1,2,3,4-TETRAPHENYLDIAZETIDINE

A REEXAMINATION[1]

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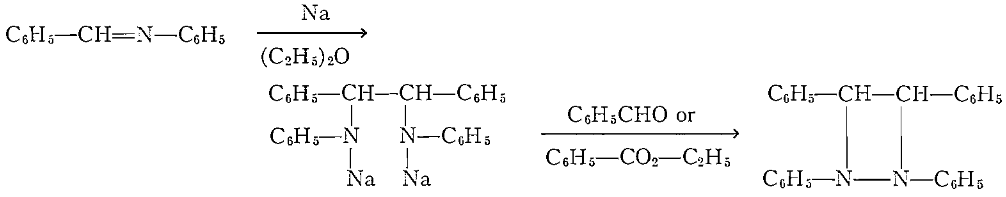
ABSTRACT

The reported synthesis of 1,2,3,4-tetraphenyldiazetidine by treating the sodium adduct of N-benzylidene aniline with benzaldehyde or benzoate ester is reexamined. It is shown that the original report is in error. The products from the reaction are the two diastereomeric N-benzoyl-N,N′,1,2-tetraphenylethylenediamines and *dd,ll*-N,N′,1,2-tetraphenylethylenediamine. When diethyl ether was used as a reaction medium, another product, N-benzoyl-N,N′-diphenylstilbene-α,α'-diamine, was formed. An explanation is offered for the formation of these compounds and for the differences in reaction products caused by the two reaction media employed, diethyl ether and tetrahydrofuran.

In 1928 it was reported (1) that the treatment of the sodium addition product (I) of N-benzylidine aniline with either ethyl benzoate or benzaldehyde produced 1,2,3,4-tetraphenyldiazetidine (II), as shown in eq. [1]. Because of the rarity of compounds such as (II) and the possibility that such a reaction may be a synthetic route to them, the reaction was reexamined.

[1]



$$C_6H_5{-}CH{=}N{-}C_6H_5 \xrightarrow[(C_2H_5)_2O]{Na} \begin{array}{c} C_6H_5{-}CH{-}CH{-}C_6H_5 \\ \quad | \qquad | \\ C_6H_5{-}N \quad N{-}C_6H_5 \\ \quad | \qquad | \\ \quad Na \quad Na \end{array} \xrightarrow[C_6H_5{-}CO_2{-}C_2H_5]{C_6H_5CHO \text{ or}} \begin{array}{c} C_6H_5{-}CH{-}CH{-}C_6H_5 \\ | \qquad | \\ C_6H_5{-}N{-}N{-}C_6H_5 \end{array}$$

I

II

RESULTS

Tetrahydrofuran was initially used as the preparative solvent and reaction medium because of the greater solubility of the organometallic compound in it. The addition of sodium to N-benzylidene aniline proceeded rapidly and smoothly to give the expected 2:2 adduct (I) (2, 3).

The reaction of this adduct with either benzaldehyde or esters of benzoic acid proceeded in a manner quite unlike that previously described. While the same compound was isolated from the two reactions, the melting point was some 30° higher than that reported.

On the basis of its analysis and its infrared spectrum, which showed a NH band at 3 380 cm^{-1} and an amide carbonyl band at 1 625 cm^{-1}, the compound was identified as N-benzoyl-N,N′,1,2-tetraphenylethylenediamine. Synthesis of the monobenzamides from the known diastereomeric N,N′,1,2-tetraphenylethylenediamines established its identity as the monobenzamide of the *dd,ll* diamine.

In addition to this, a second amide was isolated in low yield, which, on the basis of its analysis, infrared spectrum (NH band at 3 360 cm^{-1}, amide carbonyl at 1 635 cm^{-1}), and

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mixed melting point, was shown to be the N-benzoyl derivative of meso-N,N′,1,2-tetraphenylethylenediamine. The *dd,ll*-N,N′,1,2-tetraphenylethylenediamine was also detected in the products arising from the reaction with benzaldehyde.

Thinking that the course of the reaction may have been influenced by the choice of solvent, we repeated the experiments with diethyl ether, the solvent originally employed (1, 2). With methyl benzoate, no change in the course of the reaction was noticed. The products isolated were *dd,ll*-N,N′,1,2-tetraphenylethylenediamine and again the N-benzoyl derivatives of the *dd,ll* and meso diamines. There was, however, a change in the relative amounts of the two diastereomeric benzamides. With diethyl ether as solvent approximately equal quantities were formed, whereas with tetrahydrofuran the benzamide was largely derived from *dd,ll*-N,N′,1,2-tetraphenylethylenediamine.

Benzaldehyde generated a new compound which appeared as a yellow precipitate when the reaction mixture was hydrolyzed with water. This material decomposed at its melting point, was oxidized in boiling solvents, and lost its yellow color on treatment with acids. Its infrared spectrum showed a NH band at 3 340 cm^{-1} and an amide carbonyl band at 1 645 cm^{-1}. The chemical properties matched closely those described (4) for N-benzoyl-N,N′-diphenylstilbene-α,α'-diamine. Its identity was established by synthesis, by comparison of its infrared spectrum, and by the mixed melting point of its picrate.

Table I summarizes the reaction products and yields obtained.

TABLE I
Summary of reaction products and yields

			Products and yields			
Reagent	Solvent	Mole ratio*	*dd,ll*-TPED,† % yield	N-Benzoyl-TPED,† % yield	*dd,ll*/meso	Others, % yield
Methyl benzoate	Tetrahydrofuran	1	3	77	10	5‡
Methyl benzoate	Diethyl ether	1	30	62	0.35	
Benzaldehyde	Tetrahydrofuran	0.5	72	4	—	
Benzaldehyde	Tetrahydrofuran	1	28	63	20	
Benzaldehyde	Tetrahydrofuran	2	—	90	—	
Benzaldehyde	Diethyl ether	1	33	38	2.1	21§
Benzaldehyde	Diethyl ether	2	32	52	0.7	

*Moles of reagent/moles N-benzylidene aniline.
†N,N′,1,2-Tetraphenylethylenediamine.
‡N-Benzylidene aniline.
§N-Benzoyl-N,N′-diphenylstilbene-α,α'-diamine.

DISCUSSION

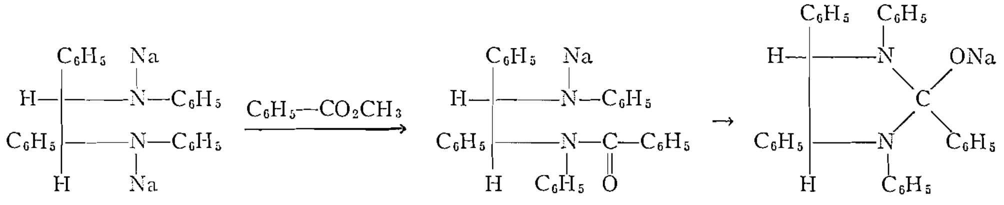
It must be concluded that 1,2,3,4-tetraphenyldiazetidine is not formed in any significant quantity in these reactions. The question remains concerning the identity of the compound isolated by Schlenk and Bergmann (1). Two pieces of evidence were offered for its identity, its analysis and its melting point, 153–154°, which differed markedly from that (136–139°) of the N,N′,1,2-tetraphenylethylenediamine obtained on hydrolysis of the organosodium compound.

At the time of the original work the fact was not appreciated that the hydrolysis product is actually a mixture of the meso and *dd,ll* diastereomers, whose individual melting points are 167° and 153° respectively (5). It seems likely that the reported compound was *dd,ll*-N,N′,1,2-tetraphenylethylenediamine, whose melting point and analysis agree with those reported. Its formation was probably due to premature hydrolysis of the reaction mixture.

Treatment of the sodium compound in ether with benzaldehyde results in the immediate formation of a yellow precipitate. Hydrolysis of the reaction mixture at this point produced only the diastereomeric mixture of the tetraphenylethylenediamines. It is only after the reaction mixture has been allowed to stand at room temperature for several hours before hydrolysis that appreciable quantities of benzoylated products are detected.

The formation of N-benzoylated derivatives with benzoate esters is to be expected. The interesting feature is the formation of only the monobenzamide. Possibly, after the formation of the monobenzamide, further reaction occurs intramolecularly to form (III),

[2]



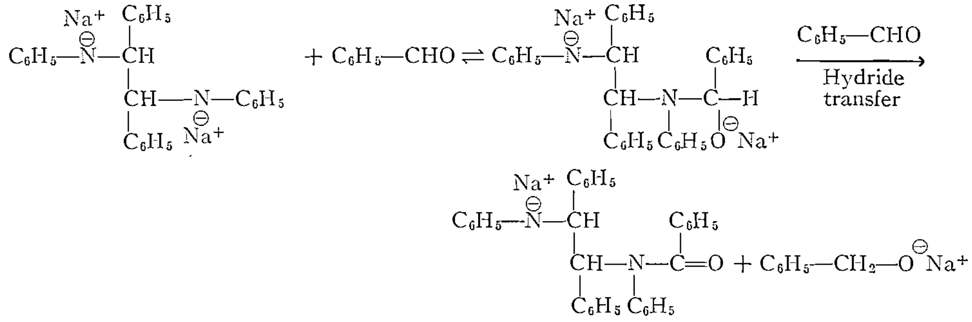
III

as shown in eq. [2]. Hydrolysis of the reaction product results in the ring opening of (III), thereby forming the N-benzoyl derivative.

Differences in the ratio of the monobenzamides of meso- and *dd,ll*-N,N′,1,2-tetraphenylethylenediamine formed in tetrahydrofuran versus those formed in diethyl ether are due to the difference in the ratio of the diastereomeric N,N′-disodio-N,N′,1,2-tetraphenylethylenediamines formed in the two solvents. It has been established (5*b*) that the ratio of the diastereomeric diamines formed by reductive dimerization of N-benzylidene aniline in wet ether is approximately 1:1. By using this published melting point – composition phase diagram, the diamine mixture obtained on hydrolysis of the sodium compound formed in tetrahydrofuran contained approximately 10% of the meso diamine.

In the case of the reaction with benzaldehyde, the substituted benzamide can arise from two sources. The amine anion can take part in a Cannizzaro reaction, as shown in eq. [3],

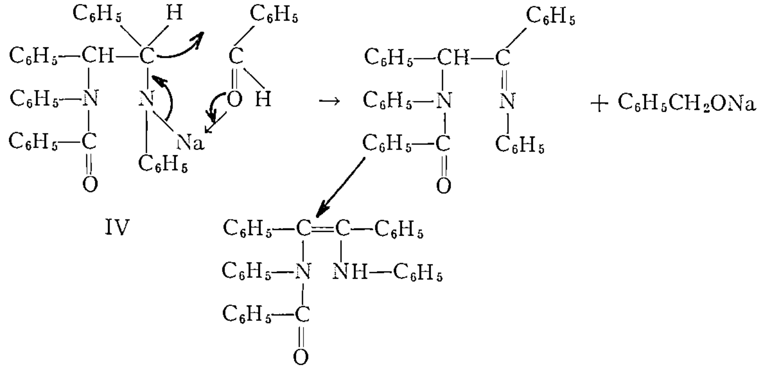
[3]



to produce the product and an alkoxide ion. This anion in turn can react with benzaldehyde in a Cannizzaro reaction to produce benzyl benzoate, which acts as a second source of the benzamide.

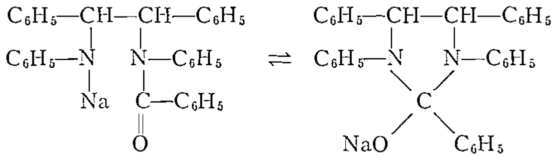
Since the stilbene derivative arises in diethyl ether, it is a reasonable assumption that the meso-disodio compound, which is formed in large amounts in diethyl ether, is its source. Presumably it is formed by a hydride transfer within a cyclic complex (IV), as shown in eq. [4]. A similar hydride transfer has been noted in the reactions of lithium diethylamide with benzophenone (6).

[4]



The ability of the meso-disodio derivative to engage in this reaction is probably connected with the position of the equilibrium between the "open" mono-N-benzoyl compound (V) and the cyclic isomer (III), as shown in eq. [5]. It will be noted that the *dd,ll* isomer of (V) produces the *trans* arrangement of the two phenyl groups in (III) whereas the diastereomeric *dl,ld* isomer of (V) produces the *cis* arrangement. It would be anticipated that, in the latter case, a higher concentration of the open structure (V) would exist in the equilibrium because of the greater steric interaction of the phenyl groups in the corresponding stereoisomer of (III).

[5]


V III

An increase in the benzaldehyde concentration increases the rate of the Cannizarro reaction much faster than it increases the rate of the cyclic hydride transfer. The benzyl benzoate so formed reacts with the sodium compound, producing the monobenzamide before the internal hydride transfer can occur within the complex to produce the stilbene derivative.

EXPERIMENTAL

Melting points are uncorrected and were determined in an open capillary in a Gallenkamp melting point apparatus. Infrared spectra were taken on a Beckmann IR9 or a Perkin–Elmer 421G.

All operations involving the organometallic compound were performed under a positive head of purified nitrogen (7). N,N′,1,2-Tetraphenylethylenediamine (TPED) was prepared by an aluminium amalgam reduction of N-benzylidene aniline in wet ether (5*b*). The diastereomers were separated by means of their complexes with N,N-dimethylformamide (5*a*); *dd,ll*-TPED had m.p. 150–153°, meso-TPED m.p. 167–168°.

The tetrahydrofuran and diethyl ether used in the experiments were purified by refluxing them under nitrogen over sodium metal until the addition of benzophenone produced the permanent blue color of the ketyl. The solvent was then distilled onto lithium aluminium hydride and stored in this fashion. When needed, the solvent was refluxed over the lithium aluminium hydride for 2 to 4 h and then distilled into the reaction vessel, a modified Schlenk tube (8).

Preparation of the Organosodium Compound

The Schlenk tube containing the freshly distilled solvent was transferred to a dry box where the N-benzylidene aniline and sodium metal (freshly cut) were weighed and added. The tube was removed from the dry box and shaken in a horizontal shaker. The reaction began at once, accompanied by the formation of an orange or orange-red color. The completeness of reaction was determined by permitting weighed amounts of the solution to flow into 50% aqueous ethanol. The solution was then titrated with standardized hydrochloric acid and phenolphthalein indicator. Under these conditions the TPED is not titrated. Table II demonstrates that the reaction is quite rapid.

Table III summarizes the properties of the mixed diastereomeric diamines isolated from the hydrolysis.

TABLE II

Reaction of N-benzylidene aniline with sodium

Duration of agitation, min	Equivalents NaOH per mole $C_6H_5CH{=}NC_6H_5$	
	Tetrahydrofuran*	Diethyl ether†
15	0.425	—
45	0.93	0.99
100	1.02	0.98
180	1.03	0.99
1 225	1.02	—

*N-Benzylidene aniline (0.01 mole) and tetrahydrofuran (35 g).
†N-Benzylidene aniline (0.01 mole) and diethyl ether (50 g).

TABLE III

N,N′,1,2-Tetraphenylethylenediamines formed on hydrolysis

Solvent	Melting point	% meso*	% meso†
Tetrahydrofuran	135–139	50	46
Diethyl ether	144.5–149	10	6.6

*From the melting point – composition data of Stuhmer and Messwarb (*5b*).
†Isolated through the complex with N,N-dimethylformamide (*5a*).

Preparation of Monobenzamide of Meso-N,N′,1,2-tetraphenylethylenediamine

Meso-N,N′,1,2-tetraphenylethylenediamine (1.09 g, 0.003 mole) was dissolved in 15 ml of benzene and 15 ml of pyridine. Benzoyl chloride (0.632 g, 0.0045 mole) was added and the solution refluxed for 18 h. To the cooled mixture, 15 ml of benzene and 15 ml of 10% aqueous potassium hydroxide was added. The aqueous phase was separated, and the organic phase was washed once with 10 ml of 10% potassium hydroxide and three times with 15 ml portions of water, and then dried over magnesium sulfate. Evaporation of the solution gave 1.332 g of solid, m.p. 170–182 °C. The material was dissolved in 30 ml of hot carbon tetrachloride, the solution was filtered hot, and when the solution was allowed to cool 1.133 g of a voluminous white precipitate separated, m.p. 188–192 °C. The infrared spectrum (Nujol mull) showed a NH band at 3 360 cm^{-1} and an amide carbonyl band at 1 635 cm^{-1}.

Anal. Calcd. for $C_{33}H_{28}N_2O$: C, 84.59; H, 6.02; N, 5.97. Found: C, 84.90; H, 5.92; N, 6.00.

Preparation of Monobenzamide of dd,ll-N,N′,1,2-Tetraphenylethylenediamine

dd,ll-N,N′,1,2-Tetraphenylethylenediamine (0.723 g, 0.002 mole) was dissolved in 25 ml of diethyl ether and 5 ml of benzene. Benzoyl chloride (0.912 g, 0.0021 mole) was added and the solution was allowed to stand at room temperature for 40 h. A white precipitate separated. The mixture was evaporated to dryness and the residue dissolved, with heating, in 15 ml of ethanol and 5 ml of water. Potassium hydroxide (0.40 g) dissolved in 10 ml of ethanol and 2 ml of water was added to the hot solution. The precipitate which formed was dissolved in 20 ml of benzene, and the organic phase was separated, washed twice with 10 ml of water, and dried over magnesium sulfate. Evaporation gave 0.882 g of a glassy residue. Treatment with 10 ml of diethyl ether effected crystallization. Filtration gave 0.349 g of derivative, m.p. 176.5–182 °C. Recrystallization from 5 ml of *n*-butanol gave 0.336 g, m.p. 180–183 °C. The infrared spectrum (Nujol mull) showed a NH band at 3 380 cm^{-1} and an amide carbonyl band at 1 625 cm^{-1}.

Anal. Calcd. for $C_{33}H_{28}N_2O$: C, 84.59; H, 6.02; N, 5.97. Found: C, 84.79; H, 5.97; N, 6.08.

Reaction in Tetrahydrofuran with Methyl Benzoate

The sodium adduct from 5.43 g (0.03 mole) of N-benzylidene aniline, 75.3 g of tetrahydrofuran, and 1.4 g (0.06 atom) of sodium was transferred to a 250 ml flask which was filled with dry nitrogen and which was equipped with a magnetic stirring bar. The solution was stirred, and 4.08 g (0.03 mole) of freshly distilled methyl benzoate dissolved in 15 ml of dry tetrahydrofuran was added all at once. A deep ruby-red color developed immediately. During the next 24 h, an orange-red precipitate formed and the color of the solution became orange. Water (25 ml) was then added and the precipitate dissolved.

The solution was transferred to a separatory funnel with 50 ml of benzene, and the aqueous phase was separated. The organic phase was washed three times with 25 ml portions of water, dried over magnesium sulfate, and evaporated, giving 6.84 g of residue. This was dissolved in 25 ml of hot benzene and treated with 40 ml of petroleum ether (b.p. 30–60°). A precipitate separated and (after 5 h) was filtered off, wt. 5.22 g, m.p. 163–175°. This material had an infrared spectrum identical with that of the N-benzoyl-*dd,ll*-TPED. However, the presence of a small amount of the diastereomer N-benzoyl-meso-TPED was demonstrated by allowing a solution of 0.6 g of the mixture in 50 ml of toluene–heptane (1:1) to evaporate to half volume spontaneously at room temperature over a period of 1 week. The crystals which separated consisted of small needles intermixed with relatively massive parallelopipeds. These were easily separated mechanically. The needles (0.05 g, m.p. 178–182°) had an infrared spectrum (Nujol mull) identical with that of the monobenzamide of the meso-TPED; the parallelopipeds (0.49 g, m.p. 165–182°) were similarly shown to be the monobenzamide of the *dd,ll* diamine.

The filtrate from the mixed monobenzamides was evaporated and the residual oil dissolved in 5 ml of methylene chloride and 25 ml of petroleum ether (b.p. 30–60 °C). The solution was chromatographed on 60 g of Woelm, grade I, basic alumina, elution being carried out with petroleum ether containing increasing amounts of methylene chloride. The first 350 ml of petroleum ether – 10% methylene chloride gave, on evaporation, 0.173 g of an amorphous solid. Crystallization from 5 ml absolute ethanol gave 0.018 g of N-benzylidene aniline, m.p. 50–54°.

The filtrate from this gave 0.086 g of the 2,4-dinitrophenylhydrazine derivative of benzaldehyde, m.p. 235–237 °C, on treatment with 2,4-dinitrophenylhydrazine reagent. An additional 0.104 g of this material was eluted with the next 200 ml of petroleum ether – 25% methylene chloride. After this, 300 ml of petroleum ether – 50% methylene chloride eluted 0.186 g of a solid which was recrystallized from 3 ml of ethanol. There was obtained 0.105 g of *dd,ll*-TPED, m.p. 148–150°, mixed melting point with an authentic sample 148–153°.

The next 275 ml of methylene chloride eluted 0.191 g of a solid which, on recrystallization from 3 ml of ethanol, gave 0.163 g of the monobenzamide of *dd,ll*-TPED, m.p. 170–176°, mixed melting point with an authentic sample 174–180°.

The yields obtained for the various compounds are: N-benzoyl-TPED (mixed isomers), 77%; *dd,ll*-TPED, 3%; N-benzylidene aniline, 5%.

Reaction in Tetrahydrofuran with Benzaldehyde (Mole Ratio 1:1)

The sodium adduct from 3.62 g (0.02 mole) of N-benzylidene aniline and 0.8 g (0.04 atom) of sodium in 62.2 g of tetrahydrofuran was transferred to a 125 ml flask which was filled with dry nitrogen and which was equipped with a magnetic stirring bar. The solution was stirred and 2.12 g (0.02 mole) of benzaldehyde was added all at once. A deep red color immediately developed. The solution was allowed to stand for 16 h, during which time a dark red precipitate formed.

Water (15 ml) was added with stirring. The color of the solution changed to orange and the precipitate dissolved. Diethyl ether (75 ml) was added, the aqueous phase was separated, and the ether layer was washed five times with 20 ml portions of water. After drying over magnesium sulfate, the solution was filtered and evaporated. The residue, a semicrystalline gummy solid, was dissolved in 20 ml of benzene and added to 50 ml of petroleum ether (b.p. 30–60°). The solid which separated was filtered off, washed with 1:1 benzene – petroleum ether, and dried; wt. 2.564 g, m.p. 174–180°. A comparison of the infrared spectrum with that of an authentic sample of N-benzoyl-*dd,ll*-TPED showed that the materials were identical.

The filtrate was evaporated, and the residue was dissolved in 20 ml of ether and 10 ml of benzene, and chromatographed on 60 g of Woelm, grade I, basic alumina. Elution with 50 ml of 1:1 petroleum ether – diethyl ether and then 100 ml of diethyl ether removed 1.02 g of *dd,ll*-N,N′,1,2-tetraphenylethylenediamine, m.p. 145–148°. Recrystallization from absolute ethanol raised the melting point to 150–153°; the mixed melting point with an authentic sample was 151–153°. The next 200 ml of ether containing 10% benzene eluted 0.161 g of N-benzoyl-meso-TPED, m.p. 180–186°, which after recrystallization from toluene melted at 186–192°; the mixed melting point with an authentic sample was 186–192°. The next 200 ml of ether containing 25% benzene, 150 ml of 1:1 ether–benzene, 200 ml of 1:1 ether–benzene containing 0.5% methanol, and 200 ml of 1:1 ether–benzene containing 2% methanol yielded a total of 0.25 g of N-benzoyl-*dd,ll*-TPED. The yields of these various compounds are: *dd,ll*-TPED, 28%; N-benzoyl-*dd,ll*-TPED, 60%; N-benzoyl meso-TPED, 3%.

Reaction in Tetrahydrofuran with Benzaldehyde (Mole Ratio 1:2)

This last experiment was repeated, except that only 1.06 g (0.01 mole) benzaldehyde was added. Evaporation of the solvent after washing gave a residue of 3.61 g. The infrared spectrum of this material showed only a weak band at 1 630 cm^{-1} characteristic of the amide carbonyl. The rest of the spectrum was identical with that of *dd,ll*-TPED.

Chromatography of the crude product as described above enabled 2.61 g (72% yield) of *dd,ll*-TPED, m.p. 141–153°, and 0.176 g (4% yield) of the monobenzamide, m.p. 173–184°, to be isolated.

Reaction in Tetrahydrofuran with Benzaldehyde (Mole Ratio 2:1)

The adduct prepared from 1.81 g (0.01 mole) of N-benzylidene aniline and 0.5 g (0.02 atom) of sodium in 43.6 g of tetrahydrofuran was transferred to a 125 ml flask which was filled with dry nitrogen. The solution was stirred and 2.12 g (0.02 mole) of benzaldehyde was rapidly added. A red color developed at once and deepened when the solution was allowed to stand for 20 h. Addition of water (15 ml) caused the color to change to yellow. Diethyl ether (50 ml) was added, the aqueous layer was separated, and the organic layer was washed twice with 20 ml portions of water, twice with 20 ml portions of 10% sodium bisulfite solution, and twice with 20 ml portions of water. After drying over magnesium sulfate, the solution was filtered and evaporated, giving a yellow crystalline residue.

The material was dissolved in 10 ml of benzene and added to 30 ml of petroleum ether (b.p. 30–60°). A crystalline solid separated; wt. 2.113 g, m.p. 170–180°. The infrared spectrum showed that this material was N-benzoyl-*dd,ll*-TPED (90% yield). The filtrate was not examined further.

Reaction in Diethyl Ether with Methyl Benzoate

The sodium adduct from 3.26 g (0.02 mole) of N-benzylidene aniline, 0.9 g (0.04 atom) sodium, and 103 g of diethyl ether was transferred to a 250 ml flask which was filled with dry nitrogen. The solution was stirred with a magnetic stirrer and 2.72 g (0.02 mole) of methyl benzoate added all at once. An immediate orange color developed and, when the solution was allowed to stand overnight, a precipitate formed. On the addition of 25 ml of water the color changed to yellow and the precipitate dissolved. When the solution was allowed to stand, small needle-like crystals separated. After 24 h, the precipitate was filtered off, washed with ether, and dried. This solid amounted to 0.938 g, m.p. 190–193°, mixed melting point with an authentic sample of N-benzoyl-meso-TPED 189–193°.

The ether phase was separated from the filtrate, washed twice with 25 ml portions of water, dried over magnesium sulfate, and evaporated. The residue amounted to 2.985 g and melted at 122–152°. Its infrared spectrum (Nujol mull) revealed the presence of the two diastereomeric N-benzoyl-TPED's.

A sample of material (1.50 g) was dissolved in 50 ml of ether–benzene (3:1) and chromatographed on 60 g of Woelm, grade I, basic alumina. Elution with diethyl ether gave 0.341 g (100 ml) of *dd,ll*-TPED, m.p. 127–134°; recrystallization from absolute ethanol raised the melting point to 147–153°, no depression with an authentic sample. The next 50 ml gave 0.270 g of a mixture of *dd,ll*-TPED and N-benzoyl-meso-TPED. These were separated by treating the mixture with 20 ml diethyl ether, at which time the N-benzoyl compound crystallized, giving 0.032 g, m.p. 188–191°, no depression with an authentic sample. The filtrate was evaporated and the residue recrystallized from 4 ml of absolute ethanol, giving 0.130 g of *dd,ll*-TPED, m.p. 149–153°; the mixed melting point with an authentic sample was not depressed. The next 200 ml of ether eluted an additional 0.545 g of N-benzoyl-meso-TPED, m.p. 183–187°, identified by its infrared spectrum. The next 200 ml of ether–benzene (3:1) and 350 ml ether–benzene (1:1) eluted 0.369 g of N-benzoyl-*dd,ll*-TPED; its melting point after recrystallization from ethanol was 182–184°, not depressed by an authentic sample.

Correcting the isolated samples for the aliquot sample of crude material and dividing the one mixture in the ratio of the amounts isolated gives total yields of *dd,ll*-TPED of 1.12 g (30%), N-benzoyl-meso-TPED 2.14 g (46%), and N-benzoyl-*dd,ll*-TPED 0.735 g (16%).

Reaction in Diethyl Ether with Benzaldehyde (Mole Ratio 1:1)

The sodium adduct from 3.62 g (0.02 mole) of N-benzylidene aniline, 0.9 g (0.04 atom) of sodium, and 104 g of diethyl ether was transferred to a 250 ml flask. The solution was stirred with a magnetic stirrer and 2.12 g (0.02 mole) of benzaldehyde dissolved in 10 ml of ether was added all at once. An orange color immediately developed together with a dense yellow precipitate. The mixture was stirred for 6 h, during which time the color deepened to a dark red-brown and the precipitate partially dissolved, changing color to a dark red or brown. Water (25 ml) was added with stirring. The precipitate dissolved to give a clear yellow solution, and then after 5 min a yellow solid began separating. After standing overnight, the mixture was filtered, and the solid was washed with ether. After drying it amounted to 0.996 g, m.p. 212–214°.[2] Its infrared spectrum (Nujol mull) showed a NH band at 3 340 cm^{-1} and an amide carbonyl at 1 645 cm^{-1}. Comparison of the spectrum with that of an authentic sample (4) of N-benzoyl-N,N′-diphenylstilbene-α,α'-diamine showed that they were identical. The compound yielded a picrate, m.p. 274–277°, mixed melting point with the picrate of N-benzoyl-N,N′-diphenylstilbene-α,α'-diamine 273.5–278.5°.

The filtrate was chromatographed on 60 g of Woelm, grade I, basic alumina. Elution with 300 ml of petroleum ether – benzene (2:1) removed 1.207 g of *dd,ll*-TPED, m.p. 140–153°. The next 200 ml of 2:1:1 benzene – petroleum ether – methylene chloride removed 0.561 g of the N-benzoyl derivative of meso-TPED, m.p. 148–173°. The N-benzoyl derivative was dissolved in 1 ml of hot ethyl acetate, and 5 ml of ethanol was added. The material which crystallized had m.p. 180–197°, mixed melting point with an authentic sample 188–198°. The next 900 ml of petroleum ether – methylene chloride (1:1) and 400 ml of methylene chloride eluted 1.198 g of N-benzoyl-*dd,ll*-TPED, m.p. 173–180°; the mixed melting point with an authentic sample was undepressed. The combined yields of these materials are: *dd,ll*-N,N′,1,2-tetraphenylethylenediamine, 33%; N-benzoyl-N,N′-diphenylstilbene-α,α'-diamine, 21%; N-benzoyl-N,N′,1,2-tetraphenylethylenediamine (mixed isomers), 38%.

[2] *This material was degraded during the determination of the melting point. The reported value was obtained by inserting the sample in a melting point apparatus preheated to 205 °C.*

Reaction in Diethyl Ether with Benzaldehyde (Mole Ratio 1:2)

The sodium compound from 1.81 g (0.01 mole) of N-benzylidene aniline and 0.5 g (0.02 atom) of sodium in 61 g of diethyl ether was treated with 2.12 g (0.02 mole) of benzaldehyde. An immediate formation of a yellow precipitate occurred and the solution became orange. Over the next 12 h no change occurred in the appearance of the mixture. Water (13 ml) was added and the precipitate dissolved, accompanied by a color change from orange to yellow. A small amount of a granular white precipitate remained. This was filtered off (wt. 0.243 g, m.p. 188–290°), dissolved in benzene, filtered from the insoluble material, and evaporated to give 0.167 g of N-benzoyl-meso-TPED, m.p. 180–195°.

The ether filtrate was evaporated to 2.32 g of a gummy residue. This was dissolved in 20 ml of benzene and the solution was added to 50 ml of diethyl ether. The small amount of solid which separated was filtered off to give 0.058 g, m.p. 189–195°; the mixed melting point with an authentic N-benzoyl derivative of meso-TPED was not depressed.

An aliquot portion (1.35 g solids) of filtrate was then chromatographed on 65 g of Woelm, grade I, basic alumina, diethyl ether being used as the eluting agent. The first 150 ml of eluate removed 0.666 g of gum (A). The next 150 ml eluted 0.217 g of the N-benzoyl derivative of meso-TPED, m.p. 189–192°, undepressed by an authentic sample. The next 175 ml eluted 0.122 g of a mixture of the N-benzoyl derivatives of meso- and *dd,ll*-TPED. After this, 250 ml of 3:1 ether–benzene and 150 ml of 1:1 ether – methylene chloride eluted 0.240 g of the N-benzoyl derivative of *dd,ll*-TPED, m.p. 173–177°. When it was recrystallized from absolute ethanol it had m.p. 177–180°; the mixed melting point with an authentic sample was undepressed. No further material was eluted from the column.

The infrared spectrum of gum (A) showed a NH absorption band at 3 380 cm^{-1} and a carbonyl band at 1 725 cm^{-1} but no amide carbonyl band at 1 630 – 1 650 cm^{-1}. This material was treated with 10 ml of petroleum ether (b.p. 30–60°) and allowed to stand. A solid separated, 0.339 g, m.p. 139–141°. When this solid was recrystallized from cyclohexane it had m.p. 138–146°; the mixed melting point with authentic *dd,ll*-TPED was 144–150°. The petroleum ether filtrate, on evaporation, gave a mobile yellow oil whose infrared spectrum was identical with that of benzyl benzoate. The total yields, after they were corrected for the aliquot portion chromatographed, were: *dd,ll*-TPED (0.583 g), 32%; N-benzoyl-TPED (1.221 g), 52%. If the fraction of mixed diastereomers obtained during chromatography is arbitrarily assumed to be a 1:1 mixture of the two diastereomers, then the yield of N-benzoyl-meso-TPED is 30% and that of N-benzoyl-*dd,ll*-TPED is 22%.

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