Journal of Fluorine Chemistry, 22 (1983) 115–122

Received: May 4, 1982

9-ACETOXYANTHRACENE DERIVATIVES. PART VII. SYNTHESES AND ELUCIDATION OF THE MOLECULAR STRUCTURE OF 9-ACETOXY-10-ARYLANTHRACENES FROM FLUOROPHENOLS

J.GRONOWSKA and A.DZIELEŃDZIAK

Department of Organic Chemistry, Institute of Chemistry
N.Copernicus University, 87 100 Toruń (Poland)

SUMMARY

The syntheses and elucidation of the molecular structures of the new 9-acetoxy-10-arylanthracenes from o-, m- and p-fluorophenols are described.

INTRODUCTION

In the course of our investigations [1] on 9-acetoxyanthracene derivatives, we have described the syntheses and elucidated the molecular structure of three new 9-acetoxy-10-arylanthracenes from o-, m- and p-fluorophenols. These compounds probably can be used in dye lasers for generating electromagnetic waves in the range of 360-410 nm [2].

RESULTS AND DISCUSSION

9-Acetoxy-10-arylanthracenes from o-, m- and p-fluorophenols have been obtained as a result of multi-step syntheses of the new compounds.

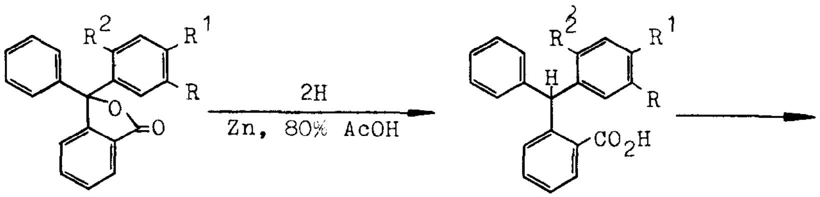
Condensation of 2-benzoylbenzoic acid with o-fluorophenol gave 3-phenyl-3-(3'-fluoro-4'-hydroxyphenyl) phthalide (1) : with m-fluorophenol, 3-phenyl-3-(2'-fluoro-4'-hydroxyphenyl)-phthalide (2): and with p-fluorophenol, 3-phenyl-3-(5'-fluoro-2'-hydroxyphenyl)phthalide (3). Acetylation of phthalides

0022-1139/83/0000-0000/$03.00

1-3 with Ac_2O/AcONa gave their acetates 1a-3a. After reduction of compounds 1-3 with Zn dust in 80% AcOH the corresponding derivatives of 2-benzhydrylbenzoic acid (1b-3b) have been obtained.

During acetylation of acids 1b-3b with Ac_2O in the presence of traces concentrated H_2SO_4 there takes place also intracyclization to:

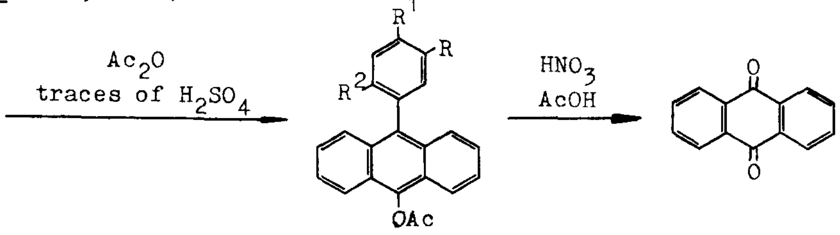
9-acetoxy-10-(4'-acetoxy-3'-fluorophenyl)anthracene (1c),
9-acetoxy-10-(4'-acetoxy-2'-fluorophenyl)anthracene (2c) and
9-acetoxy-10-(2'-acetoxy-5'-fluorophenyl)anthracene (3c).



1: R=F, R^1=OH, R^2=H;
2: R=H, R^1=OH, R^2=F;
3: R=F, R^1=H, R^2=OH;

1b, 2b, 3b — substituents as in 1-3

1a: R=F, R^1=OAc, R^2=H;
2a: R=H, R^1=OAc, R^2=F;
3a: R=F, R^1=H, R^2=OAc.



1c, 2c, 3c — substituents as in 1a-3a

4c: R=R^1=R^2=H;
5c: R=R^1=H, R^2=OAc;
6c: R=R^2=H, R^1=OAc.

The structures of compounds 1c-3c have been confirmed with the use of chemical and spectral PMR methods [3,4]. Boiling of compounds 1c-3c with HNO_3 in AcOH according to the method [3] caused their degradation to anthraquinone, which confirmed that substituents are in the phenyl ring and not in the anthracene skeleton.

The comparison of PMR spectra of 1c-3c with those of 9-acetoxy-10-phenylanthracene(4c), 9-acetoxy-10-(2'-acetoxyphenyl) anthracene (5c) and 9-acetoxy-10-(4'-acetoxyphenyl)-anthracene (6c) elucidated the exact positions of substituents in phenyl ring according to a given Scheme. For compound 4c : 9-OAc $\delta = 2.65$ ppm; 5c: 9-OAc $\delta = 2.51$, 2'-OAc $\delta = 1.35$ ppm; 6c: 9-OAc $\delta = 2.60$, 4'-OAc $\delta = 2.33$ ppm [4].

The elucidation of the molecular structures of 1c-3c indicates simultaneously also the structures of the initial compounds 1-3. This is very important especially in the case of m-fluorophenol, because in m-halogenophenols there is also very active hydrogen atom in o-position to OH group [5].

EXPERIMENTAL

All m.p.s reported below are corrected. Infrared (IR) spectra were measured in Nujol (within the ranges 650-1300 and 1500-2000 cm^{-1}) and hexachlorobutadiene (within the ranges 1300-1500 and 2000-3600 cm^{-1}) mulls on a Unicam SP-200 spectrophotometer. The ν_{max} are reported only for characteristic groups. Proton magnetic resonance (PMR) spectra were run with a Jeol LNM-4H-100 (80 MHz) spectrometer in deuteriochloroform solution; as a internal standard tetramethylsilane was used (TMS, $\delta = 0.00$ ppm).

3-Phenyl-3-(fluorohydroxyphenyl) phthalides (1-3)(nc)

To a mixture of 0.01 mole of 2-benzoylbenzoic acid and 0.011 mole of the appropriate fluorophenol, 3 g of anhydrous $ZnCl_2$ was added. The reaction mixture was heated then on an oil bath for ca 8 hrs at 120-125°C. The melt was dissolved in hot AcOH and solution poured into water. The white amorphous precipitate was filtered off, washed well with water, extracted with 5% NaOH aq.,filtered off again and washed several times with water. The precipitate (yield of crude compounds ca.80-85%) after several recrystallizations from EtOH yielded crystals (for results see Table) .

3-Phenyl-3-(acetoxyfluorophenyl)phthalides (1a-3a) (nc)

A sample of 0.5 g of phthalide (1-3) was treated with 5 ccm of Ac_2O and ca. 0.5 g of anhydrous AcONa and heated for 3 hrs on the oil bath at 120°C. Then the mixture was poured into water. The precipitate was filtered off, washed with water (yield ca. 80-85%) and recrystallized several times from EtOH. For results see Table.

2-Fluorohydroxybenzhydrylbenzoic acids (1b-3b) (nc)

A sample of 5.00 g of phthalide (1-3) was reduced with 10 g of Zn-dust in a solution of 150 ccm of 80% AcOH during 7-10 hrs heating under a reflux condenser. Then the solution was decanted into 800 ccm of water. The white amorphous precipitate was filtered off (yield ca. 90%) and recrystallized from AcOH or EtOH (for results see Table).

9-Acetoxy-10-(acetoxyfluorophenyl)anthracene (1c-3c) (nc)

By heating of 1 g of acid (1b-3b) in 5 ccm of acetic anhydride and 0.03 ccm of concd. sulfuric acid for 1 hr under reflux, pouring the solution into 500 ccm of water and recrystallizing the crude product (yield ca. 85%) from EtOH, compounds 1c-3c were obtained (for results cf. Table and Fig.). Solutions of 1c-3c in organic solvents exhibited blue fluorescence.

Compounds 1c-3c after heating in HNO_3/AcOH according to the method [3] gave anthraquinone in each case.

ACKNOWLEDGEMENT

Thanks are due to Mrs. T. Rakowska for her syntheses of two phthalides in experimental part.

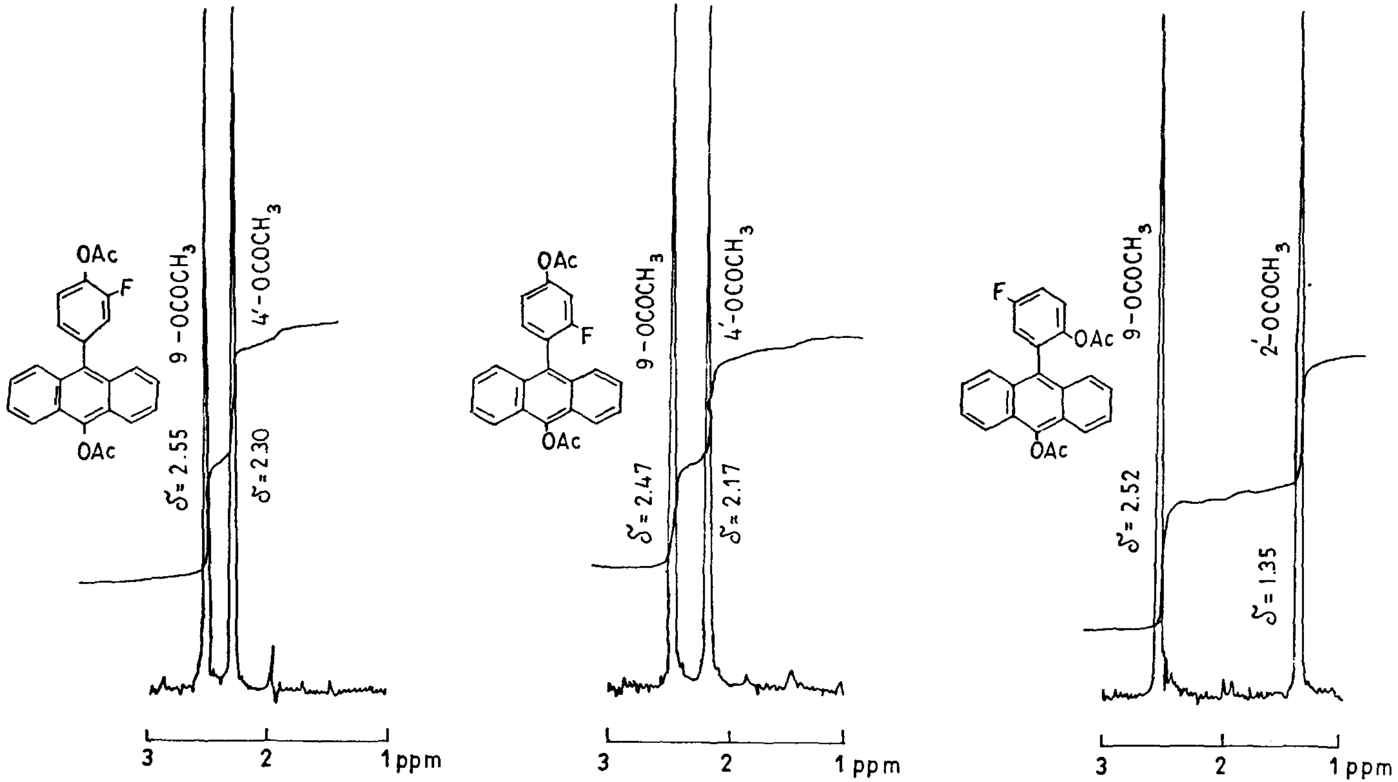


Fig. PMR spectra of 9-acetoxy-10-arylanthracenes

TABLE

Results and elemental analyses, m.p.s and IR spectra of 3-phenyl-3-(fluorohydroxyphenyl)-phthalides (1-3), their acetates (1a-3a), 2-(fluorohydroxybenzhydryl) benzoic acids (1b-3b) and 9-acetoxy-10-(acetoxyfluorophenyl) anthracene (1c-3c)

No	Compound	Formula, molecular mass	Analyses [%]		M.p. [°C] EtOH	IR spectra, cm^{-1}
			Calc.	Found		
1	3-Phenyl-3-(3'-fluoro-4'-hydroxyphenyl)-phthalide	$C_{20}H_{13}O_3F$ 320.3	C 75.0 H 4.1 F 5.9	C 75.3 H 4.2 F 5.8	200.5-202.5	1720s (C=O, γ-lactone), 1340m (C-O, phenol), 980m (C-O-C, γ-lactone);
2	3-Phenyl-3-(2'-fluoro-4'-hydroxyphenyl)-phthalide	$C_{20}H_{13}O_3F$ 320.3	-	-	-	white, amorphic substance, but crystalline are its derivatives: 2a, 2b and 2c
3	3-Phenyl-3-(5'-fluoro-2'-hydroxyphenyl)-phthalide	$C_{20}H_{13}O_3F$ 320.3	C 75.0 H 4.1 F 5.9	C 75.2 H 4.0 F 6.2	252.4-253.8	1730s (C=O, γ-lactone), 1340m (C-O, phenol), 980m (C-O-C, γ-lactone);
1a	Acetate of phthalide 1	$C_{22}H_{15}O_4F$ 362.4	C 72.9 H 4.2 F 5.2	C 72.5 H 4.1 F 5.5	132.0-133.8	1765s (C=O of $COOCH_3$), 1380s (CH_3, acetate), 1205s (C-O-C, acetate);
2a	Acetate of phthalide 2	$C_{22}H_{15}O_4F$ 362.4	C 72.9 H 4.2 F 5.2	C 72.7 H 4.0 F 5.7	132.5-134.1	1750s (C=O of $COOCH_3$), 1390s (CH_3, acetate), 1180s (C-O-C, acetate);
3a	Acetate of phthalide 3	$C_{22}H_{15}O_4F$ 362.4	C 72.9 H 4.2 F 5.2	C 72.6 H 4.0 F 5.3	122.3-124.0	1750s (C=O of $COOCH_3$), 1380s (CH_3, acetate), 1200s (C-O-C, acetate);

1b	2-(3'-Fluoro-4'-hydroxy-benzhydryl)benzoic acid	$C_{20}H_{15}O_3F$ 322.3	C 74.5 H 4.7 F 5.9	C 74.7 H 4.8 F 5.7	199.7-201.2	2770w (OH, dimer COOH), 1700s (C=O, COOH), 1290s (C-O, phenol);
2b	2-(2'-Fluoro-4'-hydroxy-benzhydryl)benzoic acid	$C_{20}H_{15}O_3F$ 322.3	C 74.5 H 4.7 F 5.9	C 74.8 H 5.1 F 5.2	219.6-221.4	2650w (OH, dimer COOH), 1720s (C=O, COOH), 1260s (C-O, phenol);
3b	2-(5'-Fluoro-2'-hydroxy-benzhydryl)benzoic acid	$C_{20}H_{15}O_3F$ 322.3	C 74.5 H 4.7 F 5.9	C 74.6 H 4.7 F 6.1	175.7-177.1	2830w (OH, dimer COOH), 1690s (C=O, COOH), 1270s (C-O, phenol);
1c	**9-Acetoxy-10-(4'-acetoxy-3'-fluorophenyl)-anthracene**	$C_{24}H_{17}O_4F$ 388.4	C 74.2 H 4.4 F 4.9	C 74.3 H 4.4	240.2-241.7	1760sb (C=O of $COOCH_3$), 1375s (CH_3, acetate), 1200s (C-O-C, acetate);
2c	9-Acetoxy-10-(4'-acetoxy-2'-fluorophenyl)-anthracene	$C_{24}H_{17}O_4F$ 388.4	C 74.2 H 4.4 F 4.9	C 73.9 H 4.6	154.6-155.8	1770sb (C=O of $COOCH_3$), 1375s (CH_3, acetate), 1175s (C-O-C, acetate);
3c	9-Acetoxy-10-(2'-acetoxy-5'-fluorophenyl)-anthracene	$C_{24}H_{17}O_4F$ 388.4	C 74.2 H 4.4 F 4.9	C 74.0 H 4.5	190.4-192.1	1765sb (C=O of $COOCH_3$), 1375s (CH_3, acetate), 1205sb (C-O-C, acetate).

REFERENCES

1 Part VI. J. Gronowska, K. Aleksandrzak, J. Heldt, Polish J. Chem., in press.

2 J.R. Heldt, J. Gronowska, J. Heldt, Acta Phys. Polon., A47 (1974) 613.

3 J. Gronowska, A. Dzieleńdziak, Polish J. Chem., 53 (1979) 517.

4 J. Gronowska, K. Aleksandrzak, J. Łukaszewicz, R. Żebrowska, Polish J. Chem., in press.

5 J. Gronowska, H.M. Mokhtar, Tetrahedron, 38 (1982) 1657.