Syntheses and Ultraviolet Spectra of Aromatic Azo Compounds.
III. Methoxyazobenzene Derivatives

By Yujiro NOMURA, Hiroyuki ANZAI, Ryokichi TARAO and Kengo SHIOMI

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In continuing our studies[1,2] of the synthesis of aromatic azo compounds by the reaction of diazonium salt with a Grignard compound, we wish in this paper to report on the synthesis of methoxyazobenzene derivatives.

Although several azobenzenes which have a methoxyl group at the ortho- or para-position with respect to the azo group are known, many other methoxyazobenzene derivatives have not hitherto been prepared.

Nine tolylazoanisoles (I—IX), six dimethoxyazobenzenes (X—XV), and six bromophenylazoanisoles (XVI—XXI) have been synthesized by the reactions of the zinc chloride double salts of diazonium chlorides with Grignard compounds following the procedure described in previous papers.[1,2] These azo compounds are listed in Table I, in which new compounds are asterisked. Although the yields of the azo compounds by this method were not always satisfactory, many of these azo compounds are also difficult to prepare by the method known hitherto.

The electronic absorption maxima of methoxyazobenzene derivatives are shown in Table II. It can be seen that the wavelengths of the *K*-bands of *m*-methoxyazobenzenes are shorter than those of the corresponding *o*- or *p*-isomers.

Experimental

2-(*o*-Tolylazo)anisole (I).—Following the procedure of a previous paper,[2] *o*-anisidine was diazotized and precipitated as the zinc chloride double salt by adding solid zinc chloride to the diazotized solution.

The suspension of 21.5 g. (0.09 mol.) of the dry powdered double salt in ether was vigorously stirred, and the ethereal solution of *o*-tolylmagnesium bromide prepared from 12 g. (0.07 mol.) of *o*-bromotoluene and the excess of magnesium was added slowly to it at the rate necessary to maintain reflux. After the mixture had been stirred for an additional 60 min. at room temperature, the deep red ether solution was separated by filtration with suction from the solid, which was then washed several times with ether. The ether filtrate and washings were combined and washed with dilute hydrochloric acid and then with water, dried over anhydrous sodium sulfate, and evaporated. The remaining crude azo compound (5.2 g.) was recrystallized twice from ethanol and then from petroleum ether (b. p. 40~60°C) to give orange crystals; m. p. 73.5~75°C; yield, 2.8 g. (18% theoretical based on *o*-bromotoluene).

2-(*p*-Tolylazo)anisole (III).—The brown red oil (2.6 g.) was obtained by the reaction of the zinc chloride double salt of *o*-methoxybenzenediazonium chloride (23.4 g., 0.098 mol.) with *p*-tolylmagnesium bromide (prepared from 0.07 mol. of *p*-bromotoluene). The oil was dissolved in petroleum ether (b. p. 40~60°C) and passed through a 40 cm. alumina column. The same solvent was employed as the eluent. Colorless crystals (0.1 g.) were isolated from the early fractions, which were identified as 4, 4′-dimethoxybiphenyl by melting point and mixed melting point determinations with an authentic sample. Deep red crystals (1.7 g., 11%) were obtained from the red elute; m. p. 56~57°C.

3-(*m*-Tolylazo)anisole (V).—The deep red oil (9.3 g.) was obtained by the reaction of the zinc chloride double salt of *m*-methoxybenzenediazonium chloride (23.9 g., 0.1 mol.) with *m*-tolylmagnesium bromide (prepared from 0.09 mol. of *m*-bromotoluene). The crude oil was extracted by petroleum ether (b. p. 40~60°C). The petroleum ether solution was evaporated and the remaining oil was distilled in vacuo to yield 4.1 g. (20%) of the azo compound (b. p. 168°C/6 mmHg), which could not be induced to crystallize.

Summary

1) Nine tolylazoanisoles, six dimethoxyazobenzenes, and six bromophenylazoanisoles have been synthesized by the reactions of Grignard reagents with zinc chloride double salts of diazonium compounds; thirteen of them are new compounds.

2) The ultraviolet and visible absorption spectra of the methoxyazobenzene derivatives have been measured, and some regularities of the absorption maxima have been observed in them.

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[1] Y. Nomura, This Bulletin, 34, 1648 (1961).
[2] Y. Nomura and H. Anzai, ibid., 35, 111 (1962).
[3] R. C. Farmer and A. Hantzsch. *Ber.*, 32, 3097 (1899).
[4] H. Wieland, ibid., 48, 1107 (1915).
[5] B. M. Bogoslovskii, *J. Gen. Chem.*, 16, 193 (1946); cf. *Chem. Abstr.*, 41, 104*i* (1947).
[6] Th. Rotarski, *Ber.*, 41, 865 (1908).
[7] K. Kinoshita, This Bulletin, 32, 777 (1959).
[8] Si-Jung Yeh and H. H. Jaffé, *J. Am. Chem. Soc.*, 81, 3274 (1959).
[9] G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 1954, 2243.

TABLE I. METHOXYAZOBENZENES PREPARED BY THE REACTION :

No.	R	R′	[M. p.], (B. p.)[a]	Yield, %[b]	Color	Found : N, %[c]
I*	2-CH_3	2′-CH_3O	[73.5∼75°C]	18	Orange	12.34
II*	3-CH_3	2′-CH_3O	(176°C/6 mmHg)	11	Deep red	12.37
III*	4-CH_3	2′-CH_3O	[56∼57°C]	11	Orange	12.14
IV*	2-CH_3	3′-CH_3O	(160∼165°C/7 mmHg)	29	Deep red	12.18
V*	3-CH_3	3′-CH_3O	(168°C/6 mmHg)	20	Deep red	12.44
VI*	4-CH_3	3′-CH_3O	[78∼79°C]	14	Orange yellow	12.43
VII	2-CH_3	4′-CH_3O	(173°C/6 mmHg) [58∼59°C][d]	8.9	Deep red	12.15
VIII*	3-CH_3	4′-CH_3O	(171°C/6 mmHg) [56∼57°C]	4.0	Orange	12.16
IX	4-CH_3	4′-CH_3O	[109∼110°C][e]	13	Orange yellow	12.18
X	2-CH_3O	2′-CH_3O	[143∼144°C][f]	1.4	Orange	11.16
XI*	3-CH_3O	2′-CH_3O	167°C/6 mmHg]	11.3	Deep red	11.50
XII*	4-CH_3O	2′-CH_3O	(165∼172°C/ 6.5 mmHg) [41∼42°C]	7.3	Deep red	11.62
XIII	3-CH_3O	3′-CH_3O	[77∼77.3°C][g]	7.6	Orange yellow	11.79
XIV*	3-CH_3O	4′-CH_3O	[41∼42°C]	34	Orange yellow	11.39
XV	4-CH_3O	4′-CH_3O	[145∼155°C][h]	6.9	Yellow	11.26
XVI*	2-CH_3O	3′-Br	[65∼65.5°C]	8.8	Orange	9.50
XVII*	3-Br	3′-CH_3O	[86∼87°C]	17.1	Yellow	9.76
XVIII	4-CH_3O	3′-Br	[59∼60°C][i]	10.3	Orange red	9.60
XIX	2-CH_3O	4′-Br	[81.5∼82.5°C][j]	2.0	Orange	9.45
XX*	3-CH_3O	4′-Br	[88.5∼89.5°C]	0.9	Orange	9.58
XXI	4-CH_3O	4′-Br	[146∼146.5°C][k]	14	Yellow	9.54

* New compound

a) M. p. and b. p. are uncorrected.

b) Based on the bromo compound used to prepared the Grignard reagent.

c) Calcd. % of N for tolylazoanisole $C_{14}H_{14}N_2O$ (I—IX) : 12.38.
Calcd. % of N for dimethoxyazobenzene $C_{14}H_{14}N_2O_2$ (X—XV) : 11.56.
Calcd. % of N for bromophenylazoanisole $C_{13}H_{11}BrN_2O$ (XVI—XXI) : 9.62.

d) The reported[3] m. p. of VII is 59°C ; it was prepared by the condensation of *o*-nitrosotoluene with *p*-anisidine.

e) The reported[4] m. p. of IX is 110∼111°C ; it was prepared by the condensation of *p*-nitrosotoluene with *p*-anisidine.

f) The reported[5] m. p. of X is 153∼153.5°C ; it was prepared by the decomposition of *o*-methoxybenzenediazonium chloride in the presence of cuprous chloride.

g) The reported[6] m. p. of XIII is 76∼77°C ; it was synthesized by the reduction of *m*-azoxyanisole, which was prepared from *m*-nitroanisole.

h) The reported[7] m. p. of XV is 162∼163°C ; it was prepared by the air oxidation of *p*-anisidine in pyridine containing cuprous chloride.

i) The repored[8] m. p. of XVIII is 62∼63°C ; it was synthesized by the methylation of 4-(*m*-bromophenylazo)phenol, which was prepared by the coupling of *m*-bromobenzenediazonium chloride with phenol.

j) The reported[9] m. p. of XIX is 83°C ; it was synthesized by heating the mixture of *o*-nitroanisole and *p*-bromoaniline with powdered sodium hydroxide.

k) The reported[8] m. p. of XXI is 148∼149°C ; it was prepared by the methylation of 4-(*p*-bromophenylazo)phenol.

TABLE II. ELECTRONIC ABSORPTION MAXIMA OF METHOXYAZOBENZENES IN ETHANOL

	λ, mμ	ε	K-band		λ, mμ	ε
			λ, mμ	ε		
I	238.5	8815	316.0	7382	435.0	1127
			352.0	7382		
II	236.3	9102	311.0	7837	435.0	1077
			353.0*	6920		
III	239.3	9852	320.0	9124	433.0	1355
			340.0*	8816		
			356.0	8559		
IV	237.0	10470	323.5	12360	440.0	773.7
V	236.0	11310	318.0	14390	435.5	782.4
VI	237.0	12180	325.6	16370	437.5	966.1
VII	239.0	11340	347.0	15470	402.5	1271
VIII	237.8	12650	344.6	20370	437.0	2009
IX	239.0	12120	346.0	21330	435.0	1428
X	243.5	8870	310.0	5059	445.0*	1537
			371.0	5497		
XI	241.5	9641	313.0	7370	430.0*	1151
			357.0	7126		
XII	242.0	11910	363.5	16600	435.0*	1943
XIII	242.9	11350	316.0	12530	436.0	881.2
XIV	243.0	13480	349.0	20260	434.0	1251
XV	241.0	12980	354.0	18370	430.0*	2160
	245.0*	12850				
XVI	238.0*	10230	315.0	9920	435.0*	1042
			363.0	8782		
XVII	237.7	11930	316.0	14660	436.0	794.7
XVIII	241.5	12780	350.0	18790	437.0	1277
XIX	239.0	9540	316.0	9700		
			364.0	8780		
XX	237.0	12200	323.0	17700	432.0	1180
XXI	241.0	6018	351.0	9511	438.0	1509
	245.5	5982				

* Wavelength of shoulder.

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