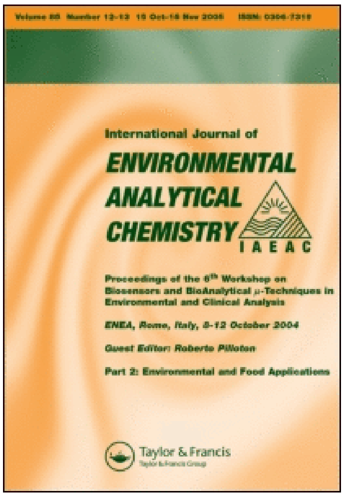


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Possible Generalized Cleavage Reaction for Mono- or Di-substituted Phenylureas Reacted with Perfluoroanhydrides

B. L. Worobey[a]; G. R. B. Webster[b]
[a] Food Research Division, Bureau of Chemical Safety, Food Directorate, Health and Welfare Canada, Ottawa, Ontario, Canada [b] Pesticide Research Laboratory, Department of Soil Science, University of Manitoba, Winnipeg, Manitoba, Canada

To cite this Article Worobey, B. L. and Webster, G. R. B.(1983) 'A Possible Generalized Cleavage Reaction for Mono- or Di-substituted Phenylureas Reacted with Perfluoroanhydrides', International Journal of Environmental Analytical Chemistry, 14: 2, 99 — 103

To link to this Article: DOI: 10.1080/03067318308071611

URL: http://dx.doi.org/10.1080/03067318308071611

Intern. J. Environ. Anal. Chem., 1983, Vol. 14, pp. 99–103
0306-7319/83/1402-0099 $18.50/0

Printed in Great Britain

A Possible Generalized Cleavage Reaction for Mono- or Di-substituted Phenylureas Reacted with Perfluoroanhydrides

B. L. WOROBEY

Food Research Division, Bureau of Chemical Safety, Food Directorate, Health and Welfare Canada, Ottawa, Ontario, Canada K1A 0L2

and

G. R. B. WEBSTER

Pesticide Research Laboratory, Department of Soil Science, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

(*Received August 17, 1982*)

Several mono- and di-substituted urea pesticides were reacted with trifluoroacetic anhydride and heptafluorobutyric anhydride to determine if the procedure normally used to derivatize tri-substituted phenylureas yielded cleavage products instead of the derivatized phenylureas. Compounds studied included 4-chlorophenylurea, N-demethoxy linuron (1-[3,4-dichlorophenyl]-3-methyl urea), siduron (1-phenyl-3-[2-methyl cyclohexyl] urea, EL-494 (1-[3-{5-methyl-6-(4-bromophenyl) pyrazinyl}] -3- [2,6-dichlorophenyl] urea), and diflubenzuron (1-[4-chlorophenyl] -3-[2,6-diflurobenzoyl] urea. All compounds yielded *N*-perfluoroacylated cleavage products, indicating a generalized cleavage reaction for mono- and di-substituted phenylureas.

INTRODUCTION

Trifluoroacetylation of thermally unstable trisubstituted urea herbicides proceeds to the expected tetra-substituted urea compounds;[1] this reaction is often used to enhance GLC stability and to increase the effective sensitivity of the electron capture detector to these compounds. Attempted derivatization of the di-substituted phenylurea diflubenzuron with trifluoroacetic anhydride (TFAA) resulted in cleavage of the molecule to yield the trifluoroacetyl derivative of 4-chloroaniline and the imide trifluoroacetyl derivative of 2,6-diflurobenzamide as the major products.[2] Worobey and Webster[2] showed that the cleavage of diflubenzuron occurred during reaction with perfluoroanhydrides and not as a result of thermal degradation during gas-liquid chromatography (GLC) or mass spectrometry (MS). Vandenheuvel *et al.*[3] reported that the reaction of heptafluorobutyric anhydride with the mono-substituted urea drug, 4-(4′-aminophenyl)-sulfonyl phenylurea, resulted in cleavage to the corresponding *N*-heptafluorobutyramide derivatives. To determine if this cleavage is a generalized reaction, several additional mono- and di-substituted phenylureas were examined.

EXPERIMENTAL

Reagents and analytical standards

All solvents were glass-distilled residue-free grade. Trifluoroacetic anhydride was purchased from Aldrich Co. (Milwaukee, WI, U.S.A.). Diflubenzuron and 4-chlorophenylurea were supplied by Thompson–Hayward Chemical Co. (Kansas City, KA, U.S.A.). EL-494 was supplied by Elanco Products Div. (Winnipeg, Manitoba, Canada), Siduron and *N*-demethoxy linuron were supplied by E. I. DuPont de Nemours & Co. (Wilmington, DE, U.S.A.). The identity of each analytical standard was confirmed from mass spectra obtained by direct insertion probe mass spectrometry (DIP-MS) with source temperature *ca.* 130°C and ionization potential of 70 ev in the EI mode.

Chromatographic conditions

A Varian 2440 gas chromatograph equipped with a tritium foil electron capture detector was used. Operating conditions: temperatures: injector 180°C, column 130 or 150°C, detector 182°C; N_2 carrier 40 ml/min. The borosilicate glass column, 1.7 m × 2 mm i.d., was packed with 5% OV-101 coated Chromosorb W (AW) DMCS (100–120 mesh).

GC-MS conditions

A DuPont Dimaspec GC-MS was used equipped with a 1.6 m × 2 mm i.d. borosilicate glass column packed with 5% OV-101 coated Chromosorb W (AW) DMCS (100–120 mesh), and was operated in either the EI or CI mode. Operating conditions: temperatures: injector 180°C, column 150°C or programmed 50–150°C at 8°C/min, glass jet separator 220°C, source 150 or 220°C; ionization potential 70 ev; CI reagent gas isobutane; CI source pressure *ca.* 65 Pa. DIP temperature was set at "off" and the source was run at its base temperature of *ca.* 130°C (filament on, heater off).

Procedure

A solution of each standard was prepared in ethyl acetate (*ca.* 100 μg/ml). In each case, 1.0 ml of solution plus 0.2 ml TFAA were placed in a glass stoppered 5 ml centrifuge tube and reacted at 50°C for 30 min. The solvent was removed just to dryness under a stream of dry N_2 and the residue made up to a final volume of 1.0 ml with hexane for GC- and DIP-MS analysis. Injections of 1–5 μl or 100–500 ng were examined in the EI and CI modes.

RESULTS AND DISCUSSION

Table 1 describes the reaction products identified in these studies in addition to those reported for diflubenzuron[2] and penfluron.[4] Both GC-MS (a) and DIP-MS (b) evidence is presented.

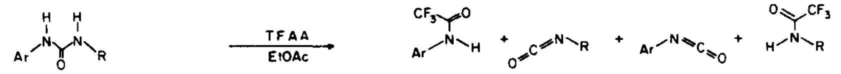
When diflubenzuron was reacted with TFAA, the major products were the TFA derivative of 4-chloraniline and the more labile TFA imide derivative of 2,6-diflurobenzamide. Other products detected included 4-chlorophenyl isocyanate and 2,6-difluorobenzoyl isocyanate. These structures were confirmed using EC-GC, GC-MS, DIP-MS and TLC followed by DIP-MS.

Similar reaction products were obtained for other mono- and di-substituted phenylureas. The metabolite of diflubenzuron, 4-chlorophenylurea, yielded the TFA derivative of 4-chloroaniline, 4-chlorophenyl trifluoroacetamide, and 4-chlorophenyl isocyanate. The *N*-demethoxy metabolite of linuron, 1-(3,4-dichlorophenyl)3-methylurea, yielded 3,4-dichlorophenyl trifluoroacetamide and 4-chlorophenyl isocyanate. The herbicide siduron yielded phenyltrifluroacetamide, phenylisocyanate, 2-methylcyclohexyl isocyanate, and 2-methylcyclohexyl trifluoroacetamide. Similarly, the new experimental chitin inhibitor, EL-494, yielded the trifluoroacetamide I, 2,6-dichlorobenzoylisocyanate, the isocyanate III, and 2,6-dichlorobenzoyl trifluoroacetamide. All products were identified using a combination of EC-GC, GC-MS, and DIP-MS.

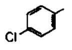
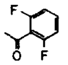
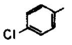
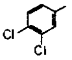
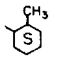
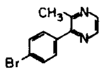
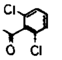
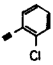
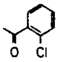
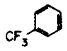
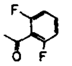
Reaction of both diflubenzuron and 4-chlorophenylurea with

TABLE I

Cleavage products from trifluoroacetylation of several mono- and di-substituted urea pesticides characterized by (a) GC-MS and (b) DIP-MS



I II III IV

COMPOUND	Ar	R	I	II	III	IV
1. Diflubenzuron			a,b	b	a,b	a,b
2. 4-Chlorophenyl Urea		H	a,b	—	a,b	—
3. N-Demethoxy Linuron		CH_3	a,b	—	b	—
4. Siduron			a,b	a,b	a,b	b
5. EL-494			a,b	—; a,b 	a,b	a, b ; b 
6. Penfluron (7)			a	—	—	—

heptafluorobutyric anhydride under the same conditions yielded products analogous to those encountered with TFAA.

Perfluoroacylation of mono- and di-substituted ureas apparently proceeds via a concomitant cleavage reaction which yields derivatized products similar to those obtained if the ureas were first hydrolyzed and then derivatized with the perfluoroacyl anhydride.

Although the perfluoroacylation of mono- and di-substituted urea pesticides does not yield the expected direct derivatization product, a new one-step quantification method is possible for each compound examined based on the formation of cleavage product I. The method may also be used as a confirmatory test.

In conclusion, the following observations can be made regarding the reaction of mono- and di-substituted phenylureas and related compounds with perfluoroacyl anhydrides:

1) The cleavage appears general for mono- and di-substituted aryl ureas.

2) The cleavage occurs during derivatization rather than as a result of thermal degradation in the GC.

3) The major quantifiable portion of the molecule is the aryl moiety; viz., 4-chloroaniline, 3,4-dichloroanile, aniline, 5-methyl-6-*p*-bromophenyl pyrazine-3-amine, and 4-trifluoromethylaniline are detectable as their *N*-perfluoroacyl derivatives.

4) Both GC-MS and DIP-MS are required to establish that this cleavage takes place *in vitro*. EC-GC is suitable for routine quantification of *N*-perfluoroacyl derivatives.

References

1. D. G. Saunders and L. E. Vanatta, *Anal. Chem.* **46**, 1319 (1974).
2. B. L. Worobey and G. R. B. Webster, *J. Chromatog.* **153**, 423 (1978).
3. W. J. A. Vandenheuvel, V. B. Gruber and R. W. Walker, *J. Chromatog.* **87**, 341 (1973).
4. A. B. DeMilo, P. H. Terry and D. M. Rains, *J. Assoc. Offic. Anal. Chem.* **61**, 629 (1978).