Journal of Fluorine Chemistry, 17 (1981) 485–487

Received: September 12, 1980

Synthesis of Some Substituted Difluoronitroacetanilides and Their Reduction to Substituted N-Difluoronitroethylanilines

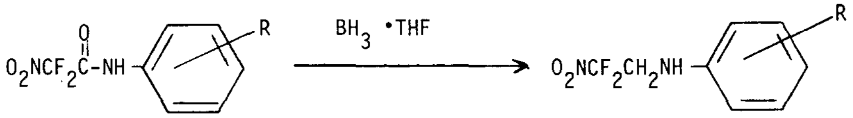
EUGENE R. BISSELL and ROSALIND W. SWANSIGER
Lawrence Livermore National Laboratory, Livermore, California 94550, (U.S.A.)

SUMMARY

The synthesis of difluoronitroacetanilide and its p-methyl and m-methoxyl derivatives and their reduction by diborane in tetrahydrofuran to the corresponding N-difluoronitroethylanilines is described. Yields on the acetanilides ranged from 13 to 43% and on the anilines from 50 to 64%.

INTRODUCTION

In an earlier report [1] we described an improved synthesis of substituted N-trifluoroethylanilines by the reduction of the corresponding trifluoroacetanilides with diborane in tetrahydrofuran [2]. We have now extended this procedure to the synthesis of N-difluoronitroethylanilines, a class of compounds not previously reported. The required difluoronitroacetanilides, which were also new compounds, were prepared by aminolysis of ethyl difluoronitroacetate. The yields, physical properties and analyses of the new compounds are listed in Table 1.



1

2

A R = H

B R = p-CH_3

C R = m-OCH_3

RESULTS

Nuclear magnetic resonance and infrared absorption spectra were obtained for all six compounds. 1B and 2B showed CH_3 singlets at 2.33 and 2.77 ppm respectively. 1C and 2C both gave OCH_3 singlets at 3.76 ppm. The CH_2 in all three anilines was a triplet (J = 10 Hz) at 4.02 ppm. The NH

TABLE 1

Substituted difluoronitroacetanilides and N-difluoronitroethylanilines

Comp.	Yield (%)	mp (^{o}C)	Calculated (%) C	Calculated (%) H	Calculated (%) N	Found (%) C	Found (%) H	Found (%) N
1A	43	73.2	44.45	2.80	12.96	44.41	2.83	12.95
1B	30	84.6	46.96	3.50	12.17	47.08	3.49	11.86
1C	13	76.7	43.91	3.28	11.38	44.26	3.44	11.52
2A	56	52.3	47.53	3.99	13.86	47.72	4.04	13.76
2B	50	65.4	50.00	4.66	12.96	49.85	4.90	13.28
2C	64	*	46.56	4.34	12.07	46.66	4.33	12.14

*liquid, n_D^{24} = 1.5193

resonance was a broad singlet at about 8.1 ppm for the acetanilides and a slightly broadened doublet (J = 12 Hz) at 4.2 ppm for the anilines. In the aromatic region 1B and 2B both showed the quartet typical of para substituted aromatics centered at 7.3 and 6.8 ppm respectively. 1A and 1C showed complex multiplets centered at 7.5 and 7.0 ppm and 2A and 2C showed similar multiplets at 6.9 and 6.6 ppm. In all cases integration gave the expected relative areas. The NH stretching band in the infrared spectrum of the amides was at 3340 ± 20 cm^{-1}, and that of the anilines was at 3400 ± 5 cm^{-1}. The amides all showed a carbonyl band at 1710 cm^{-1}, and all six compounds had NO_2 asymmetric stretching bands at 1590 ± 10 and symmetric stretching bands at 1350 ± 20 cm^{-1}.

EXPERIMENTAL

Melting points, taken on a Mettler Model FP1 apparatus at 2^{o}/min, are corrected. Nuclear magnetic resonance measurements, in deuterated chloroform, were made on a Varian EM360 spectrometer and are reported as δ relative to internal TMS. Infrared absorption spectra on neat liquids or as potassium bromide pellets were taken on a Perkin-Elmer Model 457 grating spectrometer.

Difluoronitroacetanilides (n.c.)

A mixture of the aniline (0.1 mole) and ethyl difluoronitroacetate [3] (0.10-0.14 mole) was refluxed for 18-24 h. Any volatile material was removed under a stream of argon at room temperature, and the residue was sublimed at 130-150^{0} and 1 Pa. The sublimate was recrystallized one or more times from carbon tetrachloride, and the analytical sample was resublimed. Results are listed in Table 1.

N-Difluoronitroethylanilines (n.c.)

A solution of 0.05 mole of the acetanilide in 50 ml of tetrahydrofuran (dried over sodium-lead alloy) was added under argon over a period of 20-30 min to a stirred, 1 M solution (200 ml) of diborane in tetrahydrofuran. The reaction mixture was stirred at room temperature for 2 h, then refluxed for 20-25 h, and finally cooled to room temperature. Excess hydride was destroyed by careful addition of 5 ml of absolute ethanol followed by 1 ml of water. Concentrated aqueous hydrochloric acid (15 ml) was added, and about 180 ml of the tetrahydrofuran was removed by distillation. The residue was poured into 100 ml of water, and the solution was extracted three times with 50 ml portions of ether. Drying the ether with anhydrous magnesium sulfate, filtering, and evaporating left the crude aniline. Basifying the aqueous phase and reextracting with ether yielded only traces of other products, which were not identified. 2A was recrystallized twice from aqueous ethanol. 2B was chromatographed on silica gel eluting with methylene chloride. The fractions containing the desired product were evaporated, and the residue was distilled in a short path still at 1 Pa. 2C was similarly chromatographed, eluting with toluene, and distilled.

ACKNOWLEDGEMENTS

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-Eng-48. Microchemical analyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana. Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

REFERENCES

1 E. R. Bissell and R. W. Swansiger, J. Fluorine Chem. 12 (1978) 293.

2 H. C. Brown, P. Heim, and N. M. Yoon, J. Am. Chem. Soc. 92 (1970) 1637.

3 E. R. Bissell, J. Org. Chem. 26 (1961) 5100.