Gas chromatography of halogenated carbamates

III. *meta*-Fluorosulfonylphenyl derivatives

The recent availability of a new reagent, *meta*-fluorosulfonylphenyl isocyanate[1]*, has stimulated our interest in its facile conversion to substituted carbamates via the standard isocyanate reaction[2,3] with phenolic or alcohol derivatives. Aromatic fluorinated plant growth regulators and intermediates have been the subject of studies by FINGER and his associates[4], who extended their investigations to N-fluorophenyl carbamates. Isomeric mono-fluorophenyl N-methyl carbamates were included in work concerning the anticholinesterase activity and toxicity of substituted phenyl N-methyl carbamates[5]. MCFARLAND AND HOWARD have recently reported preparations of a variety of urethanes from benzenesulfonyl isocyanate[6].

This paper cites the investigation of the gas chromatographic behavior of urethanes prepared from *meta*-fluorosulfonylphenyl isocyanate.

Experimental

The N-*meta*-fluorosulfonylphenyl carbamates were synthesized via the reaction of the isocyanate with the respective phenol or alcohol in a small amount of pyridine and were recrystallized from petroleum ether (35–60° fraction). The melting points were determined on a Fisher–Johns melting point apparatus (Fisher Scientific, Silver Spring, Md., U.S.A.). Gas chromatography was carried out on an F & M model 1609 instrument equipped with a flame ionization detector. The column employed was 6 ft. by 0.25 in. glass coil packed with 4 % QF-1 on 80–100 mesh HMDS-pretreated Chromosorb W (Applied Science Laboratories, Inc., State College, Pa., U.S.A.). Specific operating conditions are given in the footnotes to Table I.

Results and discussion

The chromatographic data are reported in Table I. The carbamates were observed to undergo degradation with the release of the appropriate phenol. A second peak common to all samples was suspected to be *meta*-fluorosulfonylaniline. The elution values are cited relative to this latter component. Isopropanol and cyclohexanol were not detected owing to their rapid elution under the experimental conditions. Interestingly enough, the cyclohexyl derivative produced a large component peak at twice the elution value of the reference peak suggesting perhaps that degradation is not complete for this derivative. The order of elution for the phenols produced via thermal cleavage is essentially the same for those released from N-trichloroacetyl carbamates in earlier studies[7]. The number of theoretical plates for the *meta*-fluorosulfoxyl aniline peak was 680.

A study of other N-haloaryl carbamate derivatives is presently underway.

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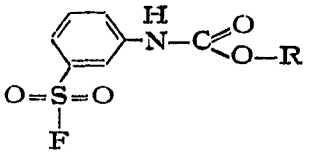
TABLE I

GAS CHROMATOGRAPHY OF N-*meta*-FLUOROSULFONYLPHENYL CARBAMATES



R	*Mol.wt.*	*M.p.* (°C)	*Relative elution*[a]
Isopropyl	261	82– 83.5	[b]
Phenyl	295	76– 78	0.041
Cyclohexyl	301	64– 66	[c]
o-Chlorophenyl	329	137–139	0.041
m-Chlorophenyl	329	111–113	0.61
2,3-Dichlorophenyl	363	133–135	0.16
2,5-Dichlorophenyl	363	88– 90	0.17
p-Chlorophenyl	329	124–126	0.18
2,6-Dichlorophenyl	363	114–116	0.19
3,5-Dichlorophenyl	363	110–112	0.35
3,4-Dichlorophenyl	363	98–100	0.48

[a] Elution of phenols released during chromatographic analysis relative to a secondary product (*m*-fluorosulfonyl aniline), present in all samples and eluting at 2.9 min. Column 4% QF-1 on 80–100 mesh HMDS pretreated Chromosorb W, 6 ft. by 0.25 in. glass coil. Operating conditions: column 140°; injection port 70 V; detector 200°; range 1000; nitrogen carrier 91 ml/min; hydrogen 77 ml/min; air 300 ml/min; flame ionization detector.

[b] Eluted in solvent peak.

[c] A major component appeared at 2.0 relative to the *m*-fluorosulfonyl aniline peak, suggestive of intact carbamate.

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1 GEVAERT PHOTOPRODUCTION N.V., *Belgian Pat.*, 634,665, Jan. 9, 1964; *C.A.*, 62 (1964) 681.
2 B. T. DEWEY AND N. F. WITT, *Ind. Eng. Chem., Anal. Ed.*, 14 (1942) 648.
3 E. LAMBLING, *Bull. Soc. Chim. France*, [3] 19 (1898) 771.
4 G. C. FINGER, D. R. DICKERSON, D. E. ORLOPP AND J. W. EHRMANTRAUT, *J. Med. Pharm. Chem.*, 7 (1964) 572.
5 R. L. METCALF, T. R. FUKUTO AND M. Y. WINTON, *J. Econ. Entomol.*, 55 (1962) 891.
6 J. W. MCFARLAND AND J. B. HOWARD, *J. Org. Chem.*, 30 (1965) 957.
7 L. FISHBEIN AND W. L. ZIELINSKI, JR., *J. Chromatog.*, 23 (1966) 298.

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