best of the known syntheses. Direct nitration of alkanes loses its cost advantage as a preparative method for higher nitroalkanes because of problems in separating the many isomers and by-products formed. Replacement reactions, such as the replacement of halogen[9] or nitrate[10] groups by nitro groups, while providing good yields with primary groups, fail with tertiary alkyl groups, are irregular with secondary alkyl groups (especially cyclohexyl groups), and require special solvents and reagents to inhibit side reactions as well as starting materials which are often less readily available in pure form than the corresponding carboxylic acids. In the aromatic series decarboxylative nitration is scarcely competitive in yields with other known methods, but it does offer for the first time a process for the direct replacement of carboxyl groups by nitro groups.

Experimental Section

Apparatus.—A 21 × 2 cm glass tube packed with glass helices and wrapped with nichrome heating ribbon was employed as the pyrolysis apparatus. The temperature was controlled with the aid of a thermocouple inserted in a smaller glass tube in the reactor.

A Welsbach Style T-23 ozonator was used as the source of ozonized oxygen (110 V, 5.6 psi O_2, 0.015 ft^3/min). A 150-ml 316 stainless steel autoclave with a magnadrive stirrer was used in the experiments with N_2O_4.

Analysis by Vpc.—Throughout this work most of the conversions and yields reported were calculated from vpc analyses using the common thermal conductivity correction factor method. An F & M Model 720 dual column temperature programmed gas chromatograph was employed. Most nitroalkanes and by-products were analyzed on either a 6.0 ft, 0.25 in., 5% FFAP liquid phase on Chromosorb W, acid washed, DMCS treated column or a 16.0 ft, 0.25 in., 15% FFAP liquid phase on Chromosorb W, acid washed, DMCS treated column at a flow rate of 10 ml/16 sec. Products were identified principally by comparing their gas chromatographic retention times and infrared spectra with those of authentic samples. Mass spectral analyses were obtained when necessary.

Materials.—All anhydrides and acid chlorides were carefully distilled. Anhydrides and acid chlorides which were unavailable were prepared by techniques described in Vogel.[11] (−)-2-Methyl-1-butanol, 99% optically pure, was obtained from the Aldrich Chemical Co.

Synthesis of Acyl Nitrates. Method A.—The acid anhydride was mixed with a sevenfold excess of liquid dinitrogen tetroxide in a stainless steel autoclave cooled in an ice bath. The resulting mixture was sealed and heated to about 100° for about 1 hr.

Method B.—A tenfold excess of the acid anhydride at room temperature was treated with 90% nitric acid at such a rate as to maintain the temperature at about 20°. The resulting mixture was dripped through the vapor phase nitrator.

Method C.—Dinitrogen pentoxide was generated by confluent mixing of streams of ozone and dinitrogen tetroxide and passed into a tenfold excess of the acid anhydride at 0° until the desired increase in weight was observed.

Method D.—Dinitrogen tetroxide was bubbled through a fivefold excess of cold acetyl peroxide prepared by Price's method.[12] When this mixture was introduced into the vapor phase nitrator, decomposition was not as smooth as in other nitrations because of the rapid decomposition of the excess acetyl peroxide.

Model E.—Equimolar amounts of silver nitrate and acyl halide were slowly mixed in acetonitrile solvent at 0° with stirring. The precipitate or silver halide was filtered off after 2 hr and before introducing the acyl nitrate solution into the nitrator.

Method F.—The carboxylic acid was dissolved in at least a twofold excess of acetic anhydride, cooled to 0°, and treated with nitric acid dropwise. With no further treatment the mixture was introduced into the nitrator.

Decarboxylative Nitration.—The liquid mixture, prepared as indicated above in methods B–F, was placed in a dropping funnel and dropped at a constant rate, approximately 3×10^{-4} mol of acyl nitrate/min, through a 2 × 20 cm glass tube packed with glass helices and heated to about 290°. The effluent vapors were condensed and analyzed by vpc or fractionally distilled (under vacuum if necessary).

In a typical experiment (method B) 0.008 mol of valeroyl nitrate was found to afford 0.0045 mol (56.5%) of 1-nitrobutane. In addition, 0.0016 mol (20.0%) of 1-butanol and 0.0008 mol (20.0%) of *n*-butyl valerate were obtained.

A temperature dependence study revealed that 135° was the lowest temperature to obtain nitromethane at a reasonable rate. An optimum temperature of 290° produced nitromethane in 54% conversion based on eq 1. Higher temperatures resulted in lower conversions to nitromethane, and at 350° considerable carbonization occurred in the pyrolysis tube.

Preparation of 2-Nitrobutane from Optically Active 2-Methylbutyric Acid.—2-Methyl-1-butanol ($[\alpha]^{26.5}D$ −8.1°) was oxidized to 2-methylbutyric acid ($[\alpha]^{26.5}D$ +19.7°) in 66% yield by the method of Marckwald[13] and converted to 2-methylbutanoyl chloride ($[\alpha]^{26.5}D$ +14.7°) in 81% yield with thionyl chloride by the method of Bartlett and Stauffer.[14] The chloride (5 ml, 0.041 mol) was added slowly to 7.65 g (0.045 mol) of silver nitrate dissolved in 17.5 ml of acetonitrile at 0°. The mixture was stirred 0.5 hr, filtered, and pyrolyzed at 260°. The condensate was fractionally distilled to obtain optically inactive 2-nitrobutane, bp 139–141°, yield 1.8 g (42.6%).

Registry No.—Nitromethane, 75-52-5; nitroethane, 79-24-3; 1-nitrobutane, 627-05-4; 1-nitroheptane, 693-39-0; nitrocyclohexane, 1122-60-7; 2-nitrobutane, 600-24-8; *tert*-nitrobutane, 594-70-7; *tert*-nitropentane, 595-42-6; 2,2-dinitropropane, 595-49-3; 3-chloro-1-nitropropane, 16694-52-3; nitrobenzene, 98-95-3; *p*-nitrotoluene, 99-99-0.

(9) N. Kornblum, *Org. React.*, **12**, 101 (1962). This review gives an excellent discussion of the relative merits of various methods of preparing nitroalkanes.

(10) G. B. Bachman and N. W. Connon, *J. Org. Chem.*, **34**, 4121 (1969).

(11) A. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1966, p 374.

(12) A. Price, *J. Amer. Chem. Soc.*, **75**, 3686 (1953).

(13) W. Marckwald, *Ber.*, **37**, 1045 (1904).

(14) P. D. Bartlett and C. H. Stauffer, *J. Amer. Chem. Soc.*, **57**, 2582 (1935).

Derivatives of Fluorene. XXXIII. Synthesis and Reactions of Hydrazofluorenes and Related Compounds[1a–c]

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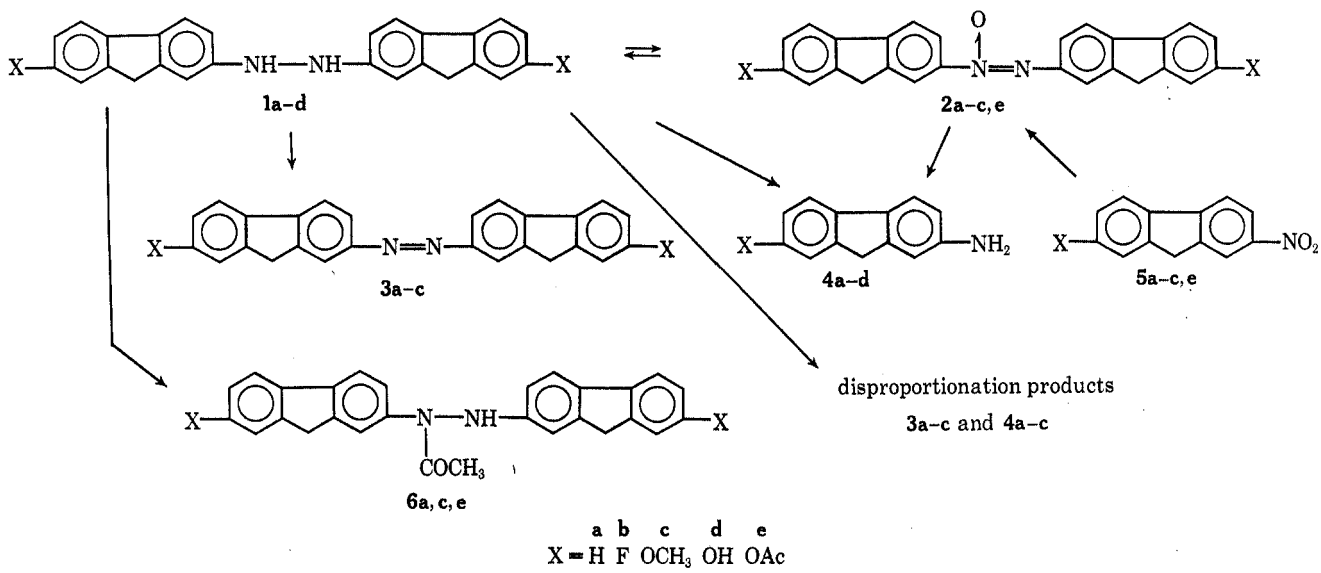
Received April 1, 1970

In a preliminary study of the synthesis of 2,2′-hydrazofluorene (**1a**) and 2,2′-azofluorene (**3a**), possible metabolites of the carcinogen *N*-(2-fluorenyl)acetamide, we reported[1c] that quantitative disproportionation occurs when **1a** is heated in alcoholic hydrochloric acid. Aware that "clean" (or 100%) disproportionation has been found with relatively few hydrazo compounds, we thought it of interest to prepare a few 7,7′-symmetrically substituted hydrazo- and azofluorenes and related compounds for comparison.[1d]

(1) (a) Supported in part by grant (CA-01744) and in part by Research Career Development Award (5-K3-CA-14,991) from the National Cancer Institute, National Institutes of Health. (b) Paper XXXII by H.-L. Pan and T. L. Fletcher appeared in *J. Med. Chem.*, **13**, 567 (1970). (c) A preliminary communication regarding this work, paper XXXI, was published in *Chem. Commun.*, 1052 (1969), by M. J. Namkung and T. L. Fletcher. (d) Biological results will be reported elsewhere.

SCHEME I



As described in the Experimental Section, 2,2′-azoxyfluorenes (**2b**, **2c**, and **2e**) (Scheme I), were made by the literature method[2] for **2a**, from the corresponding 2-nitrofluorenes (**5b**,[3] **5c**,[4] and **5e**[5]). In general, the hydrazofluorenes were made by a modified literature method,[6] by reduction of the corresponding azoxyfluorenes.

Hydrazo compounds **1a** and **1b**, in benzene, were quantitatively converted to azo compounds **3a** and **3b** by passing the solutions through alumina. Compounds **1a** and **1b** were also converted to **3a** and **3b**, with 1 equiv of *m*-chloroperoxybenzoic acid.[7] With an excess of this oxidant the azoxy compounds **2a** and **2b** were obtained.[8] Oxidation of **1c** with 1 equiv of *m*-chloroperoxybenzoic acid gave a mixture of the azo and the azoxy compounds **3c** and **2c**; with an excess of the oxidant **1c** gave pure **2c**. Pure **3c** was obtained from **1c** using 1-chlorobenzotriazole.[7,9]

As we reported for **1a**,[1c] compound **1b**, heated in alcoholic hydrochloric acid, gave **3b** and **4b**, the disproportionation products, quantitatively.[10] We were not able to alter **1c** in this way because of low solubility; however, **1c** boiled in a mixture of toluene and pyridine gave disproportionation products only. Neither alcoholic hydrochloric acid nor alcoholic potassium hydroxide nor boiling toluene–pyridine had any effect on **1d**.

In contrast, N^1-2-fluorenyl-N^2-phenylhydrazine (**7**), with alcoholic acid, gave a mixture which appeared to be free of the disproportionation product, 2-fluorenylazobenzene (**8**).

Table I gives uv absorptions for those azo and azoxy compounds which had sufficient solubility to give meaningful spectra, both in the trans form and after illumination (cis). Table II shows the per cent return of ab-

TABLE I

ABSORPTION MAXIMA[a] FOR AZO AND AZOXY COMPOUNDS

Azo compds			Azoxy compds		
Compd no.	For solutions kept in the dark (trans), λ_{max}, mμ (log ϵ)[b]	Solutions after illumination (cis), λ_{max}, mμ (log ϵ)[c]	Compd no.	For solutions kept in the dark (trans), λ_{max}, mμ (log ϵ)[b]	Solutions after illumination (cis), λ_{max}, mμ (log ϵ)[c]
3a	249 (4.21)	254 (4.25) s[d]	**2a**	245 (4.28)	250 (4.45)
	262 (4.16) s	276 (4.38)		379 (4.60)	255 (4.45) s
	292 (3.84) s	330 (4.17)			269 (4.37) s
	384 (4.69)	383 (4.10)			302 (4.20)
	396 (4.64) s	396 (4.06) s			377 (4.45)
3b	245 (4.24)	254 (4.27) s	**2b**	242 (4.29)	256 (4.32)
	383.5 (4.67)	272 (4.35)		377.5 (4.56)	306 (4.10)
		325 (4.18)			376 (4.36)
		382 (4.13)			
		398 (4.08) s			
		460 (3.70) s			
			2e	248 (4.31)	258 (4.34)
				384 (4.62)	270 (4.33) s
					306 (4.14)
					382 (4.38)
8	236 (4.06)	245 (4.10)	**9**	234 (4.07)	234 (4.04) s
	252 (3.99) s	270 (4.17)		240 (4.07) s	266 (4.14)
	262 (3.93) s	309 (4.02)		260 (3.98) s	304 (3.95) s
	362 (4.52)	437 (3.41)		354 (4.41)	361 (4.16)
	438 (3.17)				434 (3.63) s

[a] Ultraviolet and visible absorption spectra were obtained on a Beckman DK-1 automatic recording spectrophotometer in acetonitrile solution. The concentration was 2×10^{-5} *M* in all cases. [b] Solutions were kept in the dark for 40–60 hr, until no further change was observed, to obtain the highest possible maxima. [c] Values for the cis forms were obtained from solutions which had been illuminated for 4–6 hr by ultraviolet light from G. E. purple X bulbs 5 in. from the flask, with cooling by a stream of air from a portable air conditioner. [d] s = shoulder.

(2) F. E. Cislak, I. M. Eastman, and J. K. Senior, *J. Amer. Chem. Soc.*, **49**, 2318 (1927).

(3) J. A. Miller, R. B. Sandin, E. C. Miller, and H. P. Rusch, *Cancer Res.*, **15**, 188 (1955).

(4) N. Ishikawa and M. Okawaki, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 467 (1958).

(5) H. Bryant and E. Sawicki, *J. Org. Chem.*, **21**, 1322 (1956).

(6) S. Pietra and M. Res, *Ann. Chim.* (Rome), **48**, 299 (1958).

(7) Aldrich Chemical Co., Milwaukee, Wis. The *m*-chloroperoxybenzoic acid was 85% pure. Mol calculations are on this basis.

(8) It is also of interest to note that **1a** was oxidized to **2a** when it was heated in dimethyl sulfoxide to 110°; the azo compound, **3a**, was inert under these conditions.

(9) C. W. Rees and R. C. Storr, *J. Chem. Soc.*, 1474 (1969).

(10) Because some hydrazo compounds have been shown to disproportionate less at lower temperatures[11,12] than in boiling alcoholic HCl, we dissolved **1a** in acetonitrile or in *p*-dioxane at 27° and added hydrochloric acid to each. Both solutions turned to a deep reddish purple immediately. The color faded in each case (16–24 hr) and only disproportionation products were found.

(11) D. V. Banthorpe, A. Cooper, and C. K. Ingold, *Nature*, **216**, 232 (1967).

(12) H. J. Shine and J. P. Stanley, *J. Org. Chem.*, **32**, 905 (1967).

sorption maxima at 382 mμ [for **8** and 2-fluorenylazoxybenzene (**9**) these maxima are at ~360 mμ] from the fully illuminated state to the relaxed state.[13]

TABLE II

COMPARISON OF TIMES FOR CIS TO TRANS REVERSION,[a] AFTER ILLUMINATION FOR AZO AND AZOXY COMPOUNDS

Azo compds			Azoxy compds		
	% return			% return	
Compd no.	1 hr	4 hr	Compd no.	1 hr	4 hr
3a	53	77	**2a**	24	37
3b	31	75	**2b**	9	15
			2e	27	51
8	6	15	**9**	5	14

[a] Per cent return = 100 × absorbance change for a given time interval/total absorbance change (trans → cis) calculated for the peak which showed the largest difference in absorbance upon prolonged illumination in acetonitrile solution [see A. J. Ryan, *Tetrahedron*, **20**, 1547 (1964)].

Table III gives absorption maxima for hydrazo compounds and their mono-*N*-acetyl derivatives.

TABLE III

ABSORPTION MAXIMA[a] FOR HYDRAZO AND MONO-*N*-ACETYLHYDRAZO COMPOUNDS

Hydrazo compds[b]		Mono-*N*-acetylhydrazo compds	
Compd no.	λ_{max}, mμ (log ε)	Compd no.	λ_{max}, mμ (log ε)
1a	297 (4.59)	**6a**	278 (4.45)
	322 (4.39) s[c]		300 (4.33) s
	383 (3.85)		383 (4.17)
1b	281 (4.45) s		
	295 (4.52)		
	323 (4.22) s		
	384 (3.99)		
	398 (3.94) s		
1c	291 (4.50)	**6c**	280 (4.54)
	329 (4.01)		308.5 (4.26) s
	408.5 (3.65)		382 (3.95)
			396 (3.90) s
1d	288 (4.62)		
	332 (3.94)		
		6e	279 (4.65) s
			287 (4.68)
			304 (4.43) s
			314 (4.35) s
			385 (3.57)
7[b]	290 (4.42)	**10**[d]	278 (4.33)
	322 (4.03) s		301 (4.18)
	356 (3.45)		

[a] See *a* in Table I. [b] Solutions of **1a** and **1b** deepened in color upon standing, and the spectra of these compounds changed to those of the azo compounds **2a** and **2b** (complete in about 30 hr as measured by optical density at ~382 mμ). Compound **7** (*N'*-2-fluorenyl-N^2-phenylhydrazine) changed more slowly (~50 hr to completion). This appears to represent simple oxidation and not disproportionation, which also seems to be the case when solutions of these hydrazo compounds are passed through an alumina column. [c] s = shoulder. [d] *N'*-Acetyl-*N'*-2-fluorenyl-N^2-phenylhydrazine.

Experimental Section

7,7'-Difluoro-2,2'-azoxyfluorene (2b).—This compound was prepared by reduction of **5b** with Zn dust and $CaCl_2$ according to the reported method for **2a**.[2]

7,7'-Dimethoxy-2,2'-azoxyfluorene (2c) and 7,7'-Acetoxy-2,2'-azoxyfluorene (2e).—A stirred mixture of 12 g of **5c** or **5e**, 4 g of $CaCl_2$ in 5 ml of water, 10 g of Zn dust, and 200 ml of ethanol was refluxed for 2 hr. The precipitate, isolated from the cooled reaction mixture, was extracted with *o*-dichlorobenzene (for **2c**) or *p*-dioxane (for **2e**). The concentrated, cooled extract yielded the product.

2,2'-Hydrazofluorene (1a), 7,7'-Difluoro-2,2'-hydrazofluorene (1b), 7,7'-Dimethoxy-2,2'-hydrazofluorene (1c), and 7,7'-Dihydroxy-2,2'-hydrazofluorene (1d).—These compounds were prepared by reduction of **2a**, **2b**, **2c**, and **2e**,[15] respectively, in hot (80°) pyridine using hydrazine hydrate (100%) and an alcoholic slurry of Ru on C (5%) as described in detail for **1a** earlier.[16c] The isolation of **1c** was done under N_2.

2,2'-Azofluorene (3a)[16] and 7,7'-Difluoro-2,2'-azofluorene (3b). A. Alumina Oxidation.—Elution of a benzene solution (0.5 g, 500 ml) of **1a** and **1b** from an alumina column gave **3a** and **3b**, respectively.

B. *m*-Chloroperoxybenzoic Acid Oxidation.—To a solution of 0.0025 mol of either **1a** or **1b** in 100 ml of hot (100°) toluene was added 0.0025 mol[7] of *m*-chloroperoxybenzoic acid in 50 ml of toluene during a 10-min period. The mixture was boiled for 10 min, kept overnight, and filtered to give either **3a** (78%) or **3b** (88%).

7,7'-Dimethoxy-2,2'-azofluorene (3c).—To a stirred solution of 0.1 g (0.24 mmol) of **1c** in 30 ml of methylene chloride (35°) under N_2, 0.04 g (0.26 mmol) of 1-chlorobenzotriazole was added. The solution darkened and 0.08 g of a yellow compound (**3c**) precipitated.

Disproportionation of Hydrazo Compounds (1a–c). A. With Alcoholic HCl.—A mixture of 3.6 g of **1a** or 4.0 g of **1b**, 1 l. of ethanol, and 25 ml of conc HCl was boiled under reflux for 1 hr and cooled to room temperature. The precipitate was filtered off and washed with alcohol, giving 1.77 g (99%) of **3a**, mp 294–298°, or 2.0 g (100%) of **3b**, mp 275–280°. The filtrate was concentrated to ~50 ml and basified with NH_4OH. The white precipitate was filtered and dried giving 1.8 g (99%) of **4a**, mp 125–128°, or 2.0 g (100%) of **4b**, mp 135–136°. A mixture with the authentic compound[3] melted at 135–136°.

Similar results were also obtained for compounds **1a** and **1b** at a somewhat lower temperature (boiling methanolic HCl).[10]

B. With Pyridine in Boiling Toluene.—A mixture of 0.2 g of **1c**, 30 ml of toluene, and 1 ml of pyridine was boiled for 15 min and cooled. The bright yellow precipitate was filtered off, washed with benzene, and dried, giving 0.1 g of **3c**. When the filtrate was concentrated a white precipitate came out which was filtered off and dried, giving 0.1 g of **4c**, mp 190–191°.[17]

Reduction of 2,2'-Hydrazofluorenes (1a–d) and 2,2'-Azoxyfluorenes (2a–c, 2e).—Suspensions of the hydrazo or the azoxy compounds (1 g) in 100 ml of toluene–ethanol (1:1) were treated with 2 ml of hydrazine hydrate (100%) and Pd on C (5%) and boiled 10 min to give 90–98% yields of the corresponding fluoren-2-amines (**4a**, mp 128–129°; **4b**,[3] mp 135–136°; **4c**,[17] mp 189–190°; **4d**,[18] mp 270–280° dec). Mixtures of all of these with authentic compounds melted without depression.

***N*-Acetyl-2,2'-hydrazofluorene (6a), *N*-Acetyl-7,7'-dimethoxy-2,2'-hydrazofluorene (6c), and *N*-Acetyl-7,7'-diacetoxy-2,2'-hydrazofluorene (6e).**—A solution of 2 g of either **1a**, **1c**, or **1d** in 50 ml of acetic anhydride was boiled for 1 min and cooled. A creamy, white precipitate was filtered off, washed with benzene,

(13) Other examples of extremely slow transformation of azo compounds were discussed recently.[14]

(14) N. Ishikawa, M. J. Namkung, and T. L. Fletcher, *J. Org. Chem.*, **30**, 3878 (1965); M. J. Namkung, N. K. Naimy, C.-A. Cole, N. Ishikawa, and T. L. Fletcher, *ibid.*, **35**, 728 (1970).

(15) Note that reduction of **2c** led also to deacetylation giving 7,7'-dihydroxy-2,2'-hydrazofluorene (**1d**).

(16) After our preliminary note on this work[16c] had been accepted, a paper describing preparation of 2,2'-azofluorene (**3a**) by condensation of 2-nitrosofluorene and **4a** appeared [Y. Yost, *J. Med. Chem.*, **12**, 961 (1969)]. We had abandoned this method, as noted,[16c] since the product of the reaction, even when prepared under nitrogen, invariably contained a substantial amount of the azoxy compound as revealed by mass spectroscopy (maximum peak). The product mixture from our nitrosoamine condensation melted as Yost reported for his product, with decomposition, below the melting point of **2a**. Actually the melting point of pure **3a** is about 20° higher than that of the azoxy compound. In addition, all of these azofluorenes are distinguishable from the azoxy compounds in that they melt without decomposition; the azoxy compounds all decompose at their melting points.

(17) J. H. Weisburger and E. K. Weisburger, *J. Chem. Soc.*, 758 (1954).

(18) F. Bielschowsky, *Biochem. J.*, **39**, 287 (1945).

TABLE IV

YIELDS AND PHYSICAL DATA FOR THE SYNTHESIZED COMPOUNDS

Compd no.	Yield, %	Crystd from[a]	Mp, °C[b]	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, %[b] C	Found, %[b] H	Found, %[b] N
1a	77	A	183–234	$C_{26}H_{20}N_2$	86.63	5.59	7.77[c]	86.50	5.54	7.97
1b	65.5	A	199–225	$C_{26}H_{18}F_2N_2$	78.77	5.48	7.07[d]	78.86	4.86	6.78
1c	88	B[e]	190–240	$C_{28}H_{24}N_2O_2$	79.97	5.75	6.66	79.79	5.83	6.83
1d	70	B	250–280	$C_{26}H_{20}N_2O_2$	79.57	5.14	7.14	79.57	5.28	7.17
2b	63	C	273–275 dec	$C_{26}H_{16}F_2N_2O$	76.08	3.93	6.83	76.23	3.87	6.85
2c	34	D	295–297 dec	$C_{28}H_{22}N_2O_3$	77.40	5.10		77.43	5.28	
2e	63	B	260–267 dec	$C_{30}H_{22}N_2O_5$	73.46	4.52	5.71	73.78	4.57	5.67
3a	80[f]	C	299–300	$C_{26}H_{18}N_2$	87.12	5.06	7.82	86.85	5.41	7.67
3b	88[g]	C	275–280	$C_{26}H_{16}F_2N_2$	79.17	4.09	7.10	79.15	4.28	7.01
3c	100[h]	C	288–290	$C_{28}H_{22}N_2O_2$	80.35	5.30	6.69	80.30	5.14	6.85
6a	94	B	215–240	$C_{28}H_{22}N_2O$	83.55	5.51	6.96	83.57	5.55	6.97
6c	73	B	203–213	$C_{30}H_{26}N_2O_3$	77.90	5.67	6.06	77.70	5.48	6.24
6e	76	B	195–222	$C_{32}H_{26}N_2O_5$			5.40			5.32
7	70	E	137–140	$C_{19}H_{16}N_2$	83.79	5.92	10.29	84.01	5.89	9.99
9	85	C	159–160	$C_{19}H_{14}N_2O$	79.70	4.93	9.78	79.91	5.03	9.97
10	88	E	220–221	$C_{21}H_{18}N_2O$	80.23	5.77	8.91	79.97	5.77	9.11

[a] Solvent key: A (pyridine), B (*p*-dioxane), C (toluene), D (*o*-dichlorobenene), E (ethanol). [b] Melting points were determined on a Fisher–Jones apparatus and are corrected to standards. The wide ranges indicate that melting depends on the temperature at which the substance is put on the plate. If put on within a degree of the top figure, the melting range is 1°. If put on at or below the lower figure, melting begins at the given point but spreads over a wider range. Microanalyses were determined by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and A. Bernhardt, Elbach über Engelskirchen, West Germany. [c] Calcd: mol wt, 360. Found: mol wt, 365. [d] Calcd: F, 9.58. Found: F, 9.34. [e] Under N_2 atmosphere. [f] Obtained from Al_2O_3 oxidation of **1a**. [g] Obtained from the oxidation of **1b** with an equivalent amount of *m*-chloroperoxybenzoic acid. [h] Obtained from the disproportionation reaction of **1c**.

and dried giving **6a**, **6c**, or **6e**.[19] Attempts to monoacetylate **1b** or, by prolonged boiling, to diacetylate **1a** produced the corresponding azo compound in each case.

Reduction of 2,2′-Azoxyfluorene (2a) with Phenylhydrazine.—A mixture of 1 g of **2a** and 10 g of phenylhydrazine was heated to 225° for 30 min. At 165°, evolution of gas began. The resulting oil was cooled and poured into water to form a white precipitate, which was filtered off and dried to give 0.85 g (90%) of **4a**, mp 125–127°.

2-Fluorenylazobenzene (8).—To a solution of 1.8 g (0.01 mol) of **4a** in 40 ml of ethanol, 1.1 g (0.0103 mol) of nitrosobenzene and 2 ml of glacial acetic acid were added. The mixture was heated to 50° and allowed to cool. The precipitate was filtered off and recrystallized from ethanol giving 2.6 g (95%) of **8**, mp 174–175° (lit.[20] mp 173–174°).

N^1-2-Fluorenyl-N^2-phenylhydrazine (7).—A solution of 1.35 g of **8** in 10 ml of pyridine was treated with 10 mg of Ru on C (5%) and 1 ml of hydrazine hydrate (100%) and boiled until the solution was decolorized (5 min). After filtration, the solution was concentrated to 5 ml. Addition of 30 ml of petroleum ether (bp 30–60°), brought out 0.95 g of **7**, mp 137–139°.

N^1-Acetyl-N^1-2-fluorenyl-N^2-phenylhydrazine (10).—Acetylation, as above, of 2.7 g of **7** gave 2.75 g of **10**, mp, 318–321°.[21]

***N*-2-Fluorenylazoxybenzene (9).**—A solution of 2 g (0.0074 mol) of **7** in 50 ml of toluene was treated with 2 g (0.01 mol) of *m*-chloroperoxybenzoic acid, boiled for 10 min, and cooled. The yellow precipitate was filtered off, washed with ethanol, and dried, giving 1.8 g of **9**, mp 159–160°.

Registry No.—**1a**, 24247-79-8; **1b**, 26319-77-7; **1c**, 26319-78-8; **1d**, 26319-79-9; **2a** (*cis*), 26332-74-1; **2a** (*trans*), 26332-70-7; **2b** (*cis*), 26332-75-2; **2b** (*trans*), 26395-33-5; **2c**, 26319-80-2; **2e** (*cis*), 26332-76-3; **2e** (*trans*), 26347-40-0; **3a** (*cis*), 26332-77-4; **3a** (*trans*), 26332-71-8; **3b** (*cis*), 26332-78-5; **3b** (*trans*), 26332-72-9; **3c**, 26347-41-1; **4a**, 153-78-6; **4b**, 363-16-6; **6a**, 24225-71-6; **6c**, 26319-84-6; **6e**, 26319-85-7; **7**, 26319-86-8; **8** (*cis*), 26332-79-6; **8** (*trans*), 26347-42-2; **9** (*cis*), 26332-80-9; **9** (*trans*), 26332-73-0; **10**, 26319-87-9.

Acknowledgment.—The authors are greatly indebted to Miss Carol-Ann Cole for the uv studies.

(19) All of the mono-*N*-acetylhydrazo compounds were obtained analytically pure with respect to C, H, and N. However, in no case were values for *N*-acetyl correct or anywhere near correct. With **6a** this was true for two different commercial analysts. However, we were able to analyze indirectly for *N*-Ac by reductive splitting, thus recovering an equivalent of *N*-acetylated amine within reasonable limits of theoretical values. As a check on this anomalous situation we made the known mono-*N*-acetylhydrazobenzene. *N*-acetyl values for this otherwise analytically pure compound also were abnormally low (Calcd: 19.03. Found: 14.26).

(20) O. M. Friedman, R. M. Gofstein, and A. M. Seligman, *J. Amer. Chem. Soc.*, **71**, 3010 (1949).

(21) None of the other possible mono-*N*-acetyl isomer was detected. Reductive splitting of **10** led to a quantitative yield of *N*-(2-fluorenyl)acetamide.

Assignment of Ketoxime Stereochemistry by a Nuclear Magnetic Resonance Method

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Received June 1, 1970

The classical method for determining the stereochemistry of ketoximes is based upon the preferential migration of the group anti to the oximino hydroxyl group during the Beckmann rearrangement. The shortcomings of this method for stereochemical assignment are well known.[1] Recent nmr studies have provided alternate and more generally reliable techniques for assigning configuration. In the method of Karabatsos,[2] nmr spectra were obtained in carbon tetra-

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(2) G. J. Karabatsos, R. A. Taller, and F. M. Vane, *J. Amer. Chem. Soc.*, **85**, 2326 (1963).