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

Moles of each RMgX	Yield								
	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.

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

ST. LOUIS, MO.

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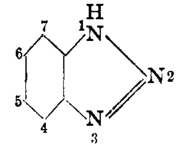
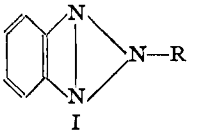
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Symmetry of Certain Types of Benzotriazoles

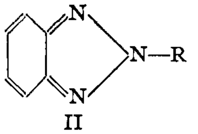
BY W. M. LAUER, W. F. FILBERT AND G. E. ULLYOT

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.

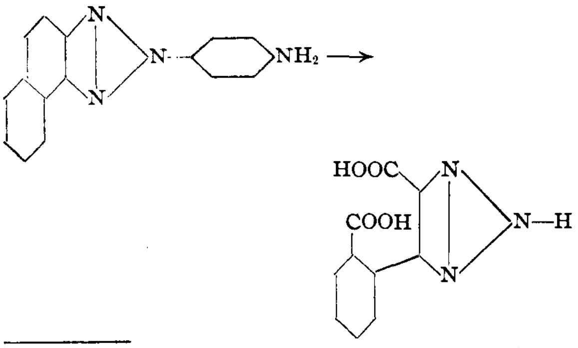


I



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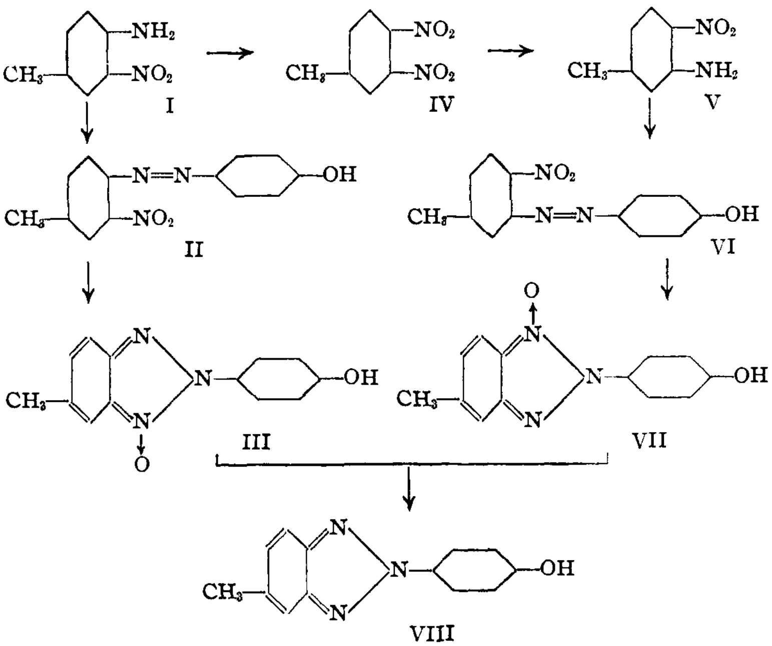
[1] For a discussion of this system see J. W. Baker, "Tautomerism," D. Van Nostrand Co., New York, 1934, pp. 143–147.

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

Again, it is evident that positions 5 and 6 in the case of either structure I or II should be equivalent. The series of reactions which is outlined below and described in the experimental part of the present paper led to two different triazole oxides, but only one triazole.



This constitutes a demonstration of the equivalence of positions 5 and 6 in the case of the benzotriazole, VIII, and of their non-equivalence in the case of the benzotriazole oxides, III and VII, and supplies further evidence for the structures commonly assigned to compounds of this type.

Experimental[3]

The preparation of **3-nitro-4-aminotoluene, I** (m. p. 116°), was carried out in accordance with the directions of Noyes.[4] It was converted to **2-nitro-4-methyl-4'-hydroxyazobenzene, II**, in the following manner: the amine (5 g.), dissolved in glacial acetic acid (60 ml.), was added to a solution of sodium nitrite (1.8 g.) in concd. sulfuric acid (12 ml.) keeping the temperature below 20°. After the addition of water (40 ml.), phenol (3.1 g.) dissolved in alcohol (5 ml.) and water (40 ml.) was added. To this mixture, potassium hydroxide (30 g.) in water (50 ml.) was added slowly with stirring. The azo compound (5.2 g.) after filtration was crystallized from dilute alcohol. After several recrystallizations, the orange needles melted at 156–157°.[5]

The method of Grandmougin[6] was used to obtain **6-methyl-2-(*p*-hydroxyphenyl)-benzotriazole-1-oxide, III.** The azo compound II (2 g.), dissolved in hot alcohol (15 ml.), was treated with a slight excess of sodium hydrosulfite (7 g.) in water (30 ml.). The solution was rapidly decolorized and colorless needles separated out. After heating on the steam-bath for fifteen to twenty minutes, the reaction was complete and the product, obtained by filtration, was crystallized from dilute alcohol; yield 1.5 g.; m. p. 242–243°.[7]

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.7; H, 4.56. Found: C, 64.7; H, 4.47.

6-Methyl-2-(*p*-hydroxyphenyl)-benzotriazole, VIII, was prepared from the oxide III by reduction with stannous chloride. The oxide (2 g.), dissolved in boiling alcohol (40 ml.) was treated with an excess of stannous chloride (10 g.) in hot hydrochloric acid (30 ml.). The reaction mixture was boiled for thirty minutes, and part of the alcohol was then removed by distillation. After cooling, colorless crystals were obtained. Recrystallization from alcohol yielded the benzotriazole (1.4 g., m. p. 217°).[8]

Anal. Calcd. for $C_{13}H_{11}N_3O$: C, 69.3; H, 4.89. Found: C, 69.3; H, 5.04.

The isomeric benzotriazole oxide, 5-methyl-2-(*p*-hydroxyphenyl)-benzotriazole-1-oxide, VII, was obtained as follows: 3-nitro-4-aminotoluene I was first transformed into **3-amino-4-nitrotoluene, V.** This was accomplished by oxidizing I with persulfuric acid to the corresponding nitroso compound, which in turn was oxidized to 3,4-dinitrotoluene, IV, with nitric acid. The dinitro compound was then converted to 3-amino-4-nitrotoluene, V, by means of alcoholic ammonia. This series of reactions has been described by Goerling and Wibaut.[9] Considerable difficulty was experienced at the next stage, but diazotization and coupling were finally achieved using the method of Witt.[10]

The amine (2 g.) and potassium bisulfite (1.8 g.) were mixed and then added portionwise with stirring to cold fuming nitric acid (12 g.). The reaction mixture was allowed to stand for two hours and then poured on ice and filtered. The cold solution (*ca.* 300 ml.) was then made slightly alkaline with potassium hydroxide and poured into an equal volume of cold alcohol containing phenol (1.24 g.) and considerable sodium acetate. The precipitate was removed by filtration after the solution had stood overnight at a temperature of 0°. The azo compound VI (1.4 g., m. p. 129–130°) was obtained in the form of dark-red needles after several recrystallization from dilute alcohol.

The benzotriazole oxide, VII, was obtained from VI in a manner analogous to that used to obtain III from II. The azo compound, VI (1.66 g.), dissolved in hot ethyl

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[3] Supported by a Research Grant of the Graduate School.

[4] Noyes, *Am. Chem. J.*, **10**, 475 (1888).

[5] Hewitt and Mitchell, *J. Chem. Soc.*, **87**, 232 (1905), give 158°.

[6] Grandmougin, *Ber.*, **39**, 3929 (1906).

[7] Rosenstiehl and Suais, *Compt. rend.*, **134**, 606 (1902), report 240–241°.

[8] Rosenstiehl and Suais[7] report 217–218°.

[9] Goerling and Wibaut, *Rec. trav. chim.*, **53**, 1014 (1934).

[10] Witt, *Ber.*, **42**, 2956 (1909).

alcohol (12 ml.) was treated with an aqueous solution (10 ml.) of sodium hydrosulfite (2.0 g.). The precipitated triazole oxide was purified by repeated crystallization from dilute alcohol: m. p. 265–266° with decomposition; mixed with the isomer III, the triazole oxide, VII, melted at 225–228°.

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.7; H, 4.60. Found: C, 64.8; H, 4.62.

The triazole, VIII, was obtained from VII by reduction with stannous chloride in the manner already described for the conversion of III to VIII; melting point and mixed melting point with triazole obtained from III 217–218°.

Anal. Calcd. for $C_{13}H_{11}N_3O$: C, 69.3; H, 4.89. Found: C, 68.8; H, 5.08.

Summary

Evidence is introduced which proves the equivalence of positions 5 and 6 in the case of benzotriazoles which are substituted in position 2.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 15, 1937

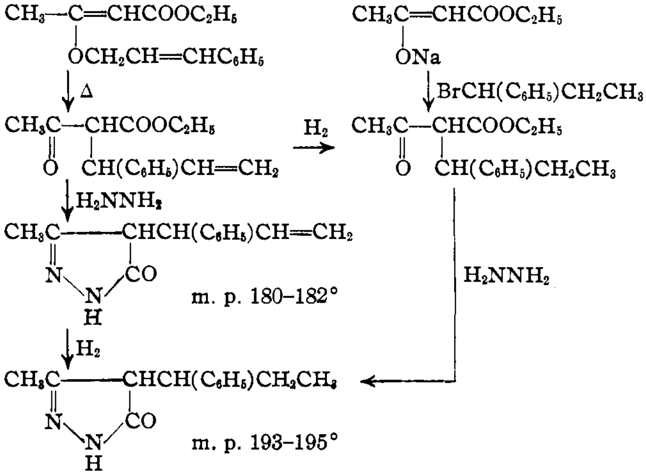
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Some Beta-Allyloxycrotonic Esters

BY WALTER M. LAUER AND ELSIE I. KILBURN[1]

Alkylation of ethyl acetoacetate cannot proceed through the intermediate formation of a β-alkoxycrotonic ester, for it has been amply demonstrated that these β-alkoxycrotonic esters are far too stable to undergo rearrangement. There is a wide difference in the thermal stability of the simple alkyl and allyl phenyl ethers and inasmuch as the ethers of β-hydroxycrotonic acid bear a formal relation to the phenol ethers, it might be expected that the β-allyloxy-crotonates would rearrange under the influence of heat even though the β-alkoxy-crotonates do not. In fact, Claisen reported[2] that O-allylacetoacetic ester rearranged to the C-allyl derivative on distillation in the presence of ammonium chloride, but apparently he never published his experimental work in support of this claim. The case of the cinnamyl ether of β-hydroxycrotonic ester is of particular interest. As is well known, when sodium phenoxide is treated with cinnamyl bromide under certain conditions, a mixture of cinnamyl phenyl ether and *o*-cinnamylphenol is obtained. The rearrangement of cinnamyl phenyl ether yields not *o*-cinnamylphenol but *o*-(α-phenylallyl)-phenol, so that in this case it is clearly evident that the *o*-cinnamylphenol must result from some other process. The present paper deals with the rearrangement of ethyl β-cinnamyloxycrotonate and also in this case the rearrangement product differed from that obtained by the direct action of cinnamyl bromide on the sodium derivative of ethyl acetoacetate. Therefore, even though ethyl β-cinnamyloxycrotonate is capable of rearrangement, the course of the reaction between the sodium derivative of ethyl acetoacetate and cinnamyl bromide cannot involve ethyl β-cinnamyloxycrotonate since its rearrangement product is not identical with the product actually obtained.

Ethyl β-cinnamyloxycrotonate was prepared by the action of sodium cinnamyl oxide on a mixture of the stereoisomers, ethyl β-chlorocrotonate and ethyl β-chloroisocrotonate. Rearrangement was accomplished at a comparatively low temperature in the presence of ammonium chloride. The reactions outlined below indicate the evidence upon which the structure of the rearrangement product is based.



A similar series of reactions was carried out in the case of the product obtained by the action of cinnamyl bromide on the sodium derivative of ethyl acetoacetate and the corresponding derivatives were prepared.

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(1) Abstract of Ph.D. Thesis submitted October, 1935.

(2) Claisen, *Ber.*, **45**, 3157 (1912). See also private communications to Beilstein [4], Supp. Vol. III/IV, p. 256.