[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Condensations of Aromatic Amines with Formaldehyde in Media Containing Acid. IV. The Conversion of Diarylaminomethanes to Substituted Dihydro- and Tetrahydroquinazolines in Non-Aqueous Media

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Interaction of aromatic amines with formaldehyde in media containing acid generally has been assumed to proceed with the primary formation of diarylaminomethane (diimine), $(ArNH)_2CH_2$ or Schiff base, $ArN=CH_2 \left(\text{or} \left(\begin{array}{c} ArN-CH_2 \\ | & | \end{array} \right)_n \right)_2$ The end-products of the condensation, however, appear to be the results of further reactions induced by the instability in an acid medium of the grouping $> N-CH_2-N <^2$. Among these secondary reactions is the isomerization of the diimine (or Schiff base) to the aminobenzylaniline or diphenylmethane bases.³

The aminobenzylaniline base may be obtained as major product from a mixture of the diimine or Schiff base with the corresponding amine and amine salt under mild conditions and in the absence of water.⁴ At higher temperatures essentially the same reaction mixture yields the diphenylmethane base,^{4,5} and as this is formed also if the aminobenzylaniline base is used instead of the diimine (or Schiff base)⁶ it is obvious and is generally accepted that the entire transformation involves two well defined steps

ArNH-CH₂-NHAr
$$\longrightarrow$$
 ArNH-CH₂-ArNH₂ \longrightarrow
II II II
NH₂Ar-CH₂-ArNH₂⁷

These behaviors appear to be general for aromatic primary amines and secondary amines of the type ArNHR, whether or not the para hydrogen is substituted. It has been shown, however, that in the case of p-toluidine the second stage of the reaction occurs less readily than with amines without para substituents.³ It was there-

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(5) German patent, 53,937, Frdl., 2, 53.

(6) German patent, 55,848, Ber., 24, ref. 504 (1891).

fore thought that the first step, e. g., conversion of di-p-toluidinomethane or of methylene-p-toluidine to o-amino-m-xylyl-p-toluidine, could be studied separately under a variety of conditions with a view to the positive elucidation of the mechanism of the change. Accordingly dip-toluidinomethane was allowed to react at 80-90° with toluidine and toluidine hydrochloride with the unexpected result that the products of the reaction were 3-p-tolyl-6-methyl-3,4-dihydroquinazoline, 3-p-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline, o-amino-m-xylyl-p-toluidine, p-toluidine and methyl-p-toluidine.

This paper presents the results of experiments in which di-*p*-toluidinomethane, methylene-*p*-toluidine and di-*p*-phenetidinomethane were treated in varying proportions and under various conditions with the corresponding amine and amine salt. Fifty to ninety per cent. of the starting materials were accounted for by the formation of di- and tetrahydroquinazolines, aminobenzylaniline bases, amines (toluidine or phenetidine) and methylated amines (methyltoluidine or methylphenetidine).

The formation of quinazolines and the occurrence of methylation during interaction of para substituted primary aromatic amines and formaldehyde in wholly or partially aqueous media containing acid has been reported by Maffei,⁸ by Eisner and Wagner,⁹ by Wagner,¹⁰ and by Cairneross and Bogert.¹¹ Several of these investigators have discussed the mechanism of heterocycle formation and of methylation.^{8c,9,10} The initial product is the diimine (or Schiff base) which rearranges to the aminobenzylaniline base. From this the several obtainable heterocyclic compounds are formed owing to the reactiv-



 ^{(8) (}a) Lepetit and Maimeri, Atti accad. Lincei, [5] 26, 558
 (1917); (b) Lepetit, Maffei and Maimeri, Gazz. chim. ital., 57, 867
 (1927); (c) Maffei, ibid., 58, 261 (1928).

- (10) Wagner, ibid., 57, 1296 (1935).
- (11) Cairneross and Bogert, Collection Czechoslov. Chem. Communications, 7, 548 (1935); 8, 57 (1936).

⁽²⁾ See Wagner, THIS JOURNAL, **55**, 724 (1933), for leading references.

⁽³⁾ Wagner, ibid., 56, 1944 (1934).

⁽⁴⁾ German patent 105,797, Frdl., 5, 84; 87,934, Frdl., 4, 66.

⁽⁷⁾ This change is superficially a two stage isomerization and is often referred to as a rearrangement [(a) Moore and Johnson, THIS JOURNAL, **57**, 1517 (1935); (b) Braun and Kruber, Ber., **45**, 2977 (1912); (c) Cohn and Fischer, *ibid.*, **33**, 2586 (1900); (d) Meyer and Rohmer, *ibid.*, **33**, 250 (1900); (e) Eberhardt and Welter, *ibid.*, **27**, 1804 (1894)]. Actually it is a fission and coupling, for by interaction of a base, its hydrochloride and the aminobenzylaniline base from a different amine there results a diphenylmethane base of "mixed" type.⁶

⁽⁹⁾ Eisner and Wagner, THIS JOURNAL, 56, 1938 (1934).

whose two amino groups are suitably disposed to permit ring closure with formic acid or formaldehyde. In these reactions the formaldehyde and formic acid needed to effect ring closure are demonstrably present so that formation of quinazolines is readily explicable. In the experiments recorded below, however, no such agents are present, the conditions being in fact those previously considered suitable for the formation of aminobenzylaniline and diphenylmethane bases. It was therefore necessary to determine the manner in which the diimine or Schiff base, by the action of amine hydrochloride and amine, yields (through the aminobenzylaniline base) the tetrahydroquinazoline, the dihydroquinazoline and methylated amine.

The probable course of the formation of such compounds from *o*-amino-*m*-xylyl-*p*-toluidine is indicated in Fig. 1.



Reaction 1 has been realized independently in the present study. It is the counterpart of the formation of II from I and formaldehyde,¹² both reactions occurring in the absence of acids. The fact that II can also be formed by the action of formaldehyde in the presence of free acid in the cold as shown by Wagner¹³ removes any doubt that the same compound may result by reaction 1, in the presence of amine salt. It is to be considered probable, however (see below), that under such conditions the reaction may be reversible.

Evidence for reaction 2, the conversion of II to III, is less direct but is circumstantially convincing. The data from experiments in which quinazolines are formed from IV show that conditions which lead to an increased yield of II bring about an approximately corresponding decrease in the yield of III and vice versa. This seems to indicate that the tetrahydro is a precursor of the dihydroquinazoline. The formation of III would accordingly require the dehydrogenation of II by some suitable hydrogen acceptor. Removal by conventional means of the two hydrogens involved was effected by mild oxidation with permanganate in acetone solution.¹⁴ It is suggested that in the conversions of diimine reported in this paper the tetrahydro compound is "oxidized" by the diimine in the presence of amine salt or the fragment CHad CH2.

As a result of such a reaction methyl-*p*-toluidine is formed. This is supported by the experimental fact that only when III was formed was there any secondary amine among the reaction products. It appears impossible to devise an experiment to test the "oxidation" of II by diimine because the diimine can only produce the fragment CH_4 N— CH_2 in the presence of an amine salt

(or acid) which was found independently to bring about a conversion of II to III.

Thus heating together II and p-toluidine hydrochloride produced III, methyl-p-toluidine and 2,2'-diamino-5,5'-dimethyldiphenylmethane. These results serve to (1) illustrate the unusual properties of the tetrahydroquinazoline and (2) support the idea of its "oxidation" by the diimine. The appearance of the diphenylmethane base suggests the intermediate formation of I by a cleavage of the tetrahydroquinazoline ring by the action of amine salt

⁽¹²⁾ Ref. 9, p. 1942.
(13) Ref. 10, p. 1297.

⁽¹⁴⁾ German patent 92,084, Frdl., 4, 131.



A similar cleavage of tetrahydroquinazolines in aqueous acids produces aminobenzylamines and aldehydes.¹⁶ Benzoyl chloride in pyridine also brings about fission,¹⁶ compound II yielding the benzoyl derivative of I. Toluidine hydrochloride, however, produces IV in addition to I so that the cleavage is actually reaction 1 reversed by the presence of amine salt. The diimine in the presence of the hydrochloride cleaves to toluidine and the fragment CH_3 N— CH_2 . Amin-

oxylyltoluidine by the action of toluidine and toluidine hydrochloride is converted to the diphenylmethane base.³ The fragment CH_2

now "oxidizes" uncleaved II, being itself reduced to methyltoluidine. In this respect the reaction would be analogous to the Doebner reaction in which secondary amine is produced from a dihydrocinchoninic acid and a methylene amine ArCH=NAr.17 The quantities of toluidine and methyltoluidine formed during the conversions of IV to III and II were observed experimentally to be in roughly quantitative agreement with the requirements of the reactions in Fig. 1. From these considerations it seems certain that in the conversion of IV to III methylation occurs during the conversion of the intermediately formed tetrahydroquinazoline to the dihydroquinazoline and that formation of the latter involves the "oxidation" of the tetrahydroquinazoline by di-p-toluidinomethane or the fragment CH_s N-CH2

A similar series of reactions explains the conversion of di-*p*-phenetidinomethane to 3-*p*-phenetyl-6-ethoxy-3,4-dihydroquinazoline and methyl*p*-phenetidine.

Experimental Part

Preparation of Materials.—Di-p-toluidinomethane, m. p. 95.5–96.0° corr., was prepared according to Eberhardt and Welter;¹⁸ di-pphenetidinomethane, m. p. 80.3–81.0° corr. by the directions of Bischoff.¹⁹ p-Toluidine and p-phenetidine hydrochlorides were crystallized from aqueous solutions by addition of strong hydrochloric acid. 3-p-Tolyl-6methyl-3,4-dihydroquinazoline hydrochloride was prepared by chilling the hot solution of the base in 1:1 hydrochloric acid. It was

crystallized from dilute acid, m. p. 219.5° obsd. (226.3° corr.). *p*-Toluidine was Eastman best grade; *p*-phenetidine was vacuum distilled before use. All melting points are corrected.

Rearrangements of Di-*p*-toluidinomethane (IV); General Procedure.—Compound IV (0.01 mole) was mixed with the desired quantities of amine and amine hydrochloride, heated for one-half to four hours at the required temperature, made alkaline and steam distilled.

The steam distillate, in experiments recorded in Table II, was then treated with benzene sulfonyl chloride by the Hinsberg-Kessler procedure to estimate quantities of primary and secondary amines.²⁰ No tertiary amine was found in these distillates. In some experiments (Nos. 34, 34R, 35, 36, 39) in which small quantities of base hydrochloride were used, preceding the Hinsberg separation the steam distillate was titrated with 0.5 N hydrochloric acid using Congo paper as indicator. This served not only as a check on the Hinsberg analysis but to separate primary and secondary amine from unreacted IV which under these conditions was not titratable and could be filtered from the solution of base hydrochloride. A test titration of 1.60 g. of p-toluidine in the presence of 0.8 g. of IV indicated 1.62 g. of p-toluidine.

Yields of I and III in the non-steam-volatile residue were estimated as follows.

The residue, separated from the alkaline solution by ether extraction or filtration, was dissolved in boiling alcohol (25-50 cc.) and benzaldehyde (1.5-2.0 cc.) added to the hot solution which was kept hot for two to three minutes. On cooling, the benzal derivative of I crystallized. The melting point of this material was usually $127^{\circ,21}$ The filtrate was then heated to boiling and a solution of picric acid (0.2-0.8 g.) in alcohol (10-15 cc.) added. The picrate of III crystallized on chilling. It melted usually at 210°.²² A test of this separation of I and III was made with 1.0 g. of I and 0.5 g. of III. The benzal compound weighed 1.24 g., 89.6%; the picrate, 1.07 g., 108%.

An over-all test of the steam distillation, ether extraction and separation using known quantities of I, III, ptoluidine and p-toluidine hydrochloride and correcting for an 89.6% recovery of I indicated 102% of I and 122% of III.

⁽¹⁵⁾ Wolff, Ber., 25, 3033-4 (1892); Busch, J. prakt. Chem., [2]
52, 413 (1895); [2] 53, 421 (1896).

⁽¹⁶⁾ Heller, Ber., 37, 3114, 3118 (1904).

⁽¹⁷⁾ Robinson and Bogert, J. Org. Chem., 1, 72 (1936); Ciusa and Musajo, Gozz. chim. ital., 59, 798 (1929); Carrara, ibid., 61, 625 (1931).

⁽¹⁸⁾ Eberhardt and Welter, Ref. (7e), p. 1808.

⁽¹⁹⁾ Bischoff, Ber., 31, 3244-3245 (1898).

⁽²⁰⁾ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. II, 1916, p. 24.

⁽²¹⁾ Von Walther and Bamberg, J. prakt. Chem., [2] 71, 157 (1905).

⁽²²⁾ Eisner and Wagner, Ref. 9, p. 1940.

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To estimate II this procedure had to be modified by extracting I and III from the ether solution of the residue with 0.5 N acid. The ether soluble portion on crystallization from ligroin (b. p. 70–90°) yielded II, m. p. $140^{\circ.33}$

The identity of III was shown by mixed melting point tests of base and/or picrate with authentic specimens. Compound I was identified by the recovery as its benzal derivative. No derivatives of II were available and its identification consisted in satisfactory mixed melting point determinations. Results are collected in Tables I, II, III.

Rearrangement of Di-*p***-phenetidinomethane.**—The diarylaminomethane (5.8 g., 0.02 mole) was heated for four hours on the boiling water-bath with 1.73 g. (0.01 mole) of *p*-phenetidine hydrochloride. The mixture was then made alkaline, steam distilled and the solid, non-volatile residue crystallized once from alcohol yielding 1.17 g. of a slightly yellow product, m. p. $141-142^{\circ}$.²⁴ The mother liquors gave no precipitate with benzaldehyde showing the absence of aminobenzylaniline base. The benzaldehyde was then removed by steam distillation and the residue converted to an impure picrate, m. p. $140-60^{\circ}$. This on recrystallization from alcohol yielded 0.58 g., m. p. 160- 70° . Total yield of 3-*p*-phenetyl-6-ethoxy-3,4-dihydroquinazoline was 1.5 g. (76%).

The steam distillate yielded the benzene sulfonyl derivatives of methyl-*p*-phenetidine, m. p. 65°, and of *p*-phenetidine, m. p. 142–143°.

A second trial of the same procedure with 20 g. (0.07 mole) of the diimine and 3.0 g. (0.01 mole) of the hydrochloride yielded 3.57 g. (52%) of the dihydroquinazoline $(2.49 \text{ g. of free base, m. p. 140-141}^\circ; 1.9 \text{ g. of the picrate, m. p. 180-183}^\circ).$

The following derivatives of phenetylethoxydihydroquinazoline were prepared.

Hydrochloride, by dissolving the base in hot dilute (1:1) acid containing a little alcohol and chilling. The product after recrystallization from dilute acid containing alcohol melted at 195.3°. The reported m. p. is 193°.^{24b}

Tetrahydroquinazoline.—Reduction of the dihydro base in alcohol with 9 times the theoretical amount of sodium gave a crude product, m. p. 131–135°. One crystallization from alcohol raised the m. p. to 143–143.5°. (Mixed with the dihydro compound melting at 141–142° the m. p. was 134–135.5°.) Another crystallization yielded pure tetrahydroquinazoline, m. p. 144–144.5°. The reported m. p. is 144°.^{24a}

3 - p - Tolyl - 6 - methyl - 3,4 - dihydroquinazoline from Methylene-*p*-toluidine.—Six grams of methylene-*p*-toluidine, 5.8 g. of *p*-toluidine, and 2.9 g. of *p*-toluidine hydrochloride were heated together at 90° for five hours. The non-steam volatile residue was crystallized twice from ligroin (b. p. 90-120°) to give 0.7 g. of III m. p. 163°. From the mother liquors there was isolated a little more of III and some I, m. p. 82°.

3 - p - Tolyl - 6 - methyl - 1,2,3,4 - tetrahydroquinazoline: Interaction of *o*-Amino-*m*-xylyl-*p*-toluidine and Di-*p*-toluidinomethane.¹⁶—A solution of IV (2.1 g.) and I (2.1 g.) in 90 cc. of alcohol was refluxed for one hour. Eighty cc. of alcohol was then distilled off and the residue allowed to crystallize. The mother liquors were diluted with water, ether was added followed by dilute hydrochloric acid (1:20) to separate toluidine and II. The solute in the ether layer was combined with the first crop of solid and crystallized from ligroin (90–120°) yielding II, m. p. 141°; yield 1.90 g., 86.3%.

The toluidine in the acid layer was recovered as the benzoyl derivative, m. p. 156° ; yield 2.1 g., 60.5%.

Oxidation to the Dihydroquinazoline

Action of p-Toluidine Hydrochloride.—Compound II (1.19 g., 0.005 mole) and p-toluidine hydrochloride (1.6 g., 0.011 mole) in 50 cc. of alcohol were refluxed four hours. The products were isolated by the usual procedure. The benzal derivative weighed 0.12 g., melted at $182-184.5^{\circ}$ and proved to be 2,2-dibenzalamino-5,5'-dimethyldiphenylmethane by mixed melting point of 183.5° with a specimen prepared as described below and melting at 186° . The yields of other products were: III, 0.40 g.; methyl-p-toluidine, 0.11 g.; p-toluidine, 0.83 g.

A duplicate experiment run at 110° for two hours without alcohol and worked up in the same way gave essentially the same yields of the same products.

Permanganate Oxidation.—Seventy-five cc. of acetone containing 0.63 g. of potassium permanganate was added in portions to II (1.19 g.), dissolved in 75 cc. of acetone. The reaction took place immediately and was allowed to proceed at room temperature. The precipitated manganese dioxide was filtered off and the product in the filtrate converted to the picrate as usual. The yield was 28.8% of picrate which after crystallization from alcohol melted at 208–209°.

Action of Di-*p*-toluidinomethane and *p*-Toluidine Hydrochloride.—A mixture of IV and II (1.2 g. each) was heated with 1.6 g. of *p*-toluidine hydrochloride in 50 cc. of alcohol for three hours at $61 \pm 1^{\circ}$. The yields were: I, 0.36 g.; III, 0.40 g.; methyl-*p*-toluidine, 0.26 g.; *p*toluidine, 1.44 g. These data indicate that 0.84 g. of IV was available to take part in reactions forming 0.40 g. of III. The ratio of 3 diimine to 1 of III indicates, however, that only 0.29 g. of III could be formed from this quantity of available IV. It may be concluded that 0.11 g. of III was formed from II.

Cleavage by Benzoyl Chloride.—One gram of II was treated in benzene solution with 2 cc. of pyridine and 1.0 cc. of benzoyl chloride. Recovery of the benzoylation product in the ordinary manner²⁸ yielded, after one crystallization, 0.45 g. of white crystalline material melting at 186–190°. Recrystallization from dilute alcohol gave a product melting at 190.2–190.5°. This material was identical with a sample melting at 188.5–189° prepared from II by the usual Schotten–Baumann procedure as shown by a mixed m. p. of 189°. Benzoylation of I in aqueous alkali gave the same compound, m. p. 189.6°, mixed m. p. 190°, shown by analysis to be the dibenzoyl derivative of I and not the monobenzoyl derivative.

Anal. Calcd. for $C_{29}H_{26}N_2O_2$: N, 6.45. Found: N, 6.50.

⁽²³⁾ Von Walther and Bamberg, J. prakt. Chem., [2] 73, 209 (1906).

^{(24) (}a) Maffei, Gazz. chim. ital., 59, 3-9 (1929); (b) Goldschmidt, Chem.-Ztg., 21, 395 (1897).

⁽²⁵⁾ Thanks are due Mr. S. A. Shrager for carrying out this experiment.

⁽²⁶⁾ Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1935, p. 146.

2,2'-Dibenzalamino - 5,5'-dimethyldiphenylmethane. The diphenylmethane base (0.24 g., 0.01 mole) in 5 cc. of alcohol was treated in the hot with 0.22 g. (0.02 mole) freshly distilled benzaldehyde. The solution was boiled for a few minutes and then chilled to give 0.38 g. of a product melting at 182-184°. One crystallization from alcohol gave the pure derivative with m. p. 186°. Analysis showed it to be a dibenzal derivative.

Anal. Calcd. for C29H26N2: N, 6.97. Found: N, 6.98.

Discussion of Results

Formation of o-Amino-m-xylyl-p-toluidine.— The data of a number of experiments performed to ascertain the effect of conditions on the production of this base from di-p-toluidinomethane are tabulated in Table I. The largest yield was 82.5% obtained by using a molar ratio of diimine: toluidine hydrochloride: toluidine of 1:1:25. The data showed that (1) the time required for reaction was not more than one-half hour, longer periods of heating had no beneficial effect; (2) the temperature at which the reaction proceeded within the limits of 60 and 100° had no effect on the yields; (3) the effect of solvent (alcohol) was to lower the yield of I and increase the quantity of III; (4) the amount of toluidine hydrochloride had to be greater than 0.01 g. (0.0001 mole) for 2.26 g. (0.01 mole) of diimine in order for any transformation to take place; (5) the best conversions were observed when there was used 0.005-0.01 mole of hydrochloride per 0.01 mole of diimine; 0.001 mole of hydrochloride resulted in smaller yields of I, larger yields of III and the formation of II.

Formation of Quinazolines.—A number of experiments were made to find out under what conditions these compounds became the major products of the transformation of IV. The data are recorded in Table II. In the absence of a solvent the greatest amount of III obtained was 0.00144 mole from 0.01 mole of dimine (43.2%). This quantity resulted when only diimine and toluidine hydrochloride reacted and was essentially the same as long as the molar ratio of hydrochloride: diimine remained larger than 0.5. When less hydrochloride was used the yield of III decreased and II was found among the products. Compound I was found under practically all conditions (up to 0.0023 mole). When alcohol was used as a solvent the quantity of III was raised to 0.0021-0.0025 mole (62-75%) while the amount of I was lowered to 0.0005 mole or less. In all of these experiments both methyl-p-toluidine and p-toluidine were produced.

In Table III are recorded the yields of III obtained from the dimine by the action of a number

Conv	ERSION OF DI-	p-TOLUIDING	METHANE TO	o-Amino-m-x	YLYL-p-TO	LUIDINE	
Effect of Conditions: Solvent: (50 mmol. (5.5	(10 mmol. (2 g.) <i>p</i> -toluidine	.26-2.3 g.) d ; 5 mmol. (liimine used i 0.7 g.) <i>p</i> -tolu	in each expt.). idine hydrochl	EFFECT oride).	of Time, Ten	MPERATURE, AND
Expt.	17	18	19	20	21	20A	15
Conditions							
Hrs, htd.	4	3	3	3	3	0.5	3
Temp., ° C.	60 = 5	60 = 1	70 ± 1	80 = 1	90 = 1	85 ± 5	78-80
Solvent		• • •	•••	•••	• • •	• • •	Alc. (50 cc.)
Products							
I, mmol.	7.43	7.19	6.90	6. 8 6	6.72	6.77	4.12
III, mmol.	0.51	0.64	0.68	0.64	0.76	0.42	1.48
Total mmol. diimine							
acctd. for	8.96	9.09	8.94	8.78	9.00	8.03	8.56
	EFFECT OF R	ATIO. D-TOL	uidine: <i>d</i> -To	LUIDINE HYDR	OCHLORID	E	
		Temp.	80 9 0°, No	Solvent			
Expt.	20A	43	20B	13	44	46	48
Conditions							
p-Tol., mmol.	50	50	5 0	50	50	250	10
p-T. HCl, mmol.	5	1	0.1	0.0	10	10	10
Molar ratio	10	5 0	50 0		5	25	1
Products							
I, mmol.	6.77	3.58	0.0	0.0	6.15	8.24	2.28
III, mmol.	0.42	0.68	0.0	0.0	0.64	0.25	1.40
Total mmol. diimine							
acctd. for	8.03	5.62		• • •	8.07	9.00	6.48

TABLE I

CONVERSION	of DI-p-	TOLUIDINO	METHANE	то 3- <i>р</i> -Тоі	LYL-6-MET	HYL-3,4-DI	HYDROQUIN	AZOLINE	
		10 mml. (2	2.26-2.3 g.) diimine 1	ised in eac	ch expt.)			
Expt.	25	16	10C	10A	35	34	34R	36	39
Reagents									
p-Tol. HCl, mmol.	10	5	10	5	5	1	1	0.5	0.1
Solvent	Alc. (50 cc.)	Alc. (50 cc.)	••	••	• •	•••		•••	• • •
Products									
I, mmol.	0.50	0.00	2.30	2.30	2.30	0.25	0.14	0.0	a
III, mmol.	2.08	2.50	1.33	1.35	1.44	1.14	0.98	0.85	
II, mmol.	b	ъ	ь	ь	ь	0.84	0.55	0.01	• • •
p-Tol., mmol.	4.6		6	2.15°	b	7.19	7.96	8.40	
Me-p-Tol., mmol.	ь	ь	ь	đ	0.69	0.96	1.03	0.77	

TABLE II

^a About 15% of unreacted dimine recovered from steam distillate. ^b Not determined. ^c Determined in a duplicate experiment. ^d Identified but not determined.

of different salts. The hydrochloride of III gave the largest yield in these trials. Small yields were obtained by the action of ammonium chloride and dimethylaniline hydrochloride. Zinc chloride yielded none of III.

TABLE III

Conversion of Di-*p*-toluidinomethane to 3-*p*-Tolyl-6-methyl-3,4-dihydroquinazoline

(10 mml. of di-*p*-toluidinomethane and various salts as catalysts; no solvent

Expt.	Salt		Mm!.	Mml. III
14	$ZnCl_2$		2 , 0	$0.0^{a,b}$
28	Dimethylaniline	hy-		
	drochloride		10.0	$0.77^{a,c}$
29	Hydrochl. of III		1.0	1.86^{a}
45	NH4Cl		10.0	0.77^{a}
34	p-Tol. HCl		1.0	1.14^{a}

^a No attempt made to isolate compd. II. ^b Isolated 0.18 g. subs. m. p. 227-230° obsd. not identified. ^c Major product was tetramethyldiaminodiphenylmethane, m. p. 87°.

Summary

1. Di-p-toluidinomethane by the action of ptoluidine and p-toluidine hydrochloride has been shown to yield o-amino-m-xylyl-p-toluidine, 3-ptolyl-6-methyl-1,2,3,4-tetrahydroquinazoline, 3*p*-tolyl-6-methyl-3,4-dihydroquinazoline, *p*-toluidine and methyl-*p*-toluidine.

2. This conversion has been studied using varying proportions of reactants and under a variety of conditions essentially those previously thought suitable for converting di-p-toluidino-methane to *o*-amino-*m*-xylyl-p-toluidine or 2,2'-diamino-5,5'-dimethyldiphenylmethane.

3. Di-*p*-phenetidinomethane similarly yielded 3-*p*-phenetyl-6-ethoxy-3,5-dihydroquinazoline and methyl-*p*-phenetidine.

4. The probable course of the formation of quinazolines under these conditions has been shown to consist in the intermediate production of a tetrahydroquinazoline from the aminobenzylaniline base followed by "oxidation" to a dihydroquinazoline effected by the diarylaminomethane in an acid medium.

5. The interaction of di-*p*-toluidinomethane and *o*-amino-*m*-xylyl-*p*-toluidine to yield 3-*p*tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline and its behavior toward a number of reagents has been described.

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