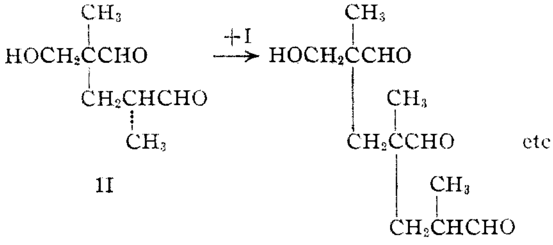


Experimental

The α-methylacrolein was purchased from the Shell Development Co. It was of about 98% purity and contained 0.05% hydroquinone as an antioxidant. Since it was desired to avoid polymerization produced by peroxides, and since the hydroquinone did not appear to inhibit the polycondensation, it was used as received without further purification.

Thirty-three grams of methylacrolein was mixed with 200 cc. of distilled water. About 50 cc. of ethyl alcohol was added to promote solution and ten cc. of 4% aqueous sodium hydroxide. A brown flash of color appeared which disappeared upon shaking. In about ten minutes turbidity appeared and a yellow oil began to settle. Heat was evolved; the flask was cooled by bathing in cold running water. After allowing the flask to stand for one hour (during which time it was shaken frequently), the solution was extracted three times with ether, and the extract was dried over sodium sulfate. The ether was removed and the oil was fractionated under reduced pressure. In the preliminary distillation three fractions were collected as follows:

(1)	Bath 165–170° (15 mm.)	141.1 g.
(2)	Bath 195–210° (10 mm.)	3.6 g.
(3)	Bath 225–250° (10 mm.)	7.6 g.

The total yield of crude oils was 71.3% of the theoretical Other experiments gave similar results.

Upon redistillation the above fractions were found to consist almost entirely of the pure polymers. The properties were determined from these purified fractions. The molecular weights were determined in freezing benzene. These and other data are listed in Table I.

Preparation of the Tri-2,4-dinitrophenylhydrazones of the Polymers.—The method employed was essentially that suggested by Shriner and Fuson.[6] An equivalent of dinitrophenylhydrazine for each aldehyde group was employed. Yellow tridinitrophenylhydrazones were obtained in each case. The derivative of the trimer separated from the reaction mixture even when boiling. Cooling was resorted to in the other cases to obtain crystallization of the derivatives. They were then recrystallized from benzene. The tridinitrophenylhydrazone of the trimer decomposed to a red liquid at 173–174° (uncorr.), but the other two derivatives decomposed indefinitely as the temperature was raised above 100°.

Anal. Trimer. Calcd. for $C_{30}H_{32}N_{12}O_{18}$: N, 21.8. Found: N (Dumas), 21.4. Tetramer. Calcd. for $C_{34}H_{38}N_{12}O_{14}$: C, 48.65; H, 4.53; N, 20.0. Found: C, 48.60; H, 4.82; N, 20.4. Pentamer. Calcd. for $C_{38}H_{44}N_{12}O_{16}$: N, 18.5. Found: N, 18.5.

Summary

α-Methylacrolein polycondenses by the Michael reaction in the presence of dilute aqueous alkali. A trimer, a tetramer, and a pentamer were isolated and characterized.

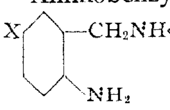
[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 148.

New Haven, Conn. Received May 23, 1938

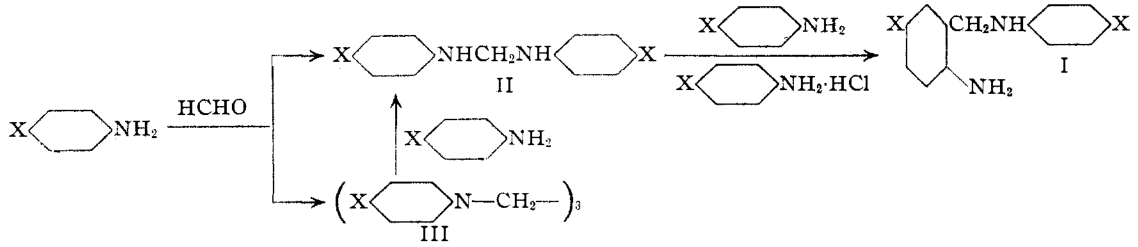
[Contribution from the Department of Chemistry and Chemical Engineering of the University of Pennsylvania]

A Study of the Conversion of Para-substituted Methylene-bis-arylamines and Trimeric Methylene-arylamines to Substituted 2-Aminobenzylarylamines

By T. R. Miller and E. C. Wagner


I

Aminobenzylarylamines of type I may be prepared from para-substituted amines through the reactions



The only published procedure[1] is cumbersome, as it requires mechanical stirring of a mixture of methylene-*p*-toluidine, *p*-toluidine and *p*-toluidine hydrochloride for forty-eight hours at 20°, in the presence of enough nitrobenzene to yield a mass which is finally liquid. The mild conditions specified (which greatly prolong the reaction period) are clearly intended to exclude or minimize

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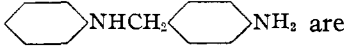
[1] German Patent 105,797; *Friedl.*, **5**, 84; v. Walther and Bamberg, *J. prakt. Chem.*, [2] **71**, 153 (1905).

the further reaction by which I is converted to the diphenylmethane base. With diimines (II) and trimeric Schiff bases (III) obtained from amines with open para-position this reaction occurs readily on warming in the presence of amine salt (or free acid),[2] and can be excluded only by operating at or below 20°, at which temperatures aminobenzylarylamines of the type  are obtainable.[3] It is now known[4] that aminobenzylarylamines of type I (from para-substituted amines) are less readily converted to diphenylmethane bases: at 100° the conversion of *o*-amino-*m*-xylyl-*p*-toluidine (I) to 2,2′-diamino-5,5′-dimethyldiphenylmethane is slight,[5] and at 125° the conversion is only 50% complete.[6] These facts suggested the possibility of converting II or III more rapidly to I by use of temperatures well above 20°. As is shown in the experimental part the reaction goes well at 80–100°, and normal yields are obtained in a few hours, the nitrobenzene and (in small runs) mechanical stirring being dispensable.

The proportions of diimine (II) or Schiff base (III), free amine and amine salt hitherto used in these reactions appear to be based upon no published experimental work. As a result of Simons' study[7] of the reactions of diimines (II) with amines and amine salts it is established that II with amine salt yields as the normal end-product the corresponding dihydroquinazoline (*e. g.*, 6-methyl-3-*p*-tolyl-3,4-dihydroquinazoline), with I formed as an intermediate, but that presence of free amine tends to exclude the later steps of the complete transformation and thus favors survival of I. With 25 molar equivalents of amine to one equivalent each of II and amine hydrochloride an 82.5% yield of I was obtained. This amount of free amine is inconveniently large, for the excess, together with amine taken as hydrochloride, must be removed subsequently by steam distillation or otherwise, in the isolation of I. Experimental trials, reported below, showed that satisfactory practical molar ratios for preparation of I are diimine:amine:amine hydrochloride = 1:10–12:0.5. When the trimeric Schiff base is used, three equivalents of amine are consumed in the initial reaction[2b] requiring for the

$$(\mathrm{ArNCH_2—})_3 + 3\mathrm{ArNH_2} \longrightarrow 3\mathrm{ArNHCH_2NHAr}$$

Schiff base the molar proportions trimer (III): amine : amine hydrochloride = 1 : 33–39 : 1.5. The proportions previously specified[1] for the cold reaction are III: amine: amine hydrochloride = 1 : 16.7 : 5.8, *i. e.*, more than the necessary amine salt (shown by Simons[7] to be 0.5–1.0 equivalent referred to the diimine), and an amount of amine less than adequate for the hot reaction. The most satisfactory combination of conditions includes the ratio of reactants stated, a temperature of 80–90°, and, for 0.01–0.1 molar quantities, a reaction period of two hours. With larger quantities the time should be extended to three to five hours and the mixture should be stirred mechanically.

The applicability of the procedure for preparative purposes appears to be limited. Satisfactory results were obtained in the preparation of the aminobenzylarylamines from *p*-toluidine, *p*-chloroaniline and *p*-bromoaniline. Attempts to prepare those from *p*-anisidine and *p*-phenetidine were unsuccessful, owing apparently to isolation difficulties, which it is safe to say would be greater with para-substituted amines not volatile with steam.

The conversion of II to I by substitutive ortho-coupling (rather than by rearrangement) suggests the possibility of making 2-aminobenzylarylamines of mixed type by warming diimines or Schiff bases with different amines and their hydrochlorides. The analogous process has been used for preparation of diphenylmethane bases of mixed type from simple aminobenzylarylamines.[8] Preliminary trials[9] yielded unpromising viscous liquids from which no well-defined product could be isolated.

Experimental

Chemicals.—Methylene-*bis*-*p*-toluidine (m. p. 95°), methylene-*bis*-*p*-chloroaniline (m. p. 59–60°) and methylene-*bis*-*p*-bromoaniline[10] (m. p. 92°) were made by the method of Eberhardt and Welter[2b] and Bischoff and Reinfeld.[11] The trimeric Schiff bases (melting respectively at 127, 151 and 166°[12]) were prepared by the procedure of J. G. Miller.[13] .

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(2) (a) German Patents 53,937, 58,072, 70,402, 107,718; *Friedl.*, **2**, 53; **3**, 79, 80; **5**, 78; (b) Eberhardt and Welter, *Ber.*, **27**, 1804 (1894); (c) Rivier and Farine, *Helv. Chim. Acta*, **12**, 865 (1929).

(3) German Patents 87,934, 104,230; *Friedl.*, **4**, 66; **5**, 83.

(4) Wagner, THIS JOURNAL, **56**, 1944 (1934).

(5) *Cf.* Eberhardt and Welter, ref. 2b, p. 1812.

(6) At higher temperatures (200–220°) diphenylmethane bases of this type, in presence of amine and amine salt, split out ammonia and yield dihydroacridines [Ullmann, *Ber.*, **36**, 1017 (1903)].

(7) Simons, THIS JOURNAL, **59**, 518 (1937).

(8) German Patent 108,064; *Friedl.*, **5**, 85; Cohn and Fischer, *Ber.*, **33**, 2586 (1900).

(9) These experiments were performed by J. R. Feldman.

(10) Wagner, *J. Org. Chem.*, **2**, 162 (1937).

(11) Bischoff and Reinfeld, *Ber.*, **36**, 41 (1903).

(12) Wagner and Eisner, THIS JOURNAL, **59**, 881 (1937).

(13) Miller and Wagner, *ibid.*, **54**, 3698 (1932).

Procedure.—The mixture of diimine or Schiff base (0.01 mole), amine and amine hydrochloride in a flask was heated in an oil-bath at the desired temperature (thermometer in the bath), and was then treated with enough sodium hydroxide solution to neutralize the acid taken as amine salt and was submitted to rapid steam distillation. When all steam-volatile material was removed the residual mixture was cooled to solidify the crude product, which was separated by filtration, washed once with water and then without drying was crystallized as follows. The moist product, in a 200-cc. flask, was heated on a water-bath, and ligroin (70–90°) was added gradually until a solution nearly saturated at the boiling point was obtained. Anhydrous potassium carbonate sufficient to "fix" the separated water was added, and the mixture was digested with about 0.5 g. of charcoal and then filtered rapidly using a heated filter. The liquid was chilled in ice, and the separated crystals were removed by filtration, washed with cold ligroin and dried in a vacuum desiccator. The yields stated represent nearly pure product but do not indicate quite the maximum yields obtainable, as the ligroin mother liquors were not worked up to recover the small amount of product still present though not readily isolable owing to presence of resinous impurities. In several experiments the mother liquors were found to contain small amounts of the dihydroquinazolines, isolated and identified as their picrates.

In the first series of experiments reported below the product was isolated and weighed as the benzal derivative.[7] This procedure indicated higher but less reproducible yields than the procedure described above.

Series 1: Effect of Temperature.—Conditions: methylene-*bis-p*-toluidine (II), 0.01 mole (2.26 g.), *p*-toluidine, 0.05 mole (5.5 g.), *p*-toluidine hydrochloride, 0.005 mole (0.70 g.); time one hour. Product isolated as benzal derivative.

Temperature, °C.	50	60	70	80	90	100
Yield of I, %	63.7	65.3	64.7	66.0	66.9	66.6

Series 2: Effect of Variation in Proportions of Reactants (and Time).—In experiments using the diimine (II) the above ratio of II to *p*-toluidine hydrochloride was held constant (being within the optimum limits reported by Simons[7]), and the ratio of *p*-toluidine to II was varied. In the experiments using the Schiff base trimer (III) the ratio of III to *p*-toluidine hydrochloride was 1:1.5, and the proportions of *p*-toluidine were varied. In the table the values for the ratio of *p*-toluidine to Schiff base refer to moles of *p*-toluidine available as "regulator," calculated in terms of equivalent moles of diimine, *viz.*, $(x - 3y)/3y$, in which x = moles of *p*-toluidine and y = moles of Schiff base; temperature, 80°.

Starting comp.	Ratio *p*-toluidine: II or III[a]	Yield of I, %	
	A, Time 0.5 hour		
III	10	50.1	51.6
III	15	57.4	
II	25	59.3	
	B, Time 1 hour		
II	5	48.7	
III	5	48.7	
III	8	50.2	
II	10	51.2	
III	10	50.0	
II	12	51.5	51.0[b]
III	12	52.0	
III	15	56.0	59.1
II	20	58.5	
III	20	60.4	
II	25	61.2	
III	25	62.0	

[a] Calculated in terms of equivalent II, as explained above. [b] Temperature 100°.

Series 3: Effect of Time.—In experiments with diimine the proportions of reactants were as in Series 1, *i. e.*, 1:10:0.5. In experiments using the Schiff base trimer the proportions were 1:33:1.5 (or 1:10:0.5 calculated to equivalent diimine); temperature 80°.

Starting compound	III	II	II	II
Time, hrs.	0.5	1	2	3
Yield, %	51.6	54.7	63.3	62.7
	50.1	54.0	60.0	

Preparative Trials

Cold Procedure.[1]—The starting compound was in all cases III, the amounts ranging from 53 to 73.5 g. The molar proportions, in terms of equivalent diimine, were 1:4.6:1.9, with nitrobenzene 1.7 cc. per gram of III. The reaction mixtures were stirred mechanically during forty-eight to fifty-three hours, at temperatures which ranged from 15 to 24° and which were for the most part not above 20°. The best yields obtained were 61.4 and 56.3%.

Hot Procedure.—The starting compound was II, the time two hours, and the temperature 80–90°. For ratio 1:12:0.5 the yield was 61.5%; for ratio 1:21:1.6 the yield was 64.5%.

The foregoing results, and those of series 1, 2 and 3 show the conversion of II or III to I to be fairly rapid at 80–90°, the yields increasing as the molar ratio of available free amine is increased. For preparative purposes a molar ratio of about 10:1 when the starting compound is II, or of 33:1 when the starting compound is III, is recommended. The yields are then satisfactory and the amount of amine to be removed during the isolation is not excessive. The diimine or the Schiff base may be used equally well as starting material.

Conversion of Diimines and Schiff Bases from *p*-Chloroaniline and *p*-Bromoaniline to Corresponding 2-Aminobenzylarylamines. Conditions.—Molar ratio for diimine 1:12:0.5, and equivalent ratio for Schiff base; temperature 80°; time two hours.

Starting compound	II	III
Yield of I, %		
Cl compound	45.3	46.3[14]
Br compound	50.2	47.3[14]

Grateful acknowledgment is made to the Faculty Research Committee of the University of Pennsylvania for a grant to assist this study.

[14] Some results by a closely similar procedure were mentioned in an earlier paper (Ref. 12, p. 879).

Summary

1. A study of the effects of variations in temperature, time and molar ratios of reactants upon the conversion of methylene-*bis*-*p*-toluidine or trimeric methylene-*p*-toluidine to N-(5-methyl-2-aminobenzyl)-*p*-toluidine, in the presence of *p*-toluidine and *p*-toluidine hydrochloride, showed: (a) at 80–100° the reaction is rapid and does not proceed beyond the aminobenzylarylamine stage. The conditions previously specified, *viz.*, a temperature of 20° and a reaction time of forty-eight hours, were based on a misconception. (b) The extent of the conversion increases with increase in the molar ratio of free amine to diimine or Schiff base. Highest yields require an inconveniently large excess of free amine. Satisfactory practical ratios, which give good yields and do not too greatly prolong the isolation procedure, are diimine : amine : amine hydrochloride = 1:10:0.5, or trimeric Schiff base : amine : amine hydrochloride = 1:33:1.5.

2. The procedure based upon the above conditions has been used for the preparation of the aminobenzylarylamines obtainable from *p*-toluidine, *p*-chloroaniline and *p*-bromoaniline. It failed in the cases of *p*-anisidine and *p*-phenetidine and its usefulness apparently is impaired by the limitations of the isolation method now available.

THE JOHN HARRISON LABORATORY OF CHEMISTRY
PHILADELPHIA, PENNA. RECEIVED MAY 11, 1938

The Structure of Beta and Gamma Tocopherols

BY OLIVER H. EMERSON

To date there have been described in the literature three tocopherols, which we designated provisionally as alpha, beta and gamma.[1,2] Alpha was obtained from wheat germ oil, cottonseed oil, palm oil, and lettuce leaves. Beta was first obtained by us from wheat germ oil, and later by Todd, Bergel, Waldmann and Work, who obtained it in addition from rice bran oil.[3,4] It was obtained subsequently from wheat germ oil by Drummond and Hoover,[5] John,[6] who suggested the name cumo-tocopherol for it, and Karrer, Salomon and Fritsche,[7] who proposed the name neo-tocopherol. Dr. John[8] kindly compared a sample of our β-tocopherol allophanate with his cumo-tocopherol allophanate and found them identical. It is interesting that the European workers found that in their preparations of wheat germ oil, β-tocopherol predominated to such an extent that the suggestion was put forward that alpha might be an artifact,[9] whereas from the Californian wheat germ oil we have regularly obtained at least twice as much alpha as beta. γ-Tocopherol has been obtained from cottonseed oil and palm oil. In our experience at the University of California and in the Research Laboratories of Merck & Co., Inc., where several hundred pounds of cottonseed oil have been worked up, the ratio of alpha to gamma varies within wide limits. Sometimes there is as much gamma as alpha but usually much less. Other oils beside wheat germ and cotton seed, notably grape seed oil, are known to vary greatly in their chemical constituents, depending not only on the locality, but also on the year of the crop.

On pyrolysis Fernholz[10] showed that α-tocopherol yields durohydroquinone. Under similar conditions, from β-tocopherol John[6] obtained trimethylhydroquinone, and Bergel, Todd and Work[9] reported a mixture of trimethylhydroquinone and durohydroquinone.

Fernholz's original view that α-tocopherol is a simple mono-ether of durohydroquinone was modified by the results of the chromic acid oxidation,[11] whereby he obtained dimethylmaleic anhydride; a lactone $C_{21}H_{40}O_2$, the hydroxy acid of which forms a characteristic benzylthiuronium salt; and an acid $C_{16}H_{32}O_2$ which on vigorous oxidation yielded two moles of acetic acid. From this evidence Fernholz proposed formula I for α-tocopherol

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[1] H. M. Evans, O. H. Emerson and G. A. Emerson, *J. Biol. Chem.*, **113**, 319 (1936).

[2] O. H. Emerson, G. A. Emerson, A. Mohammad and H. M Evans, *ibid.*, **122**, 99 (1937).

[3] A. R. Todd, F. Bergel, H. Waldmann and T. S. Work, *Nature*, **140**, 361–2 (1937).

[4] A. R. Todd, F. Bergel and T. S. Work, *Biochem. J.*, **31**, 2257 (1937).

[5] J. C. Drummond and A. A. Hoover, *ibid.*, **31**, 1852 (1937).

[6] W. John, *Z. physiol. Chem.*, **250**, 11 (1937).

[7] P. Karrer, H. Salomon and H. Fritsche, *Helv. Chim. Acta*, **20**, 1422 (1937).

[8] W. John, *Z. physiol. Chem.*, **252**, 201 (1938).

[9] F. Bergel, A. R. Todd and T. S. Work, *J. Chem. Soc.*, 253 (1938).

[10] E. Fernholz, THIS JOURNAL, **59**, 1154 (1937).

[11] E. Fernholz, *ibid.*, **60**, 700 (1938).