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

By Yujiro NOMURA and Hiroyuki ANZAI

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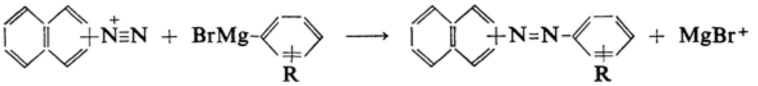
In the previous papers[1-3] of this series it was shown that many azobenzene derivatives could be prepared conveniently by the reactions of the zinc chloride double salts of

TABLE I. NAPHTHYLAZOBENZENES PREPARED BY THE REACTION:



No.	Naphthyl	R	M. p., °C[a]	Yield, %[b]	Color	Found: N, %[c]
I	α-	H	66.5∼67.5[d]	22	Red	12.00
II	β-	H	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_3O	102∼103	12	Red	10.92
X	β-	o-CH_3O	93∼94.5[h]	11	Orange	10.88
XI*	α-	m-CH_3O	55∼56	12	Orange red	10.92
XII*	β-	m-CH_3O	67∼68	6.4	Orange yellow	10.40
XIII*	α-	p-CH_3O	73∼74.5	9	Orange red	10.42
XIV*	β-	p-CH_3O	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-	m-Br	84∼85	4.2	Red	8.95
XVIII*	β-	m-Br	117∼118	12	Orange yellow	9.26
XIX*	α-	p-Br	132∼133	11.4	Orange red	9.23
XX*	β-	p-Br	142.5∼143	13	Orange red	8.85

* 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°C[4] or 70°C[5]. It was prepared by the deamination of 4-phenylazo-1-naphthylamine.

e) The reported[5] m. p. of II is 84°C. It was prepared by condensing nitrobenzene with β-naphthylamine in the presence of sodium hydroxide at 180°C.

f) The reported[4] 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 reported[6] m. p. of V is 43∼44°C. It was prepared by the reaction of N-sulfinyl-α-naphthylamine with m-tolylhydroxylamine.

h) The reported[7] 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.

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

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).

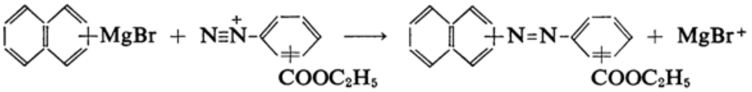
5) G. M. Badger and G. E. Lewis, *J. Chem. Soc.*, **1953**, 2151.

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

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

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

TABLE II. ETHYL NAPHTHYLAZOBENZOATES PREPARED BY THE REACTION:



No.	Naphthyl	$COOC_2H_5$	[M. p.], (B. p.), °C	Yield, %a)	Color	Found: N, %b)
XXI*	α-	o-	(170/11 mmHg)	trace	Deep red	—c)
XXII*	β-	o-	oild)	1	Deep red	8.69
XXIII*	α-	m-	[101∼102]	25	Orange	9.40
XXIV*	β-	m-	[88∼89]	1	Orange	8.96
XXV*	α-	p-	[88.5∼89]	4	Orange	9.43
XXVI*	β-	p-	[112.5∼113.5]	trace	Orange	9.22

* New compound

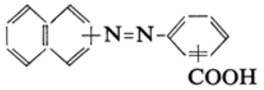
a) Based on the α- or β-bromonaphthalene used to prepare the Grignard reagent.

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).

d) Purified by column (alumina) chromatography.

TABLE III. NAPHTHYLAZOBENZOIC ACIDS



No.	Naphthyl	COOH	M. p., °C	Color	Found: N, %a)
XXVII*	α-	o-	141∼142	Orange red	10.21
XXVIII*	β-	o-	146∼146.5	Orange yellow	10.01
XXIX	α-	m-	207 and >320b)	Orange	9.97
XXX*	β-	m-	220∼221	Orange yellow	10.02
XXXI*	α-	p-	234∼234.5	Orange	10.02
XXXII*	β-	p-	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 reported[8] 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-Band			
No.	λ, mμ	ε	λ, mμ	ε	λ, mμ	ε	λ, mμ	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, mμ	ε	λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
IX			270.0*	8773	385.0	12730		
			293.2	6120				
X			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				
			285.9*	7746				
XVIII	235.9*	24410	266.0	15250	330.9	26430		
			276.3	15940				
			286.5	15610				
XIX	216.5	44690	267.6	10760	379.1	15440		
			275.4	10810				
			302.0	10270				
XX	231.5	22040	265.9	12350	335.4	28110		
			278.2	12950				
			288.8	13270				
XXII	236.5	18400	287.3	12000	325.9	19000		
XXIII			275.3	9960	378.2	9020		
XXIV	238.2	24000	274.7	15900	330.0	22100		
	247.1	23000	287.1	14700				
	255.3	23500						
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.

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 mμ 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.—α- 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.

Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo

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