters, 4219 (1983).

- D.H.R. Barton, R.S. Hay-Motherwell and W.B. Motherwell. Tetrahedron Letters, 1079 (1983).

2. Part 3 - D.H.R. Barton, A.K. Gokturk and K. Jankowski, J. Chem. Soc. Perkin Trans. I, 2109 (1985).

3. Part 5 - D.H.R. Barton, J. Boivin, W.B. Motherwell, N. Ozbalik, K.M. Schwartzentruber and K. Jankowski, Nouv. Jour. Chimie, 10, 387 (1986).

4. Part 8 - D.H.R. Barton, J.C. Beloeil, A. Billion, J. Boivin, J.Y. Lallemand, P. Lelandais, S. Mergui, N. Morellet and K. Jankowski, Nouv. Jour. Chimie, 10, 439 (1986).

5. K. Schwartzentruber, Thèse (doctorat d'état), Université de Paris Sud (XI), Orsay, 1984.

Date Received: 08/26/87
Date Accepted: 09/28/87