the 4-nitro ester. Benzoyl chloride is added gradually to the pyridine solution of the 4-amino ester.[7] The benzamido ester was refluxed for two hours with an excess of hydrazine hydrate. The mixture was then heated and stirred at 150° for an hour, and washed with hot alcohol. The benzamido phthalhydrazide melted at about 310° on the block. It was not purified further, but was acetylated by boiling for fifteen minutes in acetic anhydride; a diacetyl derivative was obtained, melting at 273–274° (corr.), on recrystallization from acetic anhydride. *Anal.* Calcd. for $C_{19}H_{15}O_5N_3$: C, 62.47; H, 4.11. Found: C, 62.37; H, 4.14.

3-Benzamidophthalhydrazide.—Dimethyl 3-nitrophthalate was prepared according to the method of Miller[10] for making the diethyl ester. The dimethyl 3-nitrophthalate was reduced catalytically (Pt) in alcohol. It was treated with benzoyl chloride in pyridine, as described for the 4-compound above. 3-Benzamidophthalhydrazide was then made from the ester and hydrazine hydrate. It was not purified further, but was acetylated directly. Its diacetyl derivative melted at 269° (corr.), upon recrystallization from acetic anhydride. *Anal.* Calcd. for $C_{19}H_{15}O_5N_3$: C, 62.47; H, 4.11. Found: C, 61.95; H, 3.94.

4-Hydroxy-N,N'-dimethylphthalhydrazide.—From 4-hydroxyphthalic acid[11] and *sym*-dimethylhydrazine acetate in acetic acid; after washing with hot water, it melted at *ca.* 290°. *Anal.* Calcd. for $C_{10}H_{10}O_3N_2$: C, 58.25; H, 4.85. Found: C, 58.45; H, 4.94.

3-Hydroxy- and 3-chlorophthalhydrazides were prepared in like manner from 3-hydroxyphthalic anhydride,[12] and 3-chlorophthalic acid,[13] respectively. These two hydrazides were not analytically pure, but seemed sufficiently pure for the light measurements described here.

o-**Methylaminobenzhydrazide** was obtained from the methyl-N-methylanthranilate[14] and hydrazine hydrate in alcohol, heated at 150° for eighteen hours. The product melts at 146–147° (corr.) after two recrystallizations from alcohol. *Anal.* Calcd. for $C_8H_{11}ON_3$: C, 58.18; H, 6.67. Found: C, 58.45; H, 6.69.

Summary

The preparation of a number of phthalhydrazide derivatives has been described. The relative chemiluminescence of these derivatives upon oxidation in alkaline solution with sodium hypochlorite has been measured.

The effect of different substituents in the benzene ring, and in the hydrazide ring, on the intensity of the light emitted was pointed out. Measurements on the rate of oxidation of these derivatives were made, and the effect of hydroxyl ion and inhibitors on the rate, and the light emitted was noted.

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[10] Miller, *Ann.*, **208**, 243 (1881).

[11] Baeyer, *Ber.*, **10**, 1079 (1877).

[12] Bernthsen and Semper, *ibid.*, **19**, 167 (1886).

[13] Bogert and Boroschek, THIS JOURNAL, **23**, 751 (1901).

[14] Schroeter and Eisleben, *Ann.*, **367**, 143 (1909).

PRINCETON, NEW JERSEY RECEIVED OCTOBER 21, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

The Coupling of Organic Radicals by the Action of Grignard Reagents on Heavy Metal Salts. II. Coupling of Dissimilar Radicals

BY JOHN H. GARDNER, LIONEL JOSEPH AND FRANK GOLLUB[1]

A number of investigators have studied the reaction of Grignard reagents with various heavy metal salts resulting in the coupling of organic radicals.[2] In only one case has there been any report of the coupling of dissimilar radicals by this method. Bennett and Turner[3] treated a mixture of phenyl- and propylmagnesium bromides with anhydrous chromic chloride and obtained a very small yield of a product which appeared to be *n*-propylbenzene. On treating other mixtures of Grignard reagents similarly, they were unable to detect any of the products formed by the union of dissimilar radicals.

Gardner and Borgstrom found that treatment of Grignard reagents with dry silver bromide resulted in the formation of the products of union of the organic radicals in quite satisfactory yield in a number of cases. They did not extend their study to include mixed Grignard reagents. That has been done in the present investigation.

It appears to be well established that, when an organomagnesium halide is treated with silver bromide, the reaction proceeds according to the equations[4]

$$\mathrm{RMgX} + \mathrm{AgBr} \longrightarrow \mathrm{RAg} + \mathrm{MgBrX} \qquad (1)$$

$$\mathrm{RAg} \longrightarrow \mathrm{R} + \mathrm{Ag} \qquad (2)$$

$$2\mathrm{R} \longrightarrow \mathrm{R_2} \qquad (3)$$

If a mixture of two Grignard reagents were to be treated with silver bromide, it would be ex-

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[1] Presented before the Division of Organic Chemistry, Kansas City, Missouri, April 14, 1936.

[2] Gardner and Borgstrom, THIS JOURNAL, **51**, 3375 (1929), give leading references. See Joseph, Dissertation, Washington University, 1937, for a bibliography and review.

[3] Bennett and Turner, *J. Chem. Soc.*, **105**, 1057 (1914).

[4] Krause and Wendt, *Ber.*, **56**, 2064 (1923); Reich, *Compt. rend.*, **177**, 322 (1923); Danehy and Nieuwland, THIS JOURNAL, **58**, 1609 (1936).

pected that the organic radicals of both would be formed, through the decomposition of the silver compounds, and that there would be formed as the final products a mixture of the compounds obtained by union of similar and dissimilar radicals.

In order to study a combination in which the products readily could be separated and identified, a mixture of the Grignard reagents prepared from bromobenzene and *p*-bromoanisole was treated with silver bromide under the conditions used by Gardner and Borgstrom for aromatic compounds. The resulting product was boiled with a mixture of constant boiling hydriodic acid and acetic acid, the biphenyl derivatives precipitated, and taken up with sodium hydroxide. The biphenyl was either filtered or steam distilled from the alkaline solution. On adding hydrochloric acid, a mixture of 4-hydroxybiphenyl and 4,4′-dihydroxybiphenyl precipitated. These were separated by fractional crystallization from benzene. It was found that symmetrical and unsymmetrical compounds were formed in considerable amounts as would be expected if the mechanism suggested above is correct.

Yields and melting points of the products are shown in Table I. Theoretical yields were calculated on the basis of all of the appropriate Grignard reagent or reagents being converted into the compound indicated. As would be expected in view of the greater difficulty of isolation, the yields of the hydroxy compounds were appreciably lower than those of biphenyl.

TABLE I

	Yield									
Moles of each RMgX	Biphenyl			4-Hydroxybiphenyl			4,4′-Dihydroxybiphenyl		
	G.	%	M. p., °C.	G.	%	M. p., °C.	G.	%	M. p., °C.
0.1	1.7	22.0	68	0.8	4.7	158–160	1.7	18.2	258–260
.1	3.6	46.8		1.4	8.2		1.8	19.4	
1.0	28.0	36.4		9.0	5.3		3.6	3.8	

For further identification, the acetate of 4-hydroxybiphenyl was prepared, m. p. 87. Kaiser[5] gives m. p. 88–89°.

Summary

The coupling of dissimilar organic radicals by means of the action of Grignard reagents on silver bromide has been accomplished.

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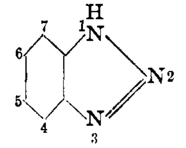
[5] Kaiser, *Ann.*, **257**, 101 (1890).

ST. LOUIS, MO. RECEIVED OCTOBER 4, 1937

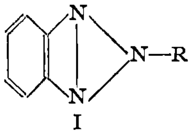
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Symmetry of Certain Types of Benzotriazoles

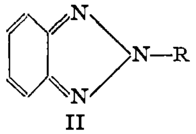
BY W. M. LAUER, W. F. FILBERT AND G. E. ULLYOT

Benzotriazoles of the type 

possess the expected lability of the three nitrogen system,[1] and as a consequence positions 5 and 6 are equivalent. The benzotriazoles in which there is a substituent in position 2 are perhaps of even greater interest since this condition necessitates a different arrangement of the valence bonds. A considerable number of representatives of this class are known and they are usually assigned structure I. Structures I and II are resonance hybrids.

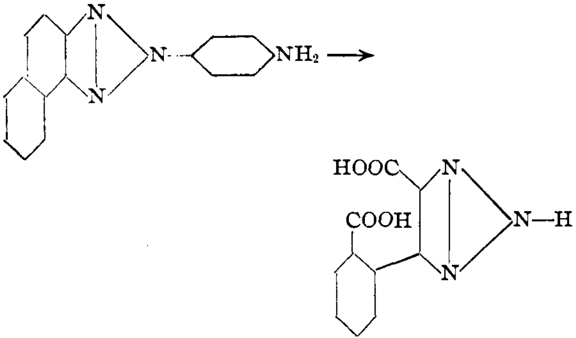


I



II

The stability of aromatic compounds to certain reagents has been associated with a sextet of electrons or with multiplicity of resonance forms. That the triazole nucleus possesses considerable stability has been demonstrated in striking manner by Charrier and Gallotti.[2] These investigators subjected 2-(*p*-aminophenyl)-α,β-naphthotriazole to oxidation with alkaline potassium permanganate and obtained 4-(*o*-carboxyphenyl)-5-carboxy-1,2,3-triazole.



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[1] For a discussion of this system see J. W. Baker, "Tautomerism," D. Van Nostrand Co., New York, 1934, pp. 143–147.

[2] Charrier and Gallotti, *Gazz. chim. ital.*, **55**, 7–11 (1925).