Syntheses and Ultraviolet Spectra of Aromatic Azo Compounds. II. Azobenzenecarboxylic Acids, Methylazobenzenecarboxylic Acids and their Ethyl Esters

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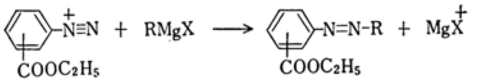
In the preceding paper of this series[1] the syntheses of twelve bromomethylazobenzenes involving ten new substances by reactions of Grignard reagents with the zinc chloride double salts of diazonium chlorides were reported. We would now like to report our extension of this investigations with the aim of preparing a number of new azobenzene derivatives carrying an ethoxycarbonyl or carboxyl group.

In the reaction of Grignard reagent with ethoxycarbonylbenzenediazonium ion, it was considered that not only the reaction 1 but also the reaction 2 or/and 3 might occur simultaneously in whichever ethoxycarbonyl group was attacked by a Grignard reagent.

Fortunately, however, the azo compound formed by 1 could be readily isolated from the ether solution of the reaction mixture, since the reaction products by 2 and 3 are insoluble in the ether employed as a solvent in this reaction.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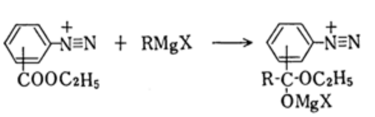
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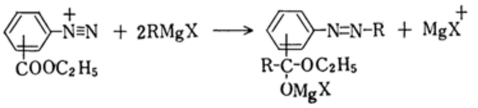
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General Procedure.—The suspension of 1.25 mol. of the zinc chloride double salt of ethoxycarbonylbenzenediazonium chloride in ether was vigorously stirred and the ethereal solution of phenyl- or tolylmagnesium bromide prepared from 1 mol. of bromobenzene or bromotoluene and the excess of magnesium was added slowly to it at a rate necessary to maintain reflux. The mixture was stirred for an additional 60 min. at room temperature,

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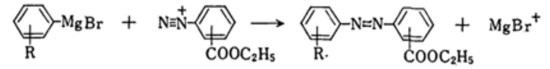
[1] Y. Nomura, This Bulletin, 34, 1648 (1960).

TABLE I. ETHYL AZOBENZENECARBOXYLATES PREPARED BY THE REACTION:



	R	$COOC_2H_5$	[M. p.], (B. p.)[a]	Color	Found: N, %[b]	Yield, %[c]
I	H	2-	(ca. 200°C/18 mmHg)	Red	—[d]	—[d]
II	H	3-	(210°C/25 mmHg)[e]	Red	11.29	42.8
III	H	4-	[83.5~84°C][f]	Red	11.02	42.4
IV	$2'-CH_3$	2-	(200°C/9 mmHg)	Deep red	10.85	36.3
V	$2'-CH_3$	3-	[36~37°C]	Red	10.32	56.5
VI	$2'-CH_3$	4-	[59~60°C]	Orange red	10.70	63.0
VII	$3'-CH_3$	2-	(195°C/9 mmHg)	Deep red	9.72	45.0
VIII	$3'-CH_3$	3-	(220°C/15 mmHg)	Deep red	10.01	53.0
IX	$3'-CH_3$	4-	[76~77°C]	Orange red	10.86	42.5
X	$4'-CH_3$	2-	(205°C/15 mmHg)	Deep red	9.72	49.5
XI	$4'-CH_3$	3-	[72~73°C]	Orange yellow	10.22	47.7
XII	$4'-CH_3$	4-	[102.5~103.5°C]	Orange	10.60	45.3

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

b Calcd. N % for ethyl azobenzenecarboxylate $C_{15}H_{14}N_2O_2$ (I—III): 11.02.
Calcd. N % for ethyl methylazobenzenecarboxylate $C_{16}H_{16}N_2O_2$ (IV—XII): 10.44.

c Based on bromobenzene or bromotoluene used to prepare Grignard reagent.

d The yield was poor, and an analytically pure sample could not be obtained even after repeated distillation in vacuo. Its structure was confirmed, however, by converting it to the known free acid (XIII).

e The reported[2)] b. p. of II is 248°C/38 mmHg; it was prepared by the esterification of azobenzene-3-carboxylic acid.

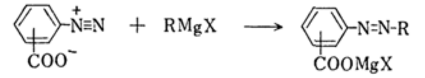
f The reported[3)] m. p. of III is 85~86°C; it was prepared from silver azobenzene-4-carboxylate and ethyl iodide.

and the dark red ether solution was then separated by filtration with suction from the unreacted diazonium salt and solid products, which were washed several times with ether. The ether filtrate and washings were combined and washed with dilute hydrochloric acid and then with water, dried and evaporated to get azo compounds as red crystals or oil, which were purified either by recrystallization from alcohol and then from ligroin or by distillation under reduced pressure, depending on their nature.

The ethyl azobenzenecarboxylates prepared by this method are shown in Table I. They are all new compounds except ethyl azobenzene-3-carboxylate (II) and 4-carboxylate (III).

Azobenzenecarboxylic acids and methylazobenzenecarboxylic acids, which were prepared by the hydrolysis of the corresponding ethyl esters in almost quantitative yields, are listed in Table II.

An attempt to prepare azobenzenecarboxylic acid from diazotized aminobenzoic acid and Grignard reagent in ether was fruitless. The ether layer remained almost colorless when the Grignard reagent was added to the suspension of diazonium salt in ether, while diazonium salt turned red brown and from it only a trace amount of azobenzenecarboxylic acid was isolated. The formation of ether-insoluble magnesium salt of azobenzenecarboxylic acid according to reaction 4 and the covering of the surface of solid diazonium salt by it was considered to be responsible for such a poor yield of azo compound.



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The wavelength and the molecular extinction coefficients, ε, of the absorption maxima of ethyl azobenzenecarboxylates and their free acids are listed in Table III.

Experimental

Zinc Chloride Double Salt of Ethoxycarbonylbenzenediazonium Chloride. — Following the procedure described in the previous paper[1)], the mixture of ethyl aminobenzoate (1 mol.) and 6 N hydrochloric acid (3 mol.) was diazotized at 0°C with aqueous sodium nitrite, and zinc chloride double salt was precipitated by adding solid zinc chloride (0.65 mol.) to the diazotized solution. Thus, from 16.5 g. of ethyl *p*-aminobenzoate, 67 ml. of 6 N hydrochloric acid and 7 g. of zinc chloride 21.8 g. of the double salt in the form of colorless crystals was obtained. In the same way, from 13.2 g. of ethyl *m*-aminobenzoate and 18.2 g. of ethyl *o*-aminobenzoate 22.0 and 24.0 g. of the respective double salt were obtained.

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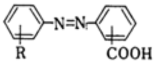
2) M. H. Duval, *Bull. soc. chim. France* [4], **11**, 19 (1912).

3) P. Jacobson and A. Steinbrenk, *Ann.*, **303**, 387 (1899).

TABLE II. AZOBENZENECARBOXYLIC ACIDS



	R	COOH	M. p., °C[a]	Color	Found : N, %[b]
XIII	H	2-	95[c]	Yellow	12.41
XIV	H	3-	168.5～169[d]	Orange yellow	12.47
XV	H	4-	237.5～238.5[e]	Orange	12.09
XVI	2'-CH_3	2-	138	Orange	11.74
XVII	2'-CH_3	3-	162.5～163	Orange	11.46
XVIII	2'-CH_3	4-	231～232	Orange	11.66
XIX	3'-CH_3	2-	97～ 98	Yellow	11.69
XX	3'-CH_3	3-	164～165	Orange yellow	11.48
XXI	3'-CH_3	4-	211～213	Orange	11.67
XXII	4'-CH_3	2-	116～117[f]	Yellow	11.38
XXIII	4'-CH_3	3-	200～201[g]	Yellow	11.61
XXIV	4'-CH_3	4-	330	Orange	11.86

a Melting points are uncorrected.

b Calcd. N % for azobenzenecarboxylic acid $C_{13}H_{10}N_2O_2$ (XIII—XV): 12.38.
Calcd. N % for methylazobenzenecarboxylic acid $C_{14}H_{12}N_2O_2$ (XVI—XXIV): 11.66.

c The reported⁴⁾ m. p. of XIII is 95°C; it was synthesized by the hydrolysis of methyl azobenzene-2-carboxylate prepared from methyl anthranilate and nitrosobenzene.

d The reported⁵⁾ m. p. of XIV is 170～171°C; it was synthesized by the hydrolysis of methyl azobenzene-3-carboxylate, m. p. 58°C, prepared from methyl *m*-aminobenzoate and nitrosobenzene.

e The reported⁶⁾ m. p. of XV is 238°C; it was prepared from *p*-aminobenzoic acid and nitrosobenzene.

f The reported⁷⁾ m. p. of XXII is 115°C; it was synthesized by the oxidation of 2-*p*-tolylindazole.

g The reported⁸⁾ m. p. of XXIII is 192°C; it was prepared from *p*-toluidine and *m*-nitrosobenzoic acid.

TABLE III. WAVELENGTHS AND INTENSITIES OF ELECTRONIC ABSORPTION MAXIMA

	λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
II	228	6960	316.5	10400	437	438
III	228	11200	323.5	22100	445	536
IV	226.5*	9550	319	8480	430	436
V	227*	11050	323.5	14900	440	559
VI	228	9720	330	20000	449	623
VII	242*	7560	303	10200	428	355
VIII	232*	16300	319	13800	435	690
IX	259	7240	326	24300	444	857
X	235.5	10000	320	10800	428	484
XI	231.5	15800	327.5	13500	440	858
XII	229	9100	335	20000	443	718
XIII	223.5	13400	319	17700	427	504
XIV	224	9720	317.5	15200	438	633
XV	230	12900	325	23700	443	848
XVI	230*	8990	323.5	12750	421	589
XVII	229*	7690	325	8140	441	813
XVIII	229.5	5210	322	10900	452	964
XIX	232*	11100	320	13600	429	471
XX	230*	14500	320	15500	437	675
XXI	230.7	7790	326	15150	443	692
XXII	229.5	16200	329	19200	432.5	995
XXIII	226	14500	326	20900	436	439
XXIV	231.5	8230	333	12200	440	590

* Wavelength of shoulder. Methylazobenzenecarboxylic acids and their ethyl esters, in which methyl and carboxyl or ethoxycarbonyl groups are not situated in the para position with respect to the azo group, have no maximum but do have a shoulder at the 220～250 mμ region.

Ethyl Azobenzenecarboxylates. — Twelve ethyl azobenzenecarboxylates were prepared following the general procedure described above. They have been summarized in Table I.

Azobenzenecarboxylic Acids. — A solution of ethyl azobenzenecarboxylate (1 mol.) in alcohol containing sodium hydroxide (1.5 mol.) was warmed on the water bath for an hour, diluted with four times its volume of water and acidified with dilute hydrochloric acid to precipitate azobenzenecarboxylic acid. The products obtained in this manner were almost pure in most cases, and analytically pure samples could be obtained by recrystallization from alcohol. They have been summarized in

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4) M. P. Freundler, *Bull. soc. chim. France*, [4], **1**, 219 (1907).

5) M. P. Freundler, *Compt. rend.*, **143**, 910 (1906).

6) H. D. Anspon, "Org. Syntheses", **25**, 86 (1946).

7) C. Paal and E. Fritzweiler, *Ber.*, **25**, 3170 (1892).

8) F. J. Alway, ibid., **37**, 335 (1904).

Table II. Yields were almost theoretical in all cases.

Measurement of Spectra.—The absorption spectra were measured in an alcoholic solution with a Hitachi EPU 2 type spectrophotometer using a 1 cm. quartz cell.

Summary

1) The zinc chloride double salts of ethoxycarbonylbenzenediazonium chlorides reacted with aryl Grignard reagents to give ethyl azobenzenecarboxylates. This provides a new method for the preparation of these compounds, as has been demonstrated by the preparation of twelve azo compounds, including ten substances not hitherto known.

2) A group of azobenzenecarboxylic acids was prepared by the hydrolysis of the corresponding ethyl esters obtained above; seven of them are new compounds.

3) The ultraviolet absorption spectra of these esters and free acids were measured.

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