[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 202.]

RESEARCHES ON QUINAZOLINES (TWENTY-NINTH PAPER). A FURTHER STUDY OF THE STILBAZOLES, HYDRAZONES AND SCHIFF BASES OF THE 4-QUINAZOLONE GROUP.[1]

BY MARSTON TAYLOR BOGERT AND GEORGE DENTON BEAL.

Received February 2, 1912.

Since the appearance of our recent paper on this subject,[2] the work has been continued and the additional results are here recorded.

In the condensation of aldehydes with α-methyl pyridines or quinolines, the alkines usually form easily and in some cases are so stable that considerable difficulty is experienced in dehydrating them to stilbazoles.[3] With the quinazolone-aldehyde condensations, on the other hand, the alkines either do not form at all under the conditions of our experiments, or are so unstable that they immediately lose water and give the stilbazole, for we have been unable to isolate alkines in any of the reactions.

Further, while it has been shown[4] that many stilbazoles add hydrogen or bromine readily, these reactions do not seem to run so smoothly with stilbazoles derived from 4-quinazolones. Hydriodic acid and red phosphorus evidently caused some reduction when brought into contact with 2-styryl-4-quinazolone, but no pure dihydro derivative could be isolated from the tarry product. The action of bromine upon this same styryl quinazolone gave rise to substitution and not to addition products. Limpricht and Schwanert[5] have observed a similar reaction with stilbene, and Dubke[6] with α'-γ-dimethyl-α-stilbazole.

In addition to the compounds described in our previous paper, the preparation of the following new aldehyde condensation products is recorded here: 6-nitro-2-styryl-4-quinazolone, 2-*o*-nitrostyryl-4-quinazolone, *p*-nitrostyryl-4-quinazolone, 6-nitro-2-*p*-nitrostyryl-4-quinazolone, 2-styryl-3-ethyl-4-quinazolone, 2-styryl-3-phenyl-4-quinazolone, 2-styryl-3-*p*-tolyl-4-quinazolone, 2-styryl-3-benzyl-4-quinazolone, 2-styryl-3-*p*-anisyl 4-quinazolone, 2-styryl-3-*p*-phenetyl-4-quinazolone, 2-styryl-3-α-naphthyl-4-quinazolone, 2-styryl-3-β-naphthyl-4-quinazolone, 2-styryl-3-anilino-4-quinazolone, 2-*o*-hydroxystyryl-3-phenyl-4-quinazolone, 2-methylenedioxystyryl-4-quinazolone, and 2-phenylbutadienyl-4-quinazolone.

[1] Read at the Washington Meeting of the Society, Dec. 29, 1911.

[2] Bogert, Beal and Amend, THIS JOURNAL, 32, 1654 (1910).

[3] For a tabulation of the condensations carried out by Ladenburg and his coworkers, see Dierig, *Inaug. Diss.*, Breslau, 1902.

[4] Baurath, *Ber.*, 20, 2719 (1887); 21, 818 (1888). Ladenburg and Krŏner, *Ibid.*, 36, 119 (1903). Tietz, *Inaug. Diss.*, Breslau, 1909, and others.

[5] *Ann.*, 145, 336.

[6] *Ber.*, 27, 82 (1894).

The condensation was generally carried out by heating an equimolecular mixture of the aldehyde and quinazolone. If the reaction was practically complete, the melt was purified by crystallization from alcohol, or some other suitable solvent, decolorizing with bone-black if necessary, while if the condensation was but a partial one, water was added, the excess of aldehyde driven out with steam, and the residue purified by crystallization.

Most of the styryl quinazolones are pale yellow or nearly colorless, and crystallize in fluffy masses of short silky needles. Frequently they exhibit tribo-electric properties. Usually they are soluble in alcohol, chloroform or glacial acetic acid; less readily in ether, carbon disulfide or benzene; and practically insoluble in water. Those with a free hydrogen in position 3 dissolve easily in aqueous solutions of the caustic alkalies and are reprecipitated by carbon dioxide or acetic acid.

Attention was called in the previous paper to the fact that 2-methyl-3-amino-4-quinazolone when treated with aldehydes condenses first with the amino group, and that the methyl group also reacts only when the attacking aldehyde is benzaldehyde. At the time, we suggested that the hydrazone group formed in position 3 prevented the reaction of the 2-methyl group by steric interference. We have since learned that an anilino group in position 3 exerts a similar influence, the 2-methyl group again condensing only with benzaldehyde.

Moore[1] has found that Schiff bases containing the chromophore group —N : CH—, together with certain auxochrome groups (for example, the —$N(CH_3)_2$ group), often form colored salts with acids. The hydrochlorides of several of our new Schiff bases were prepared by suspending the bases in dry ether and passing in dry hydrochloric acid gas, but the colors of the salts thus formed were invariably no darker than those of the bases from which they were obtained.

Fural, citral, acetophenone, and pyruvic acid failed to condense with these 2-methyl or 2-methyl-3-amino-4-quinazolones. Experiments with glyoxal also gave negative results. With benzil and 2-methyl-3-amino-4-quinazolone, some condensation occurred but the yield was too small to fully identify the product. Wislicenus[2] succeeded in condensing quinaldine with oxalic esters, in presence of sodium alcoholates, but a similar reaction does not occur when 2-methyl-4-quinazolone is substituted for the quinaldine.

By direct nitration of 2-styryl-4-quinazolone, both a mono and a dinitro derivative result. The former was proven to be the 6-nitro compound by its synthesis from 6-nitro-2-methyl-4-quinazolone and benzaldehyde; and the structure of the dinitro derivative was similarly es-

[1] THIS JOURNAL, 30, 394, 1001 (1908); 32, 382 (1910).

[2] *Ber.*, 30, 1479 (1897).

tablished by its synthesis from 6-nitro-2-methyl-4-quinazolone and *p*-nitrobenzaldehyde.

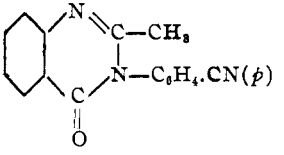
The amino group in 2-amino-4-quinazolone is decidedly inert. Although it can be acylated, it cannot be diazotized by ordinary methods, nor does it condense with aldehydes.

In the progress of the work, the following new quinazolones were prepared and studied: 2-methyl-3-*p*-cyanphenyl-4-quinazolone, 2-methyl-3-*p*-carboxyphenyl-4-quinazolone and its ethyl ester, 2-methyl-3-*p*-anisyl-4-quinazolone, 2-methyl-3-*p*-phenetyl-4-quinazolone, its sulfonic acid and the sodium salt of the latter, and 2-methyl-3-benzyl-4-quinazolone. Certain of these were prepared for the purpose of studying their physiological action upon animals. Thus, the *p*-phenetyl derivative, it was thought, might show antipyretic properties, but it proved to be too difficultly soluble. Sulfonation remedied the insolubility, but the sulfonated compound possessed no detectable therapeutic value. Similarly, the condensation product of *p*-aminobenzoic ester and acetanthranil was examined with reference to its power as a local anesthetic and found to be essentially inert. The details of these and other experiments on the physiological action of substances of this group will probably appear later in a separate paper.

Experimental.

I. Preparation of Quinazolones.

2-Methyl-3-p-cyanphenyl-4-quinazolone,



—*p*-Aminobenzonitrile and acetanthranil, in equimolecular proportion, were intimately mixed and the mixture heated for an hour at 150°. By crystallization of the reddish brown melt from alcohol, prisms were obtained of a faint pinkish cast, melting at 240° (cor.).

Calculated for $C_{16}H_{11}ON_3$: N, 16.09. Found: N, 16.37.

2-Methyl-3-p-carboxyphenyl-4-quinazolone, $HOOC.C_6H_4.N.CO.C_6H_4.N:C.CH_3$, was prepared from the above nitrile by boiling it with a 10% aqueous solution of potassium hydroxide until the evolution of ammonia ceased, cooling, and precipitating carefully with hydrochloric acid. The precipitated acid, washed with water, and recrystallized from dilute alcohol, forms short, yellowish needles, melting at about 259° (uncor.).

Calculated for $C_{16}H_{12}O_3N_2$: N, 10.00. Found: N, 10.41.

In recrystallizing this acid, prolonged boiling should be avoided, as

it tends to split out carbon dioxide from the acid and give the methyl phenyl quinazolone (m. p. 145°).

It may be recalled, in this connection, that Bogert and Klaber[1] found that anthranilic acid failed to condense with 4-nitroacetanthranil, although its methyl ester did.

Ethyl Ester.—The ester of the above acid was prepared from ethyl *p*-aminobenzoate and acetanthranil, by heating them together, in equimolecular proportion, for an hour at 150°, and crystallizing the brown melt from alcohol. Golden yellow prisms resulted which, on recrystallization, became practically colorless, and melted at 172–3° (cor.).

Calculated for $C_{18}H_{16}O_3N_2$: N, 9.09. Found: N, 9.43.

2-Methyl-3-p-anisyl-4-quinazolone, $CH_3O.C_6H_4.N.CO.C_6H_4.N : C.CH_3$, prepared in a similar manner, hy heating together *p*-anisidine and acetanthranil for an hour at 150°, and purifying the product by crystallization from alcohol, forms colorless hexagonal prisms, melting at 170° (cor.).

Calculated for $C_{16}H_{14}O_2N_2$: N, 10.52. Found: N, 10.59.

2-Methyl-3-p-phenetyl-4-quinazolone, obtained in the same way, crystallizes from alcohol in needles of a faintly pinkish cast, melting at 148° (cor.), which darken gradually on standing in the air, and are freely soluble in alcohol or ether, but practically insoluble in water.

Calculated for $C_{17}H_{16}O_2N_2$: N, 10.00. Found: N, 10.11.

Monosulfo Acid.—The compound just described was sulfonated by stirring five grams of it into a mixture of 15 cc. concentrated and 30 cc. fuming sulfuric acid, and heating the mixture at 100° for two hours. The cooled solution was poured into 500 cc. ice water and the whole concentrated to half its original volume. On cooling, small grayish prisms separated, not melting at 300°.

Calculated for $C_{17}H_{16}O_5N_2S$: N, 7.77. Found: N, 7.70.

The sodium salt forms a gray powder, easily soluble in water, and having but little taste. It is unmelted at 300°.

2-Methyl-3-benzyl-4-quinazolone, $C_6H_5CH_2.N.CO.C_6H_4.N : C.CH_3$. — Equimolecular amounts of benzylamine and acetanthranil were mixed and the mixture heated half an hour at 150°. The melt was digested with cold water, to remove unchanged benzylamine, and with sodium carbonate solution, to eliminate any acetanthranilic acid. The residual quinazolone was purified by repeated crystallization from alcohol, and was thus obtained in colorless flakes, melting at 123° (cor.).

Calculated for $C_{16}H_{14}ON_2$: N, 11.20. Found: N, 11.11.

[1] THIS JOURNAL, 30, 814 (1908).

II. Condensations of Aldehydes with 2-Methyl-4-quinazolones containing no Primary Amino Groups. Simple Styryl Quinazolones.

2-Styryl-4-quinazolone, $C_6H_5CH : CH.\overline{C : N.C_6H_4.CO.NH}$, has been described in our previous article. Its *hydrochloride* was prepared by adding concentrated hydrochloric acid to a saturated alcoholic solution of the quinazolone. Pale yellow needles separated which, when washed with alcohol and dried in a vacuum over concentrated sulfuric acid and solid potassium hydroxide, melted with decomposition at about 310°.

Calculated for $C_{16}H_{12}ON_2.HCl$: N, 9.84. Found: N, 9.99.

6-Nitro-2-styryl-4-quinazolone, $C_6H_5.CH : CH.\overline{C : N.C_6H_3(NO_2).CO.NH}$, was prepared by direct nitration of the above quinazolone (5 g.) with fuming (sp. gr. 1.52) nitric acid (50 cc.). The solution obtained was concentrated to half its original volume and then stirred into 300 cc. of ice water. The precipitated nitro compound was washed with water, then with alcohol, crystallized twice from glacial acetic acid, the crystals washed with alcohol and dried at 110°. Short, yellowish needles, melting at 323.5° (uncor).

Calculated for $C_{16}H_{11}O_3N_3$: N, 14.33. Found: N, 14.71.

That the nitro group in the above compound is in position 6 was proven by condensing benzaldehyde with 6-nitro-2-methyl-4-quinazolone, when the same substance was obtained.

Calculated for $C_{16}H_{11}O_3N_3$: N, 14.33. Found: N, 14.18.

This would appear to indicate that the benzene portion of the quinazoline nucleus nitrates more rapidly than the styryl group.

2-o-Nitrostyryl-4-quinazolone, $O_2N.C_6H_4.CH : CH.\overline{C : N.C_6H_4.CO.NH}$.—Three grams each of *o*-nitrobenzaldehyde and 2-methyl-4-quinazolone were mixed and the mixture heated for two hours at 180°. The pulverized melt was extracted with boiling alcohol, to remove unchanged initial materials, and the residue crystallized from glacial acetic acid. Minute, yellowish needles resulted, melting at 300° (uncor.).

Calculated for $C_{16}H_{11}O_3N_3$: N, 14.33. Found: N, 14.24.

2-p-Nitrostyryl-4-quinazolone was prepared in the same way. It forms bright yellow, microscopic needles, melting at 350° (uncor.).

Calculated for $C_{16}H_{11}O_3N_3$: N, 14.33. Found: N, 14.30.

6-Nitro-2-p-nitrostyryl-4-quinazolone,

$O_2N.C_6H_4.CH : CH.\overline{C : N.C_6H_3(NO_2).CO.NH}$.—Five grams of 2-styryl-4-quinazolone were nitrated with a mixture of 60 cc. fuming nitric and 30 cc. concentrated sulfuric acid. The solution was concentrated to half its original volume and poured into 250 cc. ice water, the dinitro compound separating as a curdy, orange precipitate. This precipitate was

filtered out, washed with water, and boiled with dilute potassium hydroxide solution, to remove unchanged initial materials. It was then again washed with water, and extracted twice with hot, glacial acetic acid, in which it is very difficultly soluble. The residue was washed with alcohol, dried at 110° and analyzed:

Calculated for $C_{16}H_{10}O_5N_4$: N, 16.56. Found: N, 16.60.

It is an orange-yellow solid, melting at 335° (uncor.). The same compound was obtained by heating together 6-nitro-2-methyl-4-quinazolone and *p*-nitrobenzaldehyde for four hours at 200°.

Calculated for $C_{16}H_{10}O_5N_4$: N, 16.56. Found: N, 16.56.

Monobromo-2-styryl-4-quinazolone.—On mixing glacial acetic acid solutions of bromine and 2-styryl-4-quinazolone, a yellow precipitate gradually separated. This was filtered out and crystallized from alcohol, giving yellow needles, which slowly decompose in the vicinity of 345°.

Calculated for $C_{16}H_{11}ON_2Br$: N, 8.56. Found: N, 8.75.

The filtrate from the above bromine derivative was found to contain hydrobromic acid, a further proof that substitution and not addition had occurred. The same monobrom derivative was obtained by using chloroform as the solvent and allowing the mixture to stand eight hours.

Dibromo-2-styryl-4-quinazolone was obtained when hot, glacial acetic acid solutions of the quinazolone and bromine were mixed, or when a chloroform solution of the two was allowed to stand for 24 hours. The precipitate obtained separates from hot alcohol as a colorless, amorphous solid, which turns brown at about 200°, but remains unmelted at 300° (uncor.).

Calculated for $C_{16}H_{10}ON_2Br_2$: N, 6.89. Found: N, 6.63.

The filtrate from the dibrom compound contains hydrobromic acid.

2-Styryl-3-methyl-4-quinazolone, $C_6H_5.CH : CH.\overset{|}{C} : N.C_6H_4.CO.N.CH_3$. —The preparation of this compound from 2,3-dimethyl-4-quinazolone and benzaldehyde is described in our previous paper.

We have since prepared it also from 2-styryl-4-quinazolone, by dissolving the latter in methyl alcohol, adding the calculated amounts of potassium hydroxide and then of methyl iodide, and heating with a reflux until the mixture showed a neutral reaction.

2-Styryl-3-ethyl-4-quinazolone, from 2-methyl-3-ethyl-4-quinazolone and benzaldehyde, heated in equimolecular proportion for an hour at 150°, and the crude product purified by crystallization from alcohol, forms clusters of pale yellow needles, melting at 125° (cor.).

Calculated for $C_{18}H_{16}ON_2$: N, 10.14. Found: N, 10.43.

2-Styryl-3-phenyl-4-quinazolone, from 2-methyl-3-phenyl-4-quinazolone and benzaldehyde at 180°, crystallizes from alcohol in short, lemon-yellow needles, melting at 201° (cor.).

Calculated for $C_{22}H_{16}ON_2$: N, 8.64. Found: N, 8.95.

2-Styryl-3-p-tolyl-4-quinazolone, from 2-methyl-3-*p*-tolyl-4-quinazolone and benzaldehyde at 180°, crystallizes from alcohol in fine, pale yellow needles, melting at 197° (cor.).

Calculated for $C_{23}H_{18}ON_2$: N, 8.28. Found: N, 8.30.

2-Styryl-3-benzyl-4-quinazolone, from 2-methyl-3-benzyl-4-quinazolone and benzaldehyde at 190°, crystallizes from alcohol in fine, pale yellow needles, melting at 142° (cor.), which mat together closely on the filter. Its formation has been used by us as a means of isolating and identifying the methyl benzyl quinazolone.

Calculated for $C_{23}H_{18}ON_2$: N, 8.28. Found: N, 8.37.

2-Styryl-3-p-anisyl-4-quinazolone, from 2-methyl-3-*p*-anisyl-4-quinazolone and benzaldehyde at 180°, crystallizes from alcohol in small, pale yellow needles, melting at 223° (cor.), which mat together closely.

Calculated for $C_{23}H_{18}O_2N_2$: N, 7.91. Found: N, 7.99.

2-Styryl-3-p-phenetyl-4-quinazolone, from 2-methyl-3-*p*-phenetyl-4-quinazolone and benzaldehyde at 160°, crystallizes from alcohol in minute, pale yellow crystals, melting at 204° (cor.).

Calculated for $C_{24}H_{20}O_2N_2$: N, 7.60. Found: N, 7.78.

2-Styryl-3-α-naphthyl-4-quinazolone, from 2-methyl-3-α-naphthyl-4-quinazolone and benzaldehyde at 160°, crystallizes from alcohol in short, yellowish needles, melting at 187° (uncor.).

Calculated for $C_{26}H_{18}ON_2$: N, 7.48. Found: N, 7.65.

2-Styryl-3-β-naphthyl-4-quinazolone, from 2-methyl-3-β-naphthyl-4-quinazolone and benzaldehyde at 160°, crystallizes from alcohol in short, yellowish needles, melting at 240° (uncor.).

Calculated for $C_{26}H_{18}ON_2$: N, 7.48. Found: N, 7.66.

2-Styryl-3-anilino-4-quinazolone, from 2-methyl-3-anilino-4-quinazolone and benzaldehyde at 180°, crystallizes from alcohol in dense, granular, cream colored crystals, melting at 217° (uncor.).

Calculated for $C_{22}H_{17}ON_3$: N, 12.38. Found: N, 12.62.

Attempts to condense 2-methyl-3-anilino-4-quinazolone with salicylaldehyde failed.

2-o-Hydroxystyryl-3-phenyl-4-quinazolone,

$HO.C_6H_4.CH : CH.C : N.C_6H_4.CO.N.C_6H_5$, from 2-methyl-3-phenyl-4-quinazolone and salicylaldehyde at 190°, crystallizes from alcohol in short, lemon-yellow prisms, melting at 270° (uncor.).

Calculated for $C_{22}H_{16}O_2N_2$: N, 8.23. Found: N, 8.38.

2-Methylenedioxystyryl-4-quinazolone,

$CH_2\langle\begin{smallmatrix}O\\O\end{smallmatrix}\rangle C_6H_3.CH : CH.C : N.C_6H_4.CO.NH$, from 2-methyl-4-quinazo-

lone and piperonal at 180°, crystallizes from alcohol (in which it is difficultly soluble) in minute needles of faint yellowish cast, melting at 305° (uncor.), which mat together, and show tribo-electric properties.

Calculated for $C_{17}H_{12}ON_2$: N. 9.59. Found: N, 9.76.

2-Phenylbutadiënyl-4-quinazolone,

$C_6H_5.CH : CH.CH : CH.C : N.C_6H_4.CO.NH$, was prepared from cinnamic aldehyde and 2-methyl-4-quinazolone at 190°. The aldehyde was freshly distilled in vacuum before use, and that uncombined in the reaction was blown out with steam. The residual non-volatile yellow solid was dissolved in alcohol, the solution decolorized with bone-black, and from the filtrate, on cooling, the desired compound separated in long, yellow needles, which were purified by further crystallization from alcohol, and then melted at 257–8° (uncor.).

Calculated for $C_{18}H_{14}ON_2$: N, 10.21. Found: N, 10.21.

III. Condensations of Aldehydes with Amino 2-Methyl-4-quinazolones.

In addition to the compounds described in our former article, the subjoined have been prepared and studied.

2-Styryl-3-acetamino-4-quinazolone was obtained both by the action of acetic anhydride upon the corresponding styryl amino quinazolone, and by the condensation of the methyl acetamino quinazolone with benzaldehyde. It crystallizes from alcohol in needles of a faint pinkish tinge, melting at 259° (uncor.).

Calculated for $C_{18}H_{15}O_2N_3$: N, 13.77. Found: N, 13.99.

As mentioned in the introductory portion of this paper, our attempts to condense the 2-methyl-3-amino-4-quinazolone with citral, fural, or glyoxal, proved futile.

2-Methyl-3-amino-4-quinazolone and Benzil.—An alcoholic solution of these two substances, on long boiling, deposited a very small amount of a difficultly soluble, yellow, granular solid, melting with decomposition at about 292°. Efforts to secure the condensation in other ways proved fruitless. The two substances were heated together dry and in various solvents, at ordinary pressure and in sealed tubes, alone and in presence of sodium alcoholates, traces of alkali, of acid, and of pyridine, but the experiments were unsuccessful. Only enough material was secured for a single analysis:

0.069 gram gave 7.8 cc. moist N at 24° and 766 mm.

Calculated for $C_6H_4\begin{cases} N : C—CH : C.C_6H_5 \\ CO.N—N : C.C_6H_5 \end{cases}$: N, 12.03. Found: N, 12.78.

More of the material and closer analytical results are needed before it can be said whether we really secured the product sought or not.

2-Amino-4-quinazolone and Benzaldehyde.—One gram of the quinazolone

was heated with a slight excess of benzaldehyde for an hour at 180°, but no condensation occurred.

The reaction is of interest, since we have shown that amino groups in positions 3 or 7 condense easily with benzaldehyde.

2-Methyl-4-quinazolone and Ethyl Oxalate.—Five grams of the dry quinazolone, a similar amount of ethyl oxalate, and 2 grams finely pulverized sodium ethylate, together with 100 cc. anhydrous ether, were placed in a well-stoppered flask and left at the laboratory temperature for three weeks, with occasional shaking. No condensation occurred, the quinazolone being recovered unchanged.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 203.]

RESEARCHES ON QUINAZOLINES (THIRTIETH PAPER). A STUDY OF THE BROMINATION AND NITRATION OF 4-QUINAZOLONES; THE CORRESPONDING AMINOQUINAZOLONES, AND CERTAIN OTHER NEW 4-QUINAZOLONES.[1]

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Received February 17, 1912.

The 4-quinazolones (4-hydroxyquinazolines) are not easily brominated by the action of bromine in aqueous potassium bromide solution, in glacial acetic acid or in acetic anhydride solution. By employing the Juvalta[2] process, however, the halogen may be introduced. In this way, monobromo derivatives have been obtained of 4-quinazolone and of 2-methyl-4-quinazolone.

Nor are the quinazolones readily nitrated. Griess,[3] in 1869, showed that benzoylene urea could be nitrated, but did not prove the position of the nitro group. In 1890, Dehoff[4] nitrated 2-methyl and 2,3-dimethyl-4-quinazolone, and his products were subsequently shown to be the 6-nitro derivatives by the investigations of Thieme[5] and of Bogert and Cook.[6]

According to our experience, the satisfactory nitration of 4-quinazolones requires a high temperature and the use of a mixture of fuming nitric and concentrated sulfuric acids, and but one nitro group can thus be introduced on the 4-quinazolone nucleus. Position 6 seems to be the point where the nitro group enters most readily. Of course, aryl

[1] Read at the Washington Meeting of the Society, Dec. 29, 1911.
[2] D. R. P. 50,177, *Friedländer*, **2**, 93.
[3] *Ber.*, **2**, 416 (1869).
[4] *J. prakt. Chem.*, [2] **42**, 347 (1890).
[5] Thieme, *Ibid.*, **43**, 473 (1891).
[6] THIS JOURNAL, **28**, 1449 (1906).