Syntheses and Ultraviolet Spectra of Aromatic Azo Compounds. IV. Naphthylazobenzene Derivatives

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In the previous papers¹⁻³) of this series it could be prepared conveniently by the reacwas shown that many azobenzene derivatives tions of the zinc chloride double salts of

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No.	Naphthyl	R	м. р., °Са)	Yield, % ^{b)}	Color	Found : N, %°)		
Ι	α-	н	66.5~67.5 ^d)	22	Red	12.00		
II	β-	н	81.5~82.5 ^e)	11	Orange	11.76		
III	α-	o-CH ₃	67~68 ^f)	7	Red	11.00		
IV*	β-	o-CH ₃	70~71	12	Orange	11.24		
V	α-	m-CH ₃	42~43 ^g)	23	Red	11.13		
VI*	β-	m-CH ₃	98~99.5	6	Orange yellow	11.03		
VII*	α-	p-CH ₃	81~82	20	Red	11.17		
VIII*	β-	p-CH ₃	126~127	7	Orange yellow	11.20		
IX*	α-	o-CH ₃ O	102~103	12	Red	10.92		
X	β-	o-CH₃O	93~94.5h)	11	Orange	10.88		
XI*	α-	<i>m</i> -CH₃O	55~56	12	Orange red	10.92		
XII*	β-	<i>m</i> -CH ₃ O	67~68	6.4	Orange yellow	10.40		
XIII*	α-	<i>p</i> -CH₃O	73~74.5	9	Orange red	10.42		
XIV*	β-	<i>p</i> -CH₃O	102~103	11	Orange	10.40		
XV*	α-	o-Br	103~104	3.5	Orange red	9.11		
XVI*	β-	o-Br	92.5~93	12	Orange yellow	9.08		
XVII*	α-	<i>m</i> -Br	84~85	4.2	Red	8.95		
XVIII*	β-	<i>m</i> -Br	117~118	12	Orange yellow	9.26		
XIX*	α-	<i>p</i> -Br	132~133	11.4	Orange red	9.23		
XX*	β-	<i>p</i> -Br	142.5~143	13	Orange red	8.85		

TABLE I. NAPHTHYLAZOBENZENES PREPARED BY THE REACTION:

* New compound

a) All temperatures in Tables I-III are uncorrected.

- b) Based on the bromo compound used to prepare the Grignard reagent.
- c) Calcd. % of N for naphthylazobenzene $C_{16}H_{12}N_2\ (I,\ II)$: 12.06.
 - Calcd. % of N for naphthylazotoluene $C_{17}H_{14}N_2$ (III-VIII) : 11.29.
 - Calcd. % of N for naphthylazoanisole $C_{17}H_{14}N_2O$ (IX-XIV) : 10.68.
 - Calcd. % of N for naphthylazobromobenzene $C_{16}H_{11}BrN_2$ (XV-XX) : 9.00.
- d) The reported m. p. of I is $63.5^{\circ}C^{4}$ or $70^{\circ}C^{5}$. It was prepared by the deamination of 4phenylazo-1-naphthylamine.
- The reported⁵) m. p. of II is 84°C. It was prepared by condensing nitrobenzene with β e) naphthylamine in the presence of sodium hydroxide at 180°C.
- f) The reported⁴⁾ m. p. of III is 52° C. It was synthesized by the deamination of 4-(o-tolylazo)-1-naphthylamine, which had been prepared by the coupling of o-toluenediazonium chloride with α -naphthylamine.
- g) The reported⁶⁾ m. p. of V is $43 \sim 44^{\circ}$ C. It was prepared by the reaction of N-sulfinyl- α naphthylamine with *m*-tolylhydroxylamine.
- h) The reported⁷) m. p. of X is 92.5°C. It was prepared by condensing o-nitroanisole with β -naphthylamine in the presence of sodium hydroxide at 170~180°C.

8) G. Kalischer, R. Müller and F. Frister, Friedl., 15, 716 (1925).

¹⁾ Part III: Y. Nomura, H. Anzai, R. Tarao and K. Shiomi, This Bulletin, 37, 967 (1964).

<sup>h10mi, 1 his Builetin, 37, 507 (1994).
2) Y. Nomura, ibid., 34, 1648 (1961).
3) Y. Nomura and H. Anzai, ibid., 35, 111 (1962).
4) R. Nietzki and R. Zehntner, Ber., 26, 143 (1893).
5) G. M. Badger and G. E. Lewis, J. Chem. Soc., 1953,</sup>

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⁶⁾ A. Michaelis and K. Petou, Ber., 31, 995 (1898).

⁷⁾ G. M. Badger and R. G. Buttery, J. Chem. Soc., 1954, 2243.

TABLE II. ETHYL NAPHTHYLAZOBENZOATES PREPARED BY THE REACTION :

	$+ MgBr + N = N - \langle + \rangle \longrightarrow + N = N - \langle + \rangle + MgBr^{+}$						
	•••		COOC ₂ H ₅		COOC ₂ H ₅		
No.	Naphthyl	$COOC_2H_5$	[M. p.], (B. p.), °C	Yield, % ^{a)}	Color	Found : N, % ^{b)}	
XXI*	α-	0-	(170/11 mmHg)	trace	Deep red	c)	
XXII*	β-	0-	oild)	1	Deep red	8.69	
XXIII*	α-	<i>m</i> -	[101~102]	25	Orange	9.40	
XXIV*	β-	<i>m</i> -	[88~89]	1	Orange	8.96	
XXV*	α-	р-	[88.5~89]	4	Orange	9.43	
XXVI*	β-	р-	[112.5~113.5]	trace	Orange	9.22	

* New compound

- a) Based on the α or β -bromonaphthalene used to prepare the Grignard reagent.
- b) Calcd. % of N for ethyl naphthylazobenzoate $C_{19}H_{16}N_2O_2$: 9.21.
- c) The yield was poor, and analytically pure sample could not be obtained after distillation in vacuo. However, its structure was confirmed by hydrolyzing it to the free acid (XXVII of Table III).



TABLE III. NAPHTHYLAZOBENZOIC ACIDS



V David

No.	Naphthyl	COOH	M. p., °C	Color	Found: N, % ^{a)}		
XXVII*	·α-	0-	141~142	Orange red	10.21		
XXVIII*	β-	0-	146~146.5	Orange yellow	10.01		
XXIX	α-	<i>m</i> -	207 and $> 320^{\text{b}}$	Orange	9.97		
XXX*	β-	<i>m</i> -	220~221	Orange yellow	10.02		
XXXI*	α-	<i>p</i> -	234~234.5	Orange	10.02		
XXXII*	β-	<i>p</i> -	220	Orange yellow	9.91		

* New compound

- a) Calcd. % of N for naphthylazobenzoic acid $C_{17}H_{12}N_2O_2$: 10.14.
- b) XXIX melted at 207°C and solidified above its melting point to needles, which did not melt even at 320°C. The reported⁸⁾ m. p. of XXIX is 207°C. It was prepared by the deamination of m-(4-amino-1-naphthylazo) benzoic acid, which had been obtained by coupling *m*-carboxybenzenediazonium chloride with α -naphthylamine.

TABLE IV. ELECTRONIC ABSORPTION MAXIMA OF NAPHTHYLAZOBENZENES IN ETHANOL

					K-1	banu					
No.	$\lambda, m\mu$	ε	$\lambda, m\mu$	ε	$\lambda, \widetilde{m\mu}$	ε	$\lambda, m\mu$	ε			
I	217.4	52300	270.0	12630	371.7	14390					
II	230.0*	23940	260.0*	10250	328.5	23970					
			264.2	13540							
			277.0	14420							
			287.5	14570							
III	214.7*	25840	256.9	5966	374.7	8199					
IV	229.1	21990	263.5	12280	332.4	23060	443.3	1028			
			277.6	12060							
			288.5	12320							
V			264.9	9938	371.5	12680					
			272.9*	9690							
			294.7	8101							
VI	230.0*	22880	265.9	12840	330.0	22370	440.0*	1228			
			277.6	13090							
			288.2	13350							
VII	215.3	40580	262.9	9220	373.5	12780					
			309.4	8498							
VIII	234.7	22020	262.3	12600	335.0	25510	450.0*	1295			
			278.8	12440							
			290.0	12720							

TABLE IV (Continued)

			K-Band						
No.	λ . m μ	ε	λ , m μ	ε	$\lambda, \widetilde{m\mu}$	ε	$\lambda, m\mu$	ε	
IX	,	-	270.0*	8773	385.0	12730			
			293.2	6120					
Х			263.2	12470	325.9	15820			
			278.5	11680	367.6	17140			
			289.4	11710					
XI			253.1*	12550	374.1	13620			
			292.4	7440					
XII			266.0*	13410	325.6	20430	460.0*	1018	
			276.9	12980					
			287.4	12930					
XIII			250.0*	9540	378.6	11480	490.0*	590	
			290.0*	3302					
XIV	242.4	22310	282.4	9582	345.9*	25780			
			294.1	9714	357.0	26400			
XV	245.9*	11990	268.2	9901	382.9	11820			
			276.5	9581					
			295.0*	7275					
XVI	251.8	14870	267.7*	13210	332.7	22760			
			278.3	12400					
			287.9	12040					
XVII			272.9*	9716	378.2	10680			
			276.5	9850					
3/3/111	005 0*	04410	285.9*	7746	220.0	26420			
XVIII	235.9*	24410	266.0	15250	330.9	26430			
			276.3	15940					
NIN	216 5	11(00	286.5	15610	270 1	15140			
XIX	216.5	44690	267.6	10760	3/9.1	15440			
			2/5.4	10810					
vv	221 5	22040	302.0	10270	225 4	28110			
ΛΛ	231.5	22040	203.3	12950	333.4	20110			
			278.2	13270					
XXII	236 5	18400	287.3	12000	325 9	19000			
XXIII	230.5	10400	275 3	9960	378.2	9020			
XXIV	238 2	24000	275.5	15900	330.0	22100			
	247.1	23000	287.1	14700	55010	22100			
	255.3	23500	20711	11100					
XXV	236.5	10400	276.5	15100	387.1	12500			
XXVI			268.2	15400	334.7	25200			
			277.7	15500					
			288.2	15100					
XXVII	238.7	12300	288.8	8030	372.4	11300			
XXVIII	237.6	18400	260.0	14200	330.0	19900			
			276.5	12500					
			288.8	12200					
XXIX	237.3	17600	293.5	7900	371.8	10600			
XXX	252.4	20900	275.9	12900	328.8	20200			
			288.2	12700					
XXXI	238.8	11900	263.8	11000	378.8	11800			
			300.0	8750					
XXXII			267.1	10200	337.1	22100			
			279.4	10400					
			290.9	10800					

* Wavelength of shoulder.

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diazonium chlorides with Grignard reagents. We would now like to report, in extension of this investigation, on the synthesis of naphthylazobenzenes and their derivatives by the same reaction.

 α - and β -Naphthylazobenzene (I, II) and their eighteen derivatives (III—XX) carrying a substituent such as methyl, methoxyl, or bromine on a benzene ring have been prepared by the reactions of the zinc chloride double salt of α - or β -naphthalenediazonium chloride with substituted phenylmagnesium bromides. They are summarized in Table I, in which new compounds are asterisked.

Six ethyl naphthylazobenzoates (XXI-XXVI) have been obtained by the reactions of the zinc chloride double salt of ethoxycarbonylbenzenediazonium chloride with α - or β -naphthylmagnesium bromide. They are all new compounds and are listed in Table II. By the hydrolysis of ethyl naphthylazobenzoates, the corresponding free acids (XXVII-XXXII) were prepared; they are listed in Table III.

The electronic absorption spectra of these naphthylazobenzenes were measured in ethanol solutions; their maxima are listed in Table IV.

The K-band of the α -naphthylazobenzene derivatives shifts towards a wavelength longer by about 45 m μ than that of the corresponding β -isomers, in spite of the β -naphthyl dyes having a considerably greater intensity. A similar difference of spectra between α - and β -naphthylazobenzene was pointed out and discussed theoretically by Robin and Simpson.⁹⁾

Experimental

The Preparation of Naphthylazobenzenes. $-\alpha$ -

9) M. B. Robin and W. T. Simpson, J. Chem. Phys., 36, 585 (1962).

and β -Naphthylazobenzene (I, II) and their derivatives (III—XXVI) were prepared by the method used in a previous paper.¹⁾ They have been summarized in Tables I and II.

m-(α -Naphthylazo)benzoic Acid (XXIX).—One gram of ethyl m-(α -naphthylazo)benzoate was dissolved in 10 ml. of ethanol containing 0.2 g. of sodium hydroxide. The solution was refluxed on a water bath for an hour, diluted with 50 ml. of water, and acidified with dilute hydrochloric acid to precipitate m-(α -naphthylazo)benzoic acid, which was then recrystallized from ethanol. The yield (0.9 g.) was almost that theoretically expected.

Other naphthylazobenzoic acids were also prepared by the hydrolysis of the corresponding ethyl esters. They have been summarized in Table III.

The Measurement of Spectra. — The absorption spectra were obtained in 95% ethanol as a solvent on a Cary Model 14 M self-recording spectrophotometer with 1 cm. quartz cells.

Summary

1) α - and β -Naphthylazobenzene and their twenty-four derivatives with a substituent on a benzene ring have been synthesized by the reactions of Grignard reagents with zinc chloride double salts of diazonium salts. Twenty-one of them are new compounds.

2) Six naphthylazobenzoic acids have been prepared by the hydrolysis of the corresponding ethyl esters; five of them are new compounds.

3) The ultraviolet and visible absorption spectra of these naphthylazobenzene derivatives have been measured.

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